Justification for exclusion of Fluoropolymers from the PFAS definition

PFAS (per- and polyfluoroalkyl substances) are a broad group of man-made chemicals that are characterized by strong carbon-fluorine bonds. PFAS are under regulatory scrutiny due to concerns about their presence in drinking water and potential adverse effects on human health. PFAS may be mobile, resistant to biodegradation, may accumulate over time in soil, water, and living organisms and may be toxic to human health and environment. However, the broad group of PFAS also includes substances or groups of substances which exhibit different physio-chemical properties, toxicological and environmental profiles. One such unique group is fluoropolymers.

Fluoropolymers are excluded from the PFAS definition contained in the initial draft bill issued by the Environment & Public Works Committee because of their different chemical structure, physio-chemical, environmental and toxicological properties.

This paper differentiates fluoropolymers from other PFAS of concern and provides justification for their exclusion from the PFAS definition contained in the Committee's draft PFAS legislation based on the following six factors:

1. Fluoropolymers are safe
2. Fluoropolymers offer high socio-economic value
3. Fluoropolymers are irreplaceable
4. Fluoropolymers do not degrade under intended use conditions
5. Fluoropolymers can be disposed safely at their end of life
6. Majority of fluoropolymers can be manufactured responsibly without the use of fluorinated polymerization aids

Fluoropolymers are safe

Fluoropolymers are a safe, high molecular weight group of 38 substances that are inert. Fluoropolymers are thermally, biologically, and chemically stable, insoluble in water, non-mobile, non-bioavailable, non-bioaccumulative, and non-toxic. They satisfy the internationally recognized Organization for Economic Cooperation and Development (OECD) Polymers of Low Concern (PLC) criteria. Fluoropolymers are neither soluble in water nor in other solvents and biological liquids. Fluoropolymers cannot penetrate cell membranes or bio-accumulate and therefore do not pose any risk to human health or the environment.

References:

1. *(Eco)-toxicological read across on Fluoropolymers – GSI Environmental 2023*
2. *A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers – Henry et. al., 2018*
3. *A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers – Korzeniowski et. al., 2022*
4. *Assessment of PFAS Emissions during the Lifecycle of PTFE: a case study – Report prepared by Ramboll, 2023 - CONFIDENTIAL*

Fluoropolymers offer high socio-economic value

Fluoropolymers are extremely stable, specialty materials with unique physio-chemical properties. They are chemically inert, highly resistant to temperature variability, offer good weatherability, and exhibit low flammability. They also have properties such as low coefficient of friction, dielectric strength, and flexibility. Fluoropolymers are used in a wide variety of highly critical applications due to their valuable properties and unique combination of functionalities.

Any restriction on fluoropolymers could have far reaching adverse impacts on industry as well as society, given the essentiality of fluoropolymers to a wide range of industrial applications like:

Renewable energy: Solar panels and wind energy: various components of renewable energy installations, such as photovoltaic panels and wind turbines, require fluoropolymers.

Electric Vehicles: Fluoropolymers are critical for optimal performance of lithium-ion batteries and hydrogen fuel cells. Without fluoropolymers, decarbonization and environmental sustainability goals in the U.S. would be seriously compromised.

Semiconductors: Due to their resistance to harsh chemicals, fluoropolymers are essential for manufacturing semiconductors, providing an impurity-free environment. Without fluoropolymers, the semiconductor industry will be unable to produce microchips necessary for digitalization and vital for achieving autonomy in critical technologies.

Food and Water Treatment: Fluoropolymers are utilized in water filtration systems (which avoids the need to use chemicals for water treatment), and in food processing systems to guarantee adequate sanitary conditions and protect consumers from harmful contamination.

Pharmaceutical and Medical Devices: Catheters and medical implants are made of fluoropolymers due to their biological compatibility, inertness and durability. Furthermore, the production of medicines and vaccines require ultra pure conditions which can only be achieved with equipment containing fluoropolymer materials.

Chemical Process Industry: Fluoropolymers are unmatched in resistance to chemical attack and performance under wide temperature variations. They are the safest, most secure material for processing and containing chemicals. Fluoropolymers are found in all kinds of industrial equipment, as well as joints and gaskets to secure operation and ensure safety of workers.

Transport: Fluoropolymers contribute to both fuel efficiency and safety, playing a key role in systems such as brakes in cars or wing flaps in aircrafts. They are also the best option available to protect electrical cables in aircrafts, where high reliability of such cables, which can be exposed to thermal as well as chemical pressure, is fundamental.

References:

5. *Critical use of fluoropolymers in the functioning of modern society – Sales et. al., 2023*
6. *Inclusion of fluoropolymers in the scope of the PFAS restriction proposal under EU-REACH: Impact and proportionality assessment – Report prepared by Ramboll, 2023 - CONFIDENTIAL*

Fluoropolymers are irreplaceable

Fluoropolymers provide a combination of highly desired properties for use in many industrial sectors. These properties, and particularly their combination in single products, make them irreplaceable in

many applications. In fact, it is commonly accepted that their unique set of properties cannot be matched by alternative materials, particularly in the wide range of operability they offer. While alternatives may provide one or two properties with similar behavior, they never offer the full range of benefits.

Fluoropolymers are high-cost materials, and they are only chosen where no other material is able to match the required combination of properties. Substituting fluoropolymers with substances offering inferior performance would negatively impact the safety of people and the environment compromising key sustainability objectives.

Fluoropolymers are currently irreplaceable for many critical applications, and existing potential alternatives would be associated with significant trade-offs that could compromise safety of workers, the general population, or the environment, either due to direct hazardous properties of the alternative, or by downgrading performance and life of key applications.

References:

7. *Technical report on Analysis of alternatives to fluoropolymers and potential impacts related to substitution in different sectors of use – Chemservice 2022*

Fluoropolymers do not degrade under intended use conditions

Fluoropolymers are polymers with a carbon-only backbone with Fluorine atoms directly bonded to it. The exceptional strength of the C-F bond in fluoropolymers prevents them from degrading to small molecular weight PFAS under intended use conditions under environmental conditions. As concluded in a 2013 Danish EPA report, 'Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances', the degradation of fluoropolymers cannot lead to the formation of long chain Perfluorocarboxylic acids (PFCAs), and they are not included in the OECD list of possible precursors of short chain PFAS.

Fluoropolymers are not only different from non-polymeric PFAS, but they also exhibit completely different properties from other polymeric PFAS like side-chain fluorinated polymers, particularly in relation to possible environmental degradation into smaller PFAS. Chemservice has captured in a report the main differences between fluoropolymers, perfluoropolyethers and side-chain fluorinated polymers, highlighting how those differences justify considering fluoropolymers as chemicals posing no relevant risk for human health or the environment due to degradation to small molecule PFAS of concern.

Side-chain fluorinated polymers can degrade to hazardous non-polymeric PFAS during their intended use or under environmental conditions at the end-of-life phase of their applications due to their chemical structure. Moreover, these substances are mainly used in dispersive consumer applications like coatings on carpets, paper and textiles. OECD has published a report on side chain fluorinated polymers confirming the above.

References:

8. *Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances – Danish EPA, 2013*
9. *Differentiation of fluoropolymers from other polymeric PFAS – Chemservice, 2022*

10. *Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle - OECD Series on Risk Management, No. 73, 2022*

Fluoropolymers can be disposed safely at their end of life

Fluoropolymer applications at their end of life are disposed of in landfills or waste-to-energy incineration plants as common waste treatment routes. Less than 5% of fluoropolymers at their end of life are recycled and reused.

Landfill

Fluoropolymers are inert, non-toxic and have low to no degradation potential and therefore pose no risk when disposed of in landfills. Various studies on PTFE were performed by W.L. Gore to address potential partitioning of PFAS into water, air and soil and its leaching potential. The results support the stability of PTFE and lack of transformation to other PFAS, and that PTFE will not partition to air, water, or soil. Potential inhalation, oral or dermal exposure to PTFE for biota or the environment is highly unlikely. In another example regarding the safety of fluoropolymers with respect to their exposure to soil and water, the most common fluoropolymer, PTFE, is used as a geomembrane (lining material) in pits used for landfilling to prevent contamination of groundwater through leachates emitted from hazardous waste.

Waste-to-energy incineration

An experimental project was conducted by the Karlsruhe Institute of Technology (KIT) in cooperation with Société Générale de Surveillance (SGS) under supervision of the German Federal environmental Agency (UBA) along with incineration experts worldwide to assess if fluoropolymers get fully mineralized at household and industrial waste-to-energy incineration plants without any formation of short chain or long chain PFAS.

The results confirm that fluoropolymers at their end of life when incinerated under representative waste-to-energy incineration plant conditions do not generate any measurable levels of PFAS emissions and therefore pose no risk to human health and the environment. The absence of organic fluorides and more specifically PFAS in tests representative of municipal waste incineration confirms complete mineralization of fluoropolymers to hydrogen fluoride and carbon-di-oxide and provides critical data for exclusion of Fluoropolymers from the PFAS definition.

References:

11. *Summary of the PTFE studies performed with independent laboratories to investigate Persistence, Degradation, Transformation to or Release of Substances of Concern - W. L. Gore & Associates, 2022*
12. *Contamination from a leaking geomembrane—A necessary and imminent evil? – Tippett et. al., 2023*
13. *Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers under Representative European Municipal Waste Combustor Conditions, Preliminary report – Gehrmann et. al., 2023*

Majority of fluoropolymers can be manufactured responsibly without the use of fluorinated polymerization aids

The true and main concern related to fluoropolymers is the use of fluorinated polymerization aids (PFAS) and their emissions thereof during the manufacturing of fluoropolymers. It is important to note that more than 50% of fluoropolymer production does not require the use of fluorinated polymerization aids. For the remaining fluoropolymers, industry has dedicated significant effort and investment toward developing Non-Fluorinated Polymerization Aid (NFPA) technology in the manufacture of fluoropolymers. Several manufacturers such as Gujarat Fluorochemicals, Solvay, Arkema and Honeywell have made tremendous progress in this direction and have committed to completely move away from the use of fluorinated polymerization aids in their fluoropolymer manufacturing processes. A recently published article in volume 6 of the International Chemical Regulatory and Law Review (ICRL) states that the technologies available today allow for the manufacture of more than 80% of fluoropolymers globally without the use of fluorinated polymerization aids.

References:

14. *Developments in fluoropolymer manufacturing technology to remove intentional use of PFAS as polymerization aids – Ameduri et.al., 2023*
15. *Responsible manufacturing of fluoropolymers without the use of fluorinated polymerization aids (FPAs) – Report reviewed by Ramboll, 2023 - CONFIDENTIAL*

Conclusion

Summarizing, it is abundantly clear that fluoropolymers themselves are safe, do not pose any risk to human health and the environment and that the only concern related to the fluoropolymer lifecycle is the use of fluorinated polymerization aids. Therefore, regulating the use of fluorinated polymerization aids in the manufacturing of fluoropolymers removes the only true concern related to fluoropolymers, allowing industry and society to continue benefitting from fluoropolymer applications offering safety and well-being, digitalization, decarbonization and environment protection. We fully support the exclusion of fluoropolymers from the definition of PFAS while including within the definition for future regulation fluorinated polymerization aids.



Appendices

1. *(Eco)-toxicological read across on Fluoropolymers – GSI Environmental 2023*
2. *A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers – Henry et. al., 2018*
3. *A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II – Korzeniowski et. al., 2022*
4. *Assessment of PFAS Emissions during the Lifecycle of PTFE: a case study – Report prepared by Ramboll, 2023 - CONFIDENTIAL*
5. *Critical use of fluoropolymers in the functioning of modern society – Sales et. al.,2023*
6. *Inclusion of fluoropolymers in the scope of the PFAS restriction proposal under EU-REACH: Impact and proportionality assessment – Report prepared by Ramboll, 2023 - CONFIDENTIAL*
7. *Technical report on Analysis of alternatives to fluoropolymers and potential impacts related to substitution in different sectors of use – Chemservice, 2022*
8. *Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances – Danish EPA, 2013*
9. *Differentiation of fluoropolymers from other polymeric PFAS – Chemservice, 2022*
10. *Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle - OECD Series on Risk Management, No. 73, 2022*
11. *Summary of the PTFE studies performed with independent laboratories to investigate Persistence, Degradation, Transformation to or Release of Substances of Concern - W. L. Gore & Associates, 2022*
12. *Contamination from a leaking geomembrane—A necessary and imminent evil? – Tippett et. al., 2023*
13. *Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers under Representative European Municipal Waste Combustor Conditions, Preliminary report – Gehrmann et. al., 2023*
14. *Developments in fluoropolymer manufacturing technology to remove intentional use of PFAS as polymerization aids – Ameduri et.al., 2023*
15. *Responsible manufacturing of fluoropolymers without the use of fluorinated polymerization aids (FPAs) – Report reviewed by Ramboll, 2023 - CONFIDENTIAL*

FINAL

June 13, 2023

RE: Technical Support Document in Response to ECHA Annex XV Restriction Proposal for PFAS, Gujarat Fluorochemical's RAC Comment Letter

OVERALL COMMENT

In response to the Annex XV Restriction Report, proposal for a restriction on per- and polyfluoroalkyl substances (PFAS), we offer the following comments.

Overall, we find the proposal to be overly broad with respect to "PFAS", and scientifically distorted as it relates to fluoropolymers. The goal of reducing risks to the environment and human health from exposure to PFAS and/or their degradation products can be achieved without requiring a restriction on PFAS as single class – especially with PFAS having a broad range of chemical functional groups and physical/chemical properties. Furthermore, by essentially equating risk with persistence, the proposal significantly oversimplifies the approach to both hazard identification and risk assessment that has been central to risk management approaches under REACH and other EU regulatory frameworks for many years (see REACH Annex XIII). Fluoropolymers should be excluded from the proposed risk management option because they are not bioaccumulative, not mobile, and not toxic, and, therefore, do not pose a risk to the environment or human health.

SPECIFIC COMMENTS

1. **Persistence alone is not an appropriate measure of potential human health or environmental risk.**

   Some PFAS have been described as persistent because they degrade or transform to "terminal" persistent compounds. As stated in the restriction proposal (p.24), "[t]he persistence as the core concern of PFASs has also been pointed out by scientists for instance in the Helsingør Statement on PFASs (Scheringer et al., 2014) as well as the follow up Madrid statement (Blum et al., 2015)." The proposal omits an important detail, which is that neither of these statements refer to fluoropolymers. Scheringer et al. (2014) specifically referred to *non-polymer* perfluoroalkyl acids (PFAS) – perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs), including perfluorooctanesulfonic acid (PFOS). Likewise, Blum et al. (2015) references scientific studies that are exclusively on non-polymer perfluoroalkyl acids (PFAAs), rather than fluoropolymers.

   As described in REACH Annex XIII, several regulatory frameworks in Europe require the assessment of "persistent, bioaccumulative, toxic" (PBT) properties of chemicals, including refined classifications such as "very persistent and very bioaccumulative (vPvB)". Substances with PBT/vPvB properties **combine** the characteristics of strong persistence with the potential to accumulate in the environment and biota (Moermond et al., 2012, p. 2). Dating back to the Stockholm Convention on Persistent Organic Pollutants, the objective for evaluating PBT as combined characteristics is the "protection

of the environment and humans from substances that may harm these entities, either locally or globally, by accumulation in organisms where they then exert toxic effects" (Solomon et al., 2013, p. 1). Inherent in this objective is the understanding that the toxicity of a substance is contingent on the level present in the organism, and that chemicals with a lower bioaccumulation potential will present a lower risk.

Persistence in the environment does not indicate that the substance would accumulate in organisms, nor that environmental levels would rise to such an extent that exposure would result in toxicity. According to ECHA, substances that persist for long periods of time in the environment **and** have a high potential to accumulate in biota are of specific concern because their long-term effects are rarely predictable[1]. Importantly, the PBT criteria established under REACH has always considered the characteristics of **both** persistency and bioaccumulation **together**, as indicators of potential risk (i.e., toxicity). Potential for bioaccumulation is defined by REACH criteria (EC-1907-2006) as the condition when the bioconcentration factor (BCF) in aquatic species is higher than 2000.

PBT criteria have been applied consistently under numerous EU regulatory frameworks. The following are examples of applications of PBT concepts in regulatory programs over the past three decades (based on Table 3 from Moermond et al., 2012):

Time Period	Regulatory Program that Adopted or Applied PBT Concept
Late 1990s	Criteria Expert Group for Persistent Organic Pollutants develop criteria for categorization of POPs (Solomon et al. 2013)
1998	United Nations Economic Commission for Europe, the Convention on Long-range Transboundary Air Pollution (LRTAP)
2001	Stockholm Convention
2003	OSPAR Convention for the Protection of the Marine Environment of the Northeast Atlantic
2004	EU directives on Human & Veterinary Pharmaceuticals
	International Maritime Organization (IMO) International Convention for the Control and Management of Ship's Ballast Water and Sediments
2006	Registration, Evaluation, Authorisation and Restriction of Chemicals, (REACH)

Across each of these regulatory frameworks, the **combination** of chemical properties that comprise PBT criteria are consistently evaluated:

a. The chemical is evaluated for its persistence (P/vP) in the environment based on its half-life in environmental media (e.g., water, sediment, soil); **and**,

b. The chemical is evaluated for bioaccumulation (B/vB) in biota based on its BCF, octanol/water coefficient (log K_{OW}), or monitoring data; **and**,

c. The chemical is evaluated for toxicity (T) to biota based on observed adverse effects at concentrations exceeding specific exposure thresholds, or evidence of

[1] https://echa.europa.eu/understanding-pbt-assessment

carcinogenicity, mutagenicity, reproductive toxicity, or specific target organ toxicity after repeated exposure.

While there are differences in the specific criteria applied during PBT/vPvB evaluation, each regulatory framework makes clear that **no standalone criteria**, whether it be P/vP, B/vB, or T, is sufficient cause for PBT/vPvB status or environmental concern. In all cases, at least two of these three properties (P and B) must be established to identify a chemical as PBT/vPvB.

In fact, there is precedent within EU chemical legislation for not restricting chemicals based on persistence alone. For example, vinyl neodecanoate was evaluated by the PBT Working Group and classified as "P/vP" but "not fulfilling PBT and vP/vB criteria". Specifically, the assessment report states that vinyl neodecanoate: "is not considered to be a PBT substance. It does not meet the B criteria and does not meet the screening criteria for T. It does meet the screening criteria for P (and vP)."[2]

2. **Fluoropolymers are not bioaccumulative**.

   Available data indicate that fluoropolymers are not bioaccumulative. Bioaccumulation potential is generally assessed based on a prediction using the octanol-water coefficient (e.g., log K_{OW} > 3) or measurements in tissue and exposure media (e.g., BCF > 2000). Fluoropolymers such as polytetrafluoroethylene (PTFE, CASRN 9002-84-0), polyvinylidene fluoride (PVDF) homopolymer (CASRN 24937-79-9), perfluoroalkoxy alkane (PFA, CASRN 26655-00-5 and 31784-04-0), and fluoroelastomer (FKM, CASRNs 9011-17-0, 26424-79-6, and 25190-89-0) are insoluble in octanol and water (Henry et al., 2018; Korzeniowski et al., 2022). Therefore, the bioaccumulation potential of fluoropolymers cannot be reliably predicted from a log K_{OW}. Measured biota tissue, water, and sediment concentrations indicate there is a low bioaccumulation potential for fluoropolymers in aquatic food webs. Researchers examining benthic invertebrate exposure to PTFE and other polymers demonstrated that there was no evidence of bioaccumulation through the aquatic benthic community from lower trophic level filter-feeders and grazers to higher trophic level omnivores and predators in the Arctic (Sfriso et al., 2020) and in Norway (Bour et al., 2018).

3. **Fluoropolymers are not environmentally mobile.** The restriction proposal argues that the continuous release of PFAS will lead to the accumulation of these compounds in the environment, such that unknown toxicity thresholds will be exceeded at some unknown point in the future. Moreover, the proposal also suggests that "PFAS" as a class will be found in all environmental media. Neither of these arguments apply to fluoropolymers.

   Fluoropolymers are not water soluble and will not likely result in widespread groundwater impacts or exposures from drinking water. If released to the environment, fluoropolymers are likely to remain in the environmental matrix they contact following release, such as terrestrial soil or aquatic sediment. Because fluoropolymers are chemically inert, they cannot partition and are not chemically mobile between water and soil/sediment. Any potential movement of fluoropolymers in the environment will occur via mechanical

[2] https://echa.europa.eu/documents/10162/6af350f6-e259-4545-859f-293ce8515cb3

transport processes, such as overland flow from precipitation events (e.g., rainfall flows carrying fluoropolymers from soil to sediment via runoff). Indeed, Feng et al. (2022) recently demonstrated that PTFE in modelled tidal sediments showed enhanced retention and low likelihood of resuspension into the water column. Given their chemical inertness, non-volatility, and lack of water solubility, fluoropolymers are not highly mobile in the environment.

4. **Fluoropolymers present in the environment are not toxic to humans or ecological receptors.** Toxicity studies on fluoropolymers indicate that adverse effects are unlikely following exposure by human or ecological receptors to levels of fluoropolymer that may be present in the environment. A summary of available laboratory bioassays examining the toxicity of PTFE on test animals is provided by Radulovic and Wojcinski (2014). Given that fluoropolymers such as PTFE are insoluble in water and non-volatile, the most likely exposure route for PTFE is ingestion. In fact, acute oral toxicity of PTFE in rats is low, with a reported LD_{50} > 11,280 mg/kg. Researchers also found there were no observed adverse effects in rats exposed to up to 25% PTFE in rat diet for up to 90 days (Naftalovich et al., 2016; Radulovic & Wojcinski, 2014). The lack of toxicity of PTFE at 25% of the diet level fed to rats for 90 days was subsequently validated by peer review by the Scientific Review Panel of the Hazardous Substances Data Bank (TOXNET) (Naftalovich et al., 2016). Additionally, a four-week repeated dose study exposed mice to PTFE via their diet and reported no effects at any dose level, and no PTFE was detected in mice blood (Lee et al., 2022). The study supports an unbounded no-observed-adverse-effect-level (NOAEL) of 2,000 milligrams per kilogram (mg/kg) in mice, equivalent to approximately 9,720 mg/kg for a 60 kg human adult. The lack of toxicity from ingestion of PTFE and other fluoropolymers is attributed to their extremely high molecular weight, which renders absorption via the gastrointestinal tract negligible, and the fact that they are chemically inert compounds and not metabolized under physiological conditions (Naftalovich et al., 2016).

   Manufacturer Material Safety Data Sheets indicate that dermal contact with PTFE does not cause skin irritation in rabbits or humans. PTFE is not considered genotoxic and is so inert it has been used in genotoxicity protocols or test methodologies for *Salmonella typhimurium* mutagenicity testing of the US EPA Mobile Reaction Chamber (Naftalovich et al., 2016). The World Health Organization's International Agency for Research on Cancer concluded that organic polymeric materials (such as fluoropolymers) as a group are not classifiable as to their carcinogenicity to humans (Group 3) (IARC, 1999).

5. **The "P-sufficient" approach is novel and precedent setting, worldwide.** The Annex XV Restriction of all "PFAS" would be the first of its kind globally. The Restriction Report (p.24) references California EPA, Department of Toxic Substances and Chemicals (DTSC) as an example of established regulatory precedent, where a state regulatory agency has placed restrictions on all PFAS as class[3]. The referenced journal article (Bălan et al., 2021) written by California DTSC staff specifically refers to PFAS present in specific consumer products. It would be inaccurate to conclude from this one example that

[3] The Restriction report says: "It is noted that the first example of regulation of PFASs as a chemical class according to the P-sufficient approach has been introduced in California. Here a regulation of PFASs as a class is in place for certain consumer products under the California Safer Consumer Products Program (Balan et al., 2021)."

California has adopted the P-sufficient concept as a PFAS risk management strategy. Indeed, an examination of recent legislative developments in California clearly shows that the state is actually pursuing a **targeted** risk management strategy:

1. PFAS in fire-fighting foam
    - Effective 1 January 2022, this legislation prohibits the use of class B firefighting foam containing intentionally added PFAS chemicals in California.
2. PFAS in textiles
    - Effective 1 January 2024, will prohibit the sale of PFAS-containing textile articles and require least toxic alternatives when replacing PFAS.
3. PFAS in cosmetics
    - Effective 1 January 2025, prohibits sale of cosmetic products that contain intentionally-added PFAS.
4. PFAS in plant-based food packaging and cookware
    - Effective 1 January 2023, prohibits sale of various plant fiber-based food packaging that contains PFAS.
    - Requires disclosure of certain chemicals, including PFAS, in cookware starting January 2023.

Importantly, none of these legislative actions apply to industrial PFAS uses, where fluoropolymers are primarily utilized. Furthermore, these initiatives clearly demonstrate that California is pursuing targeted restrictions on PFAS used in specific consumer products.

Moreover, Bălan et al. (2021) inappropriately include fluoropolymers under their P-sufficient approach based solely on one false statement and a second statement that lacks important context:

1. “Fluoropolymers are characterized by large molecular sizes and do not degrade to PFAAs under typical environmental conditions, although they have been observed to release [perfluorocarboxylic acids] PFCAs, including [perfluorooctanoate] PFOA, when heated to temperatures between 180 °C and 800 °C (Schlummer et al. 2015; Feng et al. 2015).”

   This statement, while correct regarding the large molecular weight of fluoropolymers, is incorrect with regard to the release of PFCAs such as PFOA. When heated to temperatures greater than 300 °C, the potential transformation products of PTFE include trifluoroacetic acid (TFA, CASRN 76-05-1), hydrofluoric acid (CASRN 7664-39-3), tetrafluoroethylene (TFE, CASRN 116-14-3), hexafluoropropylene (CASRN 116-15-4), or perfluoroisobutylene (CASRN 382-21-8) (Ellis et al., 2001; Radulovic and Wojcinski, 2014; Henry et al., 2018; Tolkach et al., 2020). Heating PVDF homopolymer to temperatures greater than 300 °C may result in the formation of hydrogen fluoride (HF, CAS No. 7664-39-3) and oxides of carbon (Arkema, 2011). Similarly, thermal decomposition of PFA at temperatures exceeding 300 °C can produce HF, carbonyl difluoride (CASRN 353-50-4), carbon monoxide (CO, CASRN 630-08-0) and carbon dioxide (CASRN 124-38-9) (Inoflon Fluoropolymers, 2018). The potential transformation products of these fluoropolymers do not include PFCAs such as PFOA at intended use and end of life conditions.

2. “PFAAs are used in the manufacture of fluoropolymers and can occur as impurities in the final product.”

PFAAs such as fluorinated polymerization aids (FPAs), also referred to as fluorosurfactants, are currently used by some chemical manufacturers, albeit to a lesser extent, to facilitate the polymerization reaction that forms the final fluoropolymer product (Ameduri et al., 2023). PFOA and hexafluoropropylene oxide dimer acid (HFPO-DA, or GenX) are examples of these FPAs that have garnered widespread environmental concern. Furthermore, the substitution of non-fluorinated polymerization aids (NFPAs) for FPAs in the manufacture of the three main fluoropolymers by volume – PTFE, PVDF, and FKM – allows for the complete manufacture of these fluoropolymers without the use of FPAs and any resulting minor impurities (Ameduri et al., 2023). Therefore, by implementing the widespread use of NFPAs in fluoropolymer manufacturing, environmental contamination can be reduced to the maximum extent practicable.

Residual impurities from non-polymeric PFAS entrained in the final fluoropolymer product, such as low molecular weight (<1000 Da) leachables and residual monomers, are quantifiably low: <1 ppm in PTFE and <50 ppb in PFA (Henry et al., 2018). This low leaching potential is what allows PTFE to meet the requirements for use in the food and beverage, pharmaceutical, medical, and semiconductor industries (Olabisi and Adewale, 2015). The following table summarizes the numerous regulatory safety standards that fluoropolymers meet for US and EU regulations, demonstrating their safety for use across drinking water, food contact, and medical industries:

Regulation	Regulatory Program Description
EC 10/2011	EU Commission Regulation No 10/2011 of 14 January 2011 safety requirement on plastic materials and articles intended to come into contact with food (EU, 2011a).
21CFR 177.1550	US food contact regulation for perfluorocarbon resins (CFR, 2023).
2011/65/EU	Restriction of hazardous substances in electrical & electronic equipment (EU, 2011b).
USP Class VI	Biocompatibility testing requirements from the U.S. Pharmacopeia (USP). Includes safety standards for plastic, polymers, and elastomers to be applied in medical devices and surgical equipment. Testing includes acute systemic toxicity test, intracutaneous test, and implantation test (USP, n.d.).
3-A 20-27	Sanitary standards for multiple-use plastic materials as a product contact or cleaning solution contact surfaces in equipment for production, processing, and handling of milk and milk products. Test criteria includes their ability to be cleaned, to receive effective bactericidal treatment, and to maintain their essential functional properties (3-A, 2011).
Umwelt Bundesamt (UBA)	German Environmental Agency (UBA) evaluation criteria for any plastic and rubber products that come in contact with drinking water (UBA, 2022).

Sanitary Conformity Certification (ACS)	French mandatory certification for any device in contact with drinking water during production, treatment, storage, and distribution (ANSES, 2013; FR, n.d.).
Water Regulations Approval Scheme (WRAS)	United Kingdom's accreditation body for approval process of water fittings. It aims to prevent the misuse, waste, excessive consumption, and inaccurate measurement of water and, ensure that drinking water is free from contamination. Includes products used only after the time of supply (WRAS, n.d.).

References:

3-A Sanitary Standards (3-A). (2011). 3-A® Sanitary Standards for Multiple-Use Plastic Materials, Number 20-27. Accessed May 2023.

Ameduri, B., Sales, J., & Schlipf, M. (2023). Developments in fluoropolymer manufacturing technology to remove intentional use of PFAS as polymerization aids. *International Chemical Regulatory and Law Review, 6(1)*.

Arkema. (2011). *Material Safety Data Sheet, Kynar Homopolymer*.

Bălan, S. A., Mathrani, V. C., Guo, D. F., & Algazi, A. M. (2021). Regulating PFAS as a Chemical Class under the California Safer Consumer Products Program. *Environmental Health Perspectives*, *129*(2), 025001. https://doi.org/10.1289/EHP7431

Blum, A., Balan, S. A., Scheringer, M., Trier, X., Goldenman, G., Cousins, I. T., Diamond, M., Fletcher, T., Higgins, C., Lindeman, A. E., Peaslee, G., de Voogt, P., Wang, Z., & Weber, R. (2015). The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs). *Environmental Health Perspectives*, *123*(5). https://doi.org/10.1289/ehp.1509934

Bour, A., Avio, C. G., Gorbi, S., Regoli, F., & Hylland, K. (2018). Presence of microplastics in benthic and epibenthic organisms: Influence of habitat, feeding mode and trophic level. *Environmental Pollution*, *243*, 1217–1225. https://doi.org/10.1016/j.envpol.2018.09.115

Code de la Santé Publique [Public Health Code] (FR). (n.d.). Article R1321-48: Materials in contact with water. Last updated: 1 January 2023. Accessed May 2023. Available online at: https://www.legifrance.gouv.fr/codes/article_lc/LEGIARTI000006909569

Ellis, D. A., Mabury, S. A., Martin, J. W., & Muir, D. C. G. (2001). *Thermolysis of ¯uoropolymers as a potential source of halogenated organic acids in the environment*. *412*.

European Union (EU). (2011a). Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food (text with EEA relevance). Official Journal of the European Union. 14 January 2011. Accessed May 2023. Available online at: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32011R0010

European Union (EU). (2011b). Directive 2011/65/EU of The European Parliament and Of The Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (recast). Official Journal of the European Union. 8 June 2011. Accessed May 2023. Available online at: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX:32011L0065

Feng, Q., Chen, Z., Greer, C. W., An, C., & Wang, Z. (2022). Transport of Microplastics in Shore Substrates over Tidal Cycles: Roles of Polymer Characteristics and Environmental Factors. *Environmental Science & Technology*, *56*(12), 8187–8196. https://doi.org/10.1021/acs.est.2c01599

French Agency for Food, Environmental and Occupational Health and Safety (ANSES). (2013). Materials and objects in contact with water, products and processes used for treating water for public distribution. Accessed May 2023. Available online at: https://www.anses.fr/en/content/materials-and-objects-contact-water-products-and-processes-used-treating-water-public

Henry, B. J., Carlin, J. P., Hammerschmidt, J. A., Buck, R. C., Buxton, L. W., Fiedler, H., Seed, J., & Hernandez, O. (2018). A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers: Fluoropolymers PLC. *Integrated Environmental Assessment and Management*, *14*(3), 316–334. https://doi.org/10.1002/ieam.4035

IARC (Ed.). (1999). *Surgical implants and other foreign bodies.* IARC.

Inoflon Fluoropolymers. (2018). *PFA Fluoroplastic Resin SDS*. https://www.inoflon.com/pdf/PFA_Powder_Eng.pdf

Korzeniowski, S. H., Buck, R. C., Newkold, R. M., kassmi, A. E., Laganis, E., Matsuoka, Y., Dinelli, B., Beauchet, S., Adamsky, F., Weilandt, K., Soni, V. K., Kapoor, D., Gunasekar, P., Malvasi, M., Brinati, G., & Musio, S. (2022). A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers. *Integrated Environmental Assessment and Management*, ieam.4646. https://doi.org/10.1002/ieam.4646

Lee, S., Kang, K.-K., Sung, S.-E., Choi, J.-H., Sung, M., Seong, K.-Y., Lee, J., Kang, S., Yang, S. Y., Lee, S., Lee, K.-R., Seo, M.-S., & Kim, K. (2022). In Vivo Toxicity and Pharmacokinetics of Polytetrafluoroethylene Microplastics in ICR Mice. *Polymers*, *14*(11), Article 11. https://doi.org/10.3390/polym14112220

Moermond, C. T., Janssen, M. P., de Knecht, J. A., Montforts, M. H., Peijnenburg, W. J., Zweers, P. G., & Sijm, D. T. (2012). PBT assessment using the revised annex XIII of REACH: A comparison with other regulatory frameworks. *Integrated Environmental Assessment and Management*, *8*(2), 359–371. https://doi.org/10.1002/ieam.1248

Naftalovich, R., Naftalovich, D., & Greenway, F. L. (2016). Polytetrafluoroethylene Ingestion as a Way to Increase Food Volume and Hence Satiety Without Increasing Calorie Content. *Journal of Diabetes Science and Technology*, *10*(4), 971–976. https://doi.org/10.1177/1932296815626726

Radulovic, L. L., & Wojcinski, Z. W. (2014). *Encylopedia of Toxicology; PTFE (Polytetrafluoroethylene; Teflon)* (Vol. 3). Elsevier Inc.

Scheringer, M., Trier, X., Cousins, I. T., de Voogt, P., Fletcher, T., Wang, Z., & Webster, T. F. (2014). Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs). *Chemosphere*, *114*, 337–339. https://doi.org/10.1016/j.chemosphere.2014.05.044

Sfriso, A. A., Tomio, Y., Rosso, B., Gambaro, A., Sfriso, A., Corami, F., Rastelli, E., Corinaldesi, C., Mistri, M., & Munari, C. (2020). Microplastic accumulation in benthic invertebrates in Terra Nova Bay (Ross Sea, Antarctica). *Environment International*, *137*, 105587. https://doi.org/10.1016/j.envint.2020.105587

Solomon, K., Matthies, M., & Vighi, M. (2013). Assessment of PBTs in the European Union: A critical assessment of the proposed evaluation scheme with reference to plant protection products. *Environmental Sciences Europe*, *25*(1), 10. https://doi.org/10.1186/2190-4715-25-10

Tolkach, P. G., Basharin, V. A., Chepur, S. V., Gorshkov, A. N., & Sizova, D. T. (2020). Ultrastructural Changes in the Air—Blood Barrier of Rats in Acute Intoxication with Furoplast Pyrolysis Products. *Bulletin of Experimental Biology and Medicine*, *169*(2), 270–275. https://doi.org/10.1007/s10517-020-04866-x

Umweltbundesamt [German Environment Agency] (UBA). (2022). Annexes to evaluation criteria document for plastics and other organic materials in contact with drinking water (KTW-BWGL) – Polymer-specific Part. Bad Elster, Germany. Accessed May 2023. Available online at: https://www.umweltbundesamt.de/sites/default/files/medien/3521/dokumente/polymerspezifische_anlagen_der_bewertungsgrundlage_fur_kunststoffe_und_andere_organische_materialien_en.pdf

U.S. Code of Federal Regulations (CFR). (2023). Code of Federal Regulations Title 21, Volume 3, 21CFR177.1550: Title 21--Food and Drugs, Chapter I--Food and Drug

Administration, Department of Health and Human Services, Subchapter B - Food for Human Consumption (Continued), Part 177 -- Indirect Food Additives: Polymers. Last Updated: 28 March 2023. Accessed May 2023. Available online at: https://www.ecfr.gov/current/title-21/chapter-I/subchapter-B/part-177/subpart-B/section-177.1550

U.S. Pharmacopeia (USP). (n.d.). Chapter 88: Biological Reactivity Tests, in Vivo. Accessed May 2023. Available online at: http://www.pharmacopeia.cn/v29240/usp29nf24s0_c88.html

Water Regulations Approval Scheme (WRAS). (n.d.). Regulation 31. Accessed May 2023. Available online at: https://www.wrasapprovals.co.uk/approvals/products_and_materials_directory/regulation_31/#:~:text=The%20Water%20Regulations%20Advisory%20Scheme%20(WRAS)%20is%20concerned%20with%20products,distribution%20of%20public%20water%20supplies.

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Critical Review

A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a group of fluorinated substances that are in the focus of researchers and regulators due to widespread presence in the environment and biota, including humans, of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Fluoropolymers, high molecular weight polymers, have unique properties that constitute a distinct class within the PFAS group. Fluoropolymers have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability. They have negligible residual monomer and oligomer content and low to no leachables. Fluoropolymers are practically insoluble in water and not subject to long-range transport. With a molecular weight well over 100 000 Da, fluoropolymers cannot cross the cell membrane. Fluoropolymers are not bioavailable or bioaccumulative, as evidenced by toxicology studies on polytetrafluoroethylene (PTFE): acute and subchronic systemic toxicity, irritation, sensitization, local toxicity on implantation, cytotoxicity, in vitro and in vivo genotoxicity, hemolysis, complement activation, and thrombogenicity. Clinical studies of patients receiving permanently implanted PTFE cardiovascular medical devices demonstrate no chronic toxicity or carcinogenicity and no reproductive, developmental, or endocrine toxicity. This paper brings together fluoropolymer toxicity data, human clinical data, and physical, chemical, thermal, and biological data for review and assessment to show that fluoropolymers satisfy widely accepted assessment criteria to be considered as "polymers of low concern" (PLC). This review concludes that fluoropolymers are distinctly different from other polymeric and nonpolymeric PFAS and should be separated from them for hazard assessment or regulatory purposes. Grouping fluoropolymers with all classes of PFAS for "read across" or structure–activity relationship assessment is not scientifically appropriate. *Integr Environ Assess Manag* 2018;14:316–334. © 2018 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals, Inc. on behalf of Society of Environmental Toxicology & Chemistry (SETAC)

Keywords: Fluoropolymer International regulation Polytetrafluoroethylene Polymer of low concern PFAS

INTRODUCTION

The carbon–fluorine (C–F) bond is the strongest bond between C and another atom, instilling substances that contain a majority of C–F bonds with stability, inertness, and persistence (Banks et al. 1994). Per- and polyfluoroalkyl substances (PFAS) are a large group of highly fluorinated synthetic substances with diverse properties that have been used in a wide variety of industrial and consumer applications since the 1950s (Buck et al. 2011). Within the group are distinct substances with different properties: polymers and nonpolymers; solids, liquids, and gases; persistent and nonpersistent substances; highly reactive and inert substances; mobile and insoluble substances; and toxic and nontoxic chemicals.

The PFAS are a large, diverse group of substances that, in some respects, challenge easy distinction for assessment and management. A clearer understanding of the origin of PFAS found in the environment and assessment of their properties is needed to be able to determine which classes of PFAS require management action. Per- and polyfluoroalkyl substances must be assessed taking into account their differences in chemical, physical, thermal, and biological properties. A single, globally harmonized system for PFAS classification has not yet been defined, resulting in a lack of distinction between PFAS. As regulatory frameworks continue to evolve, such as the Regulation (EC) No 1907/2006 of the European

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Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (RC 2006), more work is needed to distinguish classes of PFAS to ensure that regulations are appropriate in scope and proportionality.

Two long-chain nonpolymer perfluoroalkyl acids (PFAAs), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (both PFAS), found widespread in the environment and living systems, led to regulatory assessment and management efforts in several countries (Buck et al. 2011; OECD 2017; USEPA 2017a). Management actions to curtail manufacture of long-chain PFAAs, including PFOS and PFOA, and substances that may degrade to form them (also known as "precursors") have been taken (EC 2006; ECHA 2015; USEPA 2017a). Both PFOS and PFOA have been determined by regulators to be persistent, bioaccumulative, and toxic (PBT) substances (EC 2006; ECHA 2015). A current concern is the potential for certain side-chain polymer PFAS to degrade in the environment to PFOS and PFOA or lower homologues (Liu and Mejia-Avendaño 2013). In addition, PFOS (a nonpolymeric perfluoroalkyl substance) and related substances have been listed as persistent organic pollutants (POPs) under Annex B of the Stockholm Convention (UNEP 2009), and PFOA and other related substances (UNEP 2011), as well as perfluorohexane sulfonic acid (PFHxS) and related substances are being evaluated for listing (UNEP 2017a). As a result, questions about the health and environmental safety of PFAS as a group have been raised (Scheringer et al. 2014; Blum et al. 2015).

These findings have prompted expanded regulatory interest and concern about PFAS as a group, spurring additional assessment and management actions. The German Environment Agency, Umweltbundesamt (UBA), published a proposal to implement new assessment criteria and procedures for identifying persistent (P), mobile (M), and toxic (T) substances under the European Union REACH chemical registration process (UBA 2017). The UBA has concluded that PM and/or PMT substances constitute "an irreversible threat to sources of drinking water and the quality of drinking water" in Germany. This has prompted the designation of PFAS substances as posing an "equivalent level of concern" under Article 57(f) of REACH and thereby has prompted the need for a new paradigm for chemical assessment and authorization. The Swedish Chemicals Agency, Kemikalieinspektionen (KEMI), announced agreement among 37 government agencies and research institutions in the European Union (EU) to expand cooperation to reduce the risks and increase the knowledge of PFAS, thereby endorsing the UBA view on the hazards posed by all PFAS substances (KEMI Swedish Chemicals Agency 2016). The KEMI announcement indicated that all perfluoralkyl substances should be considered as extremely persistent in the environment, and many are water soluble, mobile in soil, and likely to contaminate waterways and drinking water supplies. A risk assessment report prepared by KEMI is forthcoming (ChemNews 2016).

The PFAS are divided into 2 primary categories: nonpolymers and polymers (Figure 1). Figure 1 shows that these 2 categories are divided into 5 classes of PFAS. The fluoropolymer class of PFAS is the focus of the present paper. The nonpolymer category includes perfluoroalkyl substances and polyfluoroalkyl substances. The polymer category includes fluoropolymers, perfluoropolyethers, and side-chain fluorinated polymers. Polymers generally have very different physical, chemical, and biological properties than do nonpolymer chemical substances of low molecular weight. Precise criteria that distinguish polymers from nonpolymers have been established (OECD 1993).

There are distinct differences between the 5 classes of PFAS. For example, PFOA, in the class nonpolymer perfluoroalkyl substances, is small, mobile, and persistent; has been assessed and determined to be a PBT chemical (ECHA 2015); and is in the final stage for recommendation of listing as a POP under the Stockholm Convention (UNEP 2017b). Regulatory and industry management actions on PFOA include precursor substances that may degrade to form PFOA (USEPA 2017a). An example in the class of nonpolymer polyfluorinated substances, 8:2 fluorotelomer alcohol, is known to degrade under environmentally relevant conditions to form PFOA (Liu and Mejia-Avendaño 2013). It is therefore a precursor substance to PFOA and subject to regulatory management (Liu and Mejia-Avendaño 2013). Polymers derived from 8:2 fluorotelomer alcohol are examples of the side-chain fluorinated polymers class. These polymers may degrade to form PFOA and therefore are subject to regulatory management. Lastly, perfluoropolyethers class is a complex class of PFAS, which contains O linkages in the polymer backbone.

In the present paper, we address fluoropolymers, a class of PFAS polymers (Figure 1). Fluoropolymers are high molecular weight solid plastics that have been studied extensively.

The present paper brings together fluoropolymer toxicity data, human clinical data, and physical, chemical, thermal, and biological data for review and assessment to show that fluoropolymers satisfy widely accepted assessment criteria to be considered as "polymers of low concern" (PLC) and to show that fluoropolymers are distinctly different enough from other classes of PFAS to not be grouped with them for hazard assessment or regulatory purposes.

PERFORMANCE CHARACTERISTICS AND USES OF FLUOROPOLYMERS

Since the discovery of polytetrafluoroethylene (PTFE) in 1938 (Plunkett 1987), the use of fluoropolymers has grown considerably to take advantage of their unique physical–chemical, thermal, and biological properties. The 4 fluoropolymers addressed in the present paper, polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), and tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers (e.g., perfluoroalkoxy polymer, PFA), accounted for approximately 70% to 75% of the world fluoropolymer consumption in 2015 (IHS 2016). The representative fluoropolymer discussed in the present paper, PTFE, made up 58% (by weight) of 2015 worldwide fluoropolymer consumption (IHS 2016). Fluoropolymers are high molecular weight plastics with unique properties attributable to the strong C–F bonds, the strongest bond between C and another atom, making

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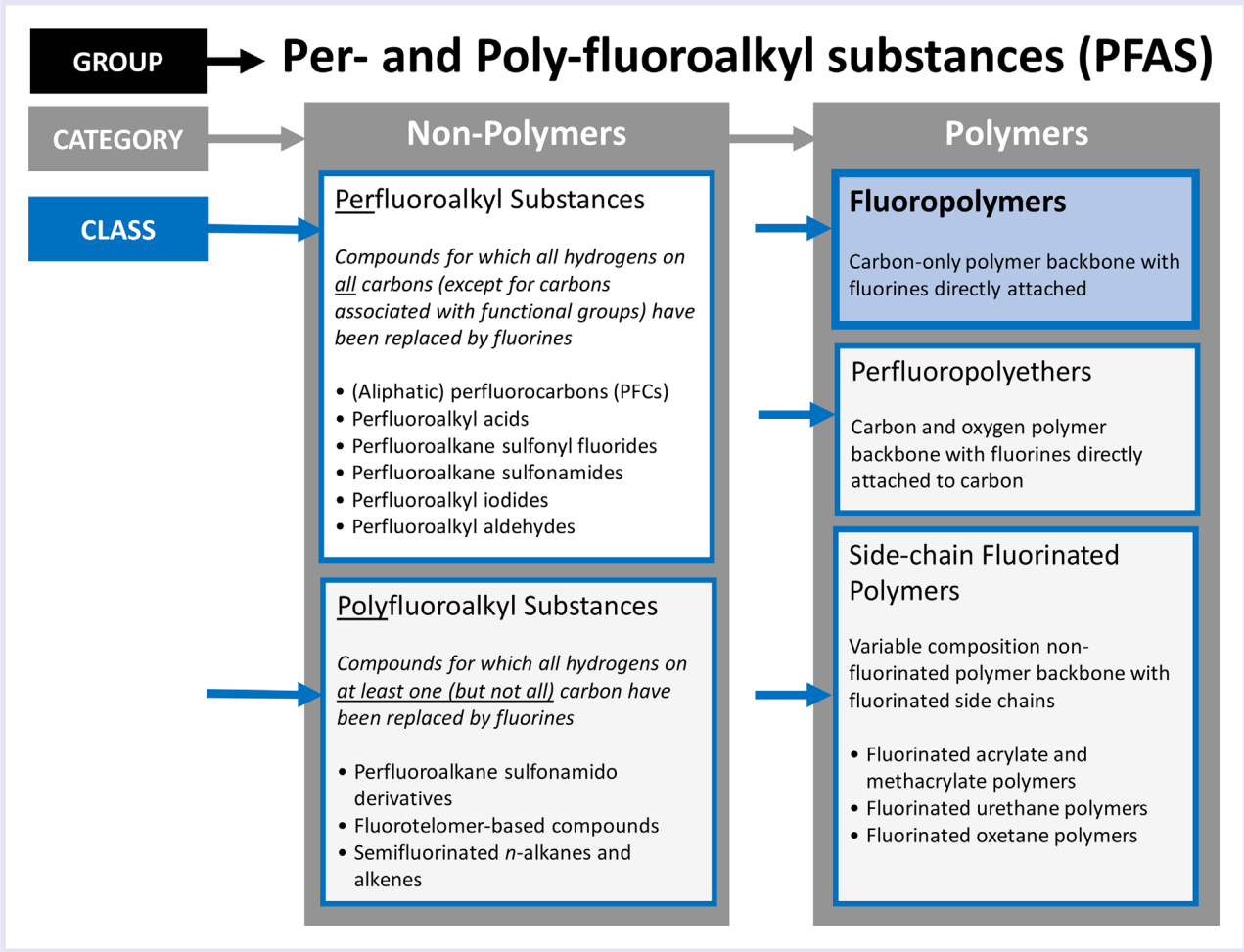


Figure 1. Per- and polyfluoroalkyl substances (PFAS).

them highly stable (Olabisi and Adewale 2015). Carbon atoms alone form the fluoropolymer backbone, each surrounded by an envelope of F atoms. Fluoropolymers are generally very high molecular weight (>100 000 Da); have high thermal, chemical, photochemical, oxidative, hydrolytic, and biological stability; have low flammability, neutral electrical charge, and resistance to degradation; have negligible residual monomers and low molecular weight oligomer content; have limited low molecular weight leachables; and have no reactive functional groups of concern (Gangal and Brothers 2015).

The unique properties of fluoropolymers include durability, mechanical strength, inertness, thermal stability in foreseeable use conditions, and resistance to chemical, biological, and physical degradation (Hougham et al. 1999). Table 1 shows performance characteristics required in various commercial fluoropolymer applications (Gangal and Brothers 2015; Dams and Hintzer 2016). For example, medical devices are successful when they are made from "biocompatible" biomaterials, that is, the material has the ability to perform with an appropriate host response in a specific situation (Williams 1987). The inertness of PTFE allows for its acceptance into the body. Moreover, PTFE flexibility and durability deliver mechanical integrity for the device's lifetime. The microstructure of PTFE can be modified to meet specific physiological needs (e.g., porous and open structure to facilitate tissue ingrowth), enhancing its utility in medical devices. In terms of end-use function, PTFE's inertness, physical properties (Ebnesajjad 2011), and the low level of residual monomer, oligomers, and low molecular weight leachables (Supplemental Data p 32–55) meet the requirements for low levels of contaminants and particulates in manufacturing environments essential for the food and beverage, pharmaceutical, medical, and semiconductor industries (Olabisi and Adewale 2015). Manufacturing applications requiring ultrapure high efficiency particulate air (HEPA) filtration use the finely controlled microporous PTFE membranes. Other components requiring a high degree of contamination control associated with patient care (e.g., dialysis tubing) also find the properties of PTFE essential. Durability in harsh conditions makes PTFE a superior material of choice in aerospace, environmental controls, energy production and storage, and electronics, as well as in technical apparel. The thermal stability of PTFE and FEP fluoropolymers provides improved fire safety risk over other polymers when used in plenums and structural

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Table 1. Fluoropolymer functionality and commercial applications

	Fluoropolymer characteristics									
	Durable		Inert		Functional			Stable		
Commercial application	Mechanical strength	Low particulation	Resistance to chemicals	Nontoxic, biocompatible, biological degradation resistant	Flexibility	Friction resistance	Low dielectric constant	Low leachables	Resistance to photolysis, oxidation, hydrolysis	Stability
Aerospace	X	—	X	—	X	X	X	—	X	X
Automotive industry	X	—	X	—	X	X	X	—	X	x
Medical devices	X	X		X	X	X	—	X	X	X
Pharmaceutical manufacture	X	X	X	X	X	—	—	X	—	X
Consumer outdoor apparel	X	—		X	X	—	—	X	—	—
Technical clothing (military, firefighters, first responders, medical personnel)	X	—	X	X	X	X	—	X	X	X
Consumer electronics	X	—	X	—	X	X	X	—	X	X
Wireless communications	X	—	X	—	X	X	X	—	X	X
Satellite navigation systems	X	—	X	—	X	X	X	—	X	X
Semiconductor industry	—	X	X	—	—	—	X	X	—	—
Building construction	X	—	—	X	X	—	X	—	X	X
Energy production and storage	X	X	—	—	—	—	X	X	X	X
Food and beverage production	X	X	X	X	X	X	—	X	X	—
Food protection and packaging	X	X	X	X	X	—	—	X		—
Drinking water filtration	—	X	X	X	—	—	—	X	X	—
Environmental protection	—	X	X	X	—	—	—	X	X	X

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geometries in aviation and standard building construction (Olabisi and Adewale 2015). In addition, chemical resistance to acids, bases, solvents, and chemical attack, combined with its unique conformable strength, makes PTFE an ideal coating for chemical process equipment, lining for process piping, sealants for gaskets and hoses, and fabricated parts for pumps, gears, and other mechanical parts that need this extreme resistance for functionality (Olabisi and Adewale 2015). The low dielectric constant of PTFE ensures the integrity of high speed–low signal loss systems as employed in the aerospace industry for flight controls, communication, and protection from extreme cold, moisture, and altitude changes (Dams and Hintzer 2016). These are lifesaving applications that are used in satellite systems for navigation, wireless communications, in-flight navigation, and shielding from electronic interference. Civil and military aviation depends on reliable performance of these systems for long service hours with minimal maintenance down times. In addition, PTFE provides reduced friction of moving parts (e.g., cable chains), preventing particulation during automated manufacturing in cleanroom environments (Dams and Hintzer 2016). This friction reduction is also uniquely beneficial in light load bearings, gears, cams, and other mechanical machine parts as well as in weaving fibers, yarns, and greases (Dams and Hintzer 2016).

ASSESSMENT OF POLYMERS

History

Prior to the mid-20th century, regulation of new chemical substances, mixtures, and polymers in general was very limited. National chemical inventories were created with notification requirements for new chemical substances, mixtures, and polymers. In the United States, new chemicals submitted to the US Environmental Protection Agency (USEPA) under the Toxic Substances Control Act (TSCA) (USC 1976) for addition to the US chemical inventory are reviewed for potential physical, chemical, and biological effects (environmental and mammalian), as well as for potential exposure to the environment and human populations. Over time, the USEPA regulatory scientists gained enough knowledge through the review of the thousands of data packages to develop tools to assist in the identification of physical–chemical properties, potential hazard, and potential exposure to assist in and expedite the chemical review and assessment process (Auer et al. 1990; Wagner et al. 1995; USEPA 2012; USEPA 2017b).

The predictive power and reliability of these approaches were tested and refined (Wagner et al. 1995). Over time, it was recognized that many of the physical–chemical properties, such as molecular weight, limit the ability of the chemical to cross the cell membrane and therefore limit its bioavailability. Further examination of general physical–chemical properties and their relationship to hazard potential of a given chemical led to the development of general principles or criteria for the identification of chemicals, including polymers, with low hazard potential. These criteria were developed for use by USEPA for its hazard evaluation of new polymers. The USEPA made this methodology available to the public to assist submitters interested in developing low hazard polymers (USEPA 1997a). In 1984, the USEPA published the polymer exemption rule to exempt low hazard polymers from certain notification requirements under the new chemicals program (USFR 1984). The polymer exemption rule incorporated the hazard criteria as part of the criteria to determine eligibility for exemption (USEPA 1997a, 2010).

The hazard criteria that support the PLC concept represent an extension of these principles and practices developed for (nonpolymeric) chemicals and rely heavily on physical–chemical properties that determine a chemical's bioavailability. In 1993, the Organisation for Economic Co-operation and Development (OECD) Expert Group on Polymers found that sufficient data existed to create a consensus document identifying the essential data elements to qualify a polymer as a PLC to human health and the environment (OECD 1993). By 2007, the OECD Expert Group on Polymers agreed that, "Polymers of low concern are those deemed to have insignificant environmental and human health impacts" (OECD 2009). Thus, there was agreement within the OECD that polymeric chemicals meeting these criteria have a low hazard potential. However, the integration of the criteria into a risk management framework may differ from country to country according to their individual regulatory mandate.

In a recent report commissioned by the European Commission (EC) (BIO by Deloitte 2015), the following countries agreed on the polymer properties predictive of adverse human health and environmental hazard: Australia, Canada, China, Japan, South Korea, Philippines, New Zealand, Taiwan, and the United States. Further, the report identified the eligibility criteria to be considered a PLC with respect to potential for adverse impact on health and the environment. The report also compiled existing polymer regulations outside the EU and proposed alternative options for EU polymer registration, including defining a category of a PLC and grouping polymers into families.

The PLC criteria are described in the following section. Note that there are some policy components, such as elemental composition, as well as the physical–chemical attributes, in the PLC criteria.

POLYMER OF LOW CONCERN CRITERIA

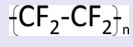
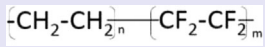
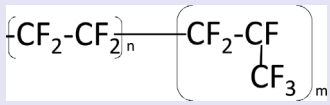
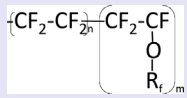
Here we describe each of the eligibility criteria for PLC and provide an assessment for the representative fluoropolymer PTFE. We will show that fluoropolymers, including PTFE, satisfy the widely accepted assessment criteria to be considered PLCs (Table 2) and therefore are considered to be of low hazard to human health and the environment.

Polymer composition

The polymer composition criterion requires structure and elemental composition of the polymer be described and identified (e.g., by Chemical Abstracts Service [CAS] number).

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Table 2. Fluoropolymers and PLC criteria

	Fluoropolymers			
	PTFE	ETFE	FEP	PFA
Assessment criteria[a]	CAS 9002-84-0	CAS 25038-71-5, 68258-85-5	CAS 25067-11-2	CAS 26655-00-5, 31784-04-0
Structure				
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to C)	Yes	Yes	Yes	Yes
Molecular weight	389 000–8 900 000[bc]	—	—	—
(M_n > 1000 Da and oligomer content < 1%)	520 000–45 000 000[bd]	530 000–1 200 000[ef]	241 000–575 000[eg]	200 000–450 000[eh]
Molecular weight distribution MW ÷ number average M_n (M_n and heterogeneity of MW distribution indicate if majority are >1000 or <1000 Da, which could penetrate the cell)	2.3[i]	1.4–2.7[f]	1.55–2.09[g]	1.7[j]
Wt % oligomer (see Figure 2) (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	Negligible	Negligible
Ionic character (cationic polymers associated with aquatic toxicity; polycationic with adverse human health effect)	Neutral	Neutral	Neutral	Neutral
RFGs[k] (some highly reactive functional groups associated with adverse human health and ecotoxicology effects, e.g., acrylates, isocyanates, anhydrides, aziridines)	<1 (see section *Reactive functional groups and RFG ratio to MW*)	<1 (see section *Reactive functional groups and RFG ratio to MW*)	<1 (see section *Reactive functional groups and RFG ratio to MW*)	<1 (see section *Reactive functional groups and RFG ratio to MW*)
FGEW[k] (typical value) (the lower the FGEW, the more reactive the polymer and the higher the potential for health and environmental impact)	$>10^5$–10^7	$>10^5$–10^6	$>10^5$	$>10^5$
Low molecular weight leachables (MW < 1000 Da able to enter cell)	<1 ppm	No active leachables by USP class VI[l] (121 °C)	No active leachables by USP class VI[l] (121 °C)	No active leachables by USP class VI[l] (121 °C)
Residual monomers (monomers have lower MW than polymers; typically more hazardous than polymers)	<1 ppm	<50 ppb	<50 ppb	<50 ppb
Ratio of residual monomers to molecular weight (typical value) (more low MW monomer content per mole increases bioavailability and hazard potential)	$\sim10^{-13}$ to 10^{-15}	$\sim10^{-13}$ to 10^{-14}	$\sim10^{-13}$	$\sim 10^{-13}$
Structural similarities to RFG of concern (increases potential risk of adverse effects)	None	None	None	None
Reference standard see also ISO 1133 (ISO 2011), ISO 12086 (ISO 2006)	ASTM D 4894 (ASTM 2015a), D 4895 (ASTM 2015b)	ASTM D 2116 (ASTM 2016a)	ASTM D 3159 (ASTM 2015c)	ASTM D 3307 (ASTM 2016b)

(*Continued*)

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Table 2. (*Continued*)

	Fluoropolymers			
	PTFE	ETFE	FEP	PFA
Assessment criteria[a]	CAS 9002-84-0	CAS 25038-71-5, 68258-85-5	CAS 25067-11-2	CAS 26655-00-5, 31784-04-0
Physical–chemical properties				
Water solubility (per USP 2011) (water solubility <10 mg/L showed generally low health concerns; 10 mL/L to 10000 mg/L had potential health concern)	Practically insoluble or insoluble (1×10^{-5} mg/L)	Practically insoluble or insoluble	Practically insoluble or insoluble	Practically insoluble or insoluble
Octanol–water partition coefficient, K_{OW} (higher K_{OW} associated with lipophilicity and a high potential to bioaccumulate or bioconcentrate)	NA	NA	NA	NA
Particle size (median mass aerodynamic diameter, MMAD, should be >5 μm)	100–500 μm (powders)	50–250 μm (powders)	50–250 μm (powders)	50–250 μm (powders)
	—	2–4 mm (pellets)	2–4 mm (pellets)	2–4 mm (pellets)
Stability				
Hydrolysis (breaking into M_n < 1000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Light (hν) (breaking into M_n < 1 000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Oxidation (breaking into M_n < 1000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Biodegradation (aerobic and anaerobic) (breaking into M_n < 1000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp (°C) (breaking into M_n < 1000 Da increases hazard potential)	260	150	200	260
Meets PLC criteria[a] (Y/N)	Yes	Yes	Yes	Yes

ASTM = American Society for Testing and Materials; CAS = Chemical Abstracts Service; Da = dalton; ETFE = ethylene tetrafluoroethylene; FEP = fluorinated ethylene propylene; FGEW = functional group equivalent weight; ISO = International Organization for Standardization; MMAD = median mass aerodynamic diameter; M_n = number average molecular weight; MW = molecular weight; MWD = molecular weight distribution; OECD = Organisation for Economic Co-operation and Development; PFA = perfluoroalkoxy polymer; PFPE = perfluoropolyether; PLC = polymer of low concern; PTFE = polytetrafluoroethylene; PVDF = polyvinylidene fluoride; PVF = polyvinyl fluoride; RFG = reactive functional groups; USEPA = US Environmental Protection Agency; USP = US Pharmacopeia.

[a]See OECD 2009 and BIO by Deloitte 2015 for details on characteristics of a "polymer of low concern."

[b]Molecular weight is number average molecular weight.

[c]Berry and Peterson 1951; Doban et al. 1956.

[d]Suwa et al. 1973.

[e]Molecular weight is weight average molecular weight.

[f]Tuminello et al. 1993.

[g]Tuminello 1989.

[h]Putnam 1986.

[i]Chu et al. 1989.

[j]Frick et al. 2012.

[k]For definition of reactive functional group; lists of low-, moderate-, and high-concern functional groups; and FGEW limits, see USEPA Polymer Exemption Guidance Manual (USEPA 1997b), BIO by Deloitte 2015 (p 191–192), and USEPA 2010. See Supplemental Data.

[l]In the USP<88> testing for "class VI," 2 g of the plastic (e.g., FEP, ETFE, or PFA) were extracted at 121 °C in: 1) 0.9% sodium chloride solution, 2) sesame oil, NF, 3) alcohol saline, and d) polyethylene glycol. The acute systemic toxicity and intracutaneous reactivity tests were conducted with those extracts. The intramuscular implantation was conducted with the plastic. Passing these 3 tests indicates that any leachables were not released in concentrations capable of causing these adverse effects, but does not result in a quantitative concentration of leachables. (See USP 2018.)

Note: The following are not addressed in this paper: PFPEs, side-chain fluorinated polymers, fluoroelastomers, PVF, and PVDF.

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Molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da

The number average molecular weight (M_n) and oligomer content are the most commonly used criteria for PLC assessment. The EU assessment report (BIO by Deloitte 2015) states that the "most potential health concern polymers have a number average molecular weight, Mn, < 1000 Da and oligomer content >1%." The higher the oligomeric content, the more likely a polymer is to be a health or ecotoxicological (OECD 2009, p 9). In fact, when comparing the potential health concern of polymers with varying percent oligomer content, "...the distribution of potential health concern polymers showed an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content" (OECD 2009, p 24).

Molecular weight (MW) is an important predictor of biological effect because very large molecules (>1000–10 000 Da) are too large to penetrate cell membranes (Supplemental Data in Beyer 1993, p 14). Because large molecular weight polymers cannot enter the cell, they cannot react with "target organs," such as the reproductive system, and are not bioavailable. "Therefore, as the M_n of a polymer increases, a reduced incidence of potential health concern effects might be expected" (OECD 2009, p 20).

An additional PLC consideration is the weight percent oligomers <1000 Da. Oligomers may be composed of, for example, dimers, trimmers, and tetramers, meaning they have 2-, 3-, and 4-monomer units, respectively. The EU report (BIO by Deloitte 2015) concluded that most potential health concern polymers have M_n of <1000 Da and oligomer content of >1%: "...the distribution of potential health concern polymers showed an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content" (OECD 2009, p 24).

Molecular weight distribution (MWD), also known as "polydispersity index," measures the heterogeneity of size of polymer molecules in a polymer. The MWD is an important parameter for predicting potential biological effects of polymers because although M_n may be a large value, low MW oligomers <1000 Da may be present, which could penetrate the cell.

Electrical charge (ionic character)

Electrical charge or ionic character can be anionic, cationic, amphoteric, or nonionic. Specifically, cationic polymers have been associated with aquatic toxicity (Auer et al. 1990; USEPA 1997a). Polycationic polymers that are water soluble or dispersible are of concern due to adverse human health (inhalation) effects (NICNAS 2016).

Reactive functional groups and RFG ratio to MW

A "reactive functional group" (RFG) is defined as an atom or associated group of atoms in a chemical substance that is intended or can be reasonably anticipated to undergo facile chemical reaction (USFR 2012). Some highly reactive functional groups (or a high ratio of RFGs per mole) have been associated with adverse human health and ecotoxicology (e.g., acrylates, methacrylates, isocyanates, anhydrides, aziridines) (USEPA 2010). Methods have been demonstrated to identify the functional end groups on fluoropolymers (Pianca et al. 1999).

The functional group equivalent weight (FGEW) is used to determine if the RFGs in a polymer are substantially diluted by polymeric material to allow the polymer to be a PLC (USEPA 1997b). The FGEW of a polymer is defined as the ratio of the M_n to the number of functional groups in the polymer. It is the weight of a polymer that contains 1 formula weight of the functional group. The FGEW is used as an indication of the degree of reactivity of the polymer; the lower the FGEW, the more reactive the polymer and the higher the potential for health and environmental impact (OECD 2009, p 10).

Low MW leachables

Low MW leachables are chemical molecules, either inorganic or organic, that migrate (i.e., leach) out of the polymer. These could be residual monomers or oligomers resulting from incomplete polymerization processes, surface residues, or other chemicals used in the manufacturing processes (e.g., initiators, catalysts, chain transfer agents, surfactants). Chemical analysis, by techniques such as thermal gravimetric analysis (TGA), gas chromatography mass spectrometry (GC-MS), or liquid chromatography mass spectrometry (LC-MS) are used to identify low MW leachables.

Low MW leachables are critically important to the potential for a polymer to affect health and the environment, given that they may be able to migrate out of the polymer and cross cell membranes to potentially react with biomolecules. In a report to the EU (BIO by Deloitte 2015) the polymer policies for 10 countries around the world, including the EU REACH handling of polymers, were reviewed. The report concluded that "Polymers with <1% MW <1000 Da and low water extractivity are not able to cause systemic effects which are toxicologically or ecotoxicologically relevant."

Monomers, by nature, are reactive. Unreacted monomer left in a polymer may migrate out of the polymer to react with biomolecules to cause potential adverse effects. Regulatory authorities (BIO by Deloitte 2015) and the OECD Expert Group on Polymers (OECD 2009) agree that the residual monomer content of a polymer is critical to determining if it qualifies to be a PLC.

Particle size

Particle size is also a PLC criterion. Particles that are small enough to reach the deep lung upon inhalation are often associated with adverse health effects. Therefore, to qualify as a PLC, median mass aerodynamic diameter (MMAD) of the polymer particle size should be greater than 5 μm.

Structural and elemental composition

In the United States, Chemical Categories of Concern are the result of the review of new chemicals by the USEPA under the TSCA (see https://www.epa.gov/reviewing-new-chemicals-under-toxic-substances-control-act-tsca/chemical-categories-used-review-new). New chemicals submitted to the USEPA

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under the TSCA for addition to the US chemical inventory are reviewed for potential chemical, physical, and biological effects (environmental and mammalian). The USEPA groups Premanufacture Notice (PMN) chemicals with shared chemical and toxicological properties into categories, enabling both PMN submitters and USEPA reviewers to benefit from the accumulated data and past decisional precedents, allowing reviews to be facilitated. The categories describe the molecular structure, boundary conditions such as MW, equivalent weight, the log of the octanol–water partition coefficient, log P, or water solubility, and standard hazard (mammalian and ecological) and (environmental) fate tests to address concerns. The categories include chemicals for which sufficient history has been accumulated so that hazard concerns and testing recommendations vary little from chemical to chemical within the category. (See Supplemental Data, p 30, for details on USEPA's chemical categories.)

Elemental composition

The elemental composition is a factor in the assessment of the eligibility of polymers for reduced notification requirements. The exclusion of polymers under this step is not a conclusion of hazard but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process. These elemental requirements differ across jurisdictions as covered in the report to the EU on global regulatory approaches to polymer assessment (BIO by Deloitte 2015). For example, in the EU under REACH it is proposed that polymers composed from among these elements, covalently bound to C, have reduced hazard: H, N, O, Si, S, F, Cl, Br, or I (BIO by Deloitte 2015). In contrast, the USEPA Polymer Exemption Rule states that a polymer is eligible for reduced agency review when it has at least 2 of the following elements: C, H, O, N, S, or Si (USFR 1995).

Water and lipid solubility and the octanol–water partition coefficient

Water solubility is the extent to which a compound will dissolve in water. According to the OECD 2009 meeting of the Expert Group on Polymers, polymers with "negligible" water solubility, or those described as "hydrophobic" have been represented with a water solubility of 0.000001 mg/L (1×10^{-6} mg/L; assigned arbitrarily) (OECD 2009). That is equivalent to 1 ppt, a very conservative definition.

Based on the data set studied, the OECD Expert Group on Polymers concluded "A higher proportion of polymers with intermediate water solubility values (10 mL/L–10 000 mg/L) displayed potential health concern. Polymers with water solubility <10 mg/L showed generally low health concerns" (OECD 2009, p 10). Although not a solubility metric, a polymer capable of absorbing its weight in water was associated with increased inhalation cancer risk in rats (OECD 2009).

The octanol–water partition coefficient (K_{OW}) is another criterion to assess chemicals and their environmental and health impact. The K_{OW} is a physical–chemical property at equilibrium to represent the lipophilic or hydrophilic nature of a chemical, the distribution of a compound in octanol, representing the lipophilic nature, to its solubility in water, representing the aqueous nature. The higher the K_{OW}, the more lipophilic the compound. Typically, a K_{OW} >5000 or a log K_{OW} >5 means high lipophilicity and, thus, a high potential to bioaccumulate or bioconcentrate. Numerous studies showed that K_{OW} was useful for correlating structural changes of drug chemicals with the change observed in some biological, biochemical, or toxic effect (LaGrega et al. 2010). It has been found to be related to water solubility, soil or sediment adsorption coefficients, and bioconcentration factors for aquatic life. According to the Stockholm Convention, a bioconcentration factor of >5000 and a log K_{OW} >5 is used as a criterion for bioaccumulation.

Stability

Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. As was previously described in the Polymer of Low Concern section under the *Molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da* heading, molecules with M_n <1000 Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment.

Abiotic stability

Polymers are stable; monomers are not. Abiotic degradation may involve sunlight, water, or oxygen. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Hydrolytic degradation of polymers is another potential way to break the polymer bonds, creating smaller oligomers that may be bioavailable. Chemical oxidation is a reaction involving the loss of electrons from 1 atom to another.

Biotic stability: aerobic, anaerobic, and in vivo

Biotic stability is assessed by whether or not the polymer is degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic) conditions; in vitro and in vivo stability studies demonstrate this. In vivo biodegradation involves the breaking of the polymer bonds by the action of bacteria, enzymes, and oxidants within the organism.

Thermal stability

Thermal stability of a polymer can be assessed when used as intended under normal, foreseeable use conditions or in extreme temperatures during disposal, such as by incineration. Thermal stability testing may involve Thermal Gravimetric Analysis (TGA), which determines mass loss over time and temperature of a test substance.

ASSESSMENT OF FLUOROPOLYMERS ACCORDING TO PLC CRITERIA

Characteristics of a PLC have been described in the preceding section. These criteria represent the combined

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experience and knowledge of global regulatory authorities on factors demonstrated to be predictive of health and environmental hazards of polymers (OECD 2009; BIO by Deloitte 2015). Four fluoropolymers were assessed according to the PLC criteria. The results are summarized in Table 2, and an expanded discussion on specific criteria is provided in the remainder of this section.

Polymer composition

Fluoropolymers satisfy the PLC criterion of polymer composition. Polytetrafluoroethylene is a homopolymer of tetrafluoroethylene (TFE). Polytetrafluoroethylene can be a homopolymer (1 monomer) or it can be a modified homopolymer containing TFE widely and not more than 1% of another fluoromonomer (see ASTM 2015). Polytetrafluoroethylene contains only C and F having a $–CF_2–$ backbone terminated on both ends of each polymer chain with $–CF_3$. In unique cases, based on production method and ingredients used, commercial PTFE may have end groups that contain O, H, N, or S, depending on the initiator or chain transfer agent used in polymerization (Pianca et al. 1999). Polytetrafluoroethylene meets the compositional criterion to be a PLC.

Molecular weight, M_n, MWD, and % oligomer <1000

Fluoropolymers satisfy the PLC criterion of MW, M_n, MWD, and % oligomer <1000. Fluoropolymers are practically insoluble in water and all organic solvents. Therefore, standard MW methods are not applicable for fluoropolymers like PTFE and have been replaced by standardized indirect methods that use specific gravity and melt flow index to determine MW of PTFE and fluoropolymers (see Supplemental Data, p 27–28). Standard Specific Gravity (SSG) and Melt Flow Rate (MFR) are more conveniently and frequently used with fluoropolymers rather than rheological and dynamic light scattering methods (Chu et al. 1989; Starkweather and Wu 1989; Tuminello 1989; Tuminello et al. 1993). Polytetrafluoroethylene has an M_n of 500 000 to 9 000 000 Da (Berry and Peterson 1951; Doban et al. 1956; Suwa et al. 1973; Putnam 1986; Chu et al. 1989; Tuminello 1989; Tuminello et al. 1993; Frick et al. 2012). Therefore, PTFE, as a very high molecular weight polymer, cannot cross cell membranes, is not bioavailable, and cannot bioaccumulate or be toxic (see Supplemental Data, p 14). High molecular weight fluoropolymers, such as PTFE, therefore meet the PLC criterion for having MW that prevents them from entering the cells. Polytetrafluoroethylene has negligible (<<1%) oligomeric content (Starkweather and Wu 1989), as does FEP (Figure 2.) In summary, fluoropolymers are high molecular weight polymers with narrow MWD and negligible oligomer content.

Reactive functional groups and RFG ratio to MW

Fluoropolymers satisfy the PLC criterion of RFGs and RFG ratio to MW. Polytetrafluoroethylene most typically has a terminal $–CF_3$ group that is not an RFG. When this is not the case, the most common terminal group is –COOH, which is

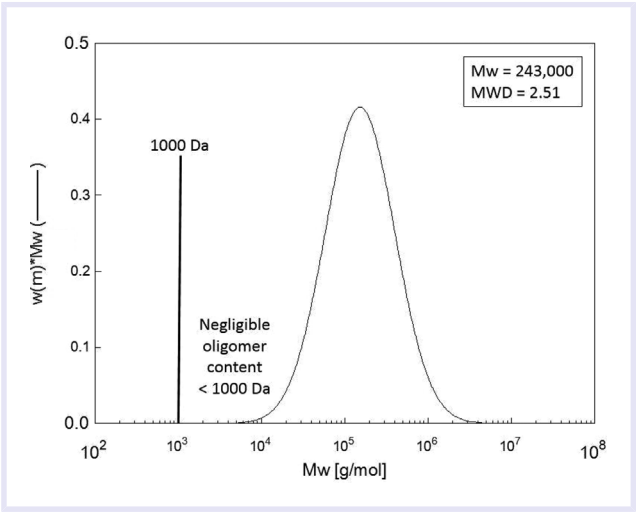


Figure 2. A fluorinated ethylene propylene (FEP) fluoropolymer molecular weight distribution from a rheological study. MW = molecular weight; MWD = molecular weight distribution.

categorized by the USEPA as a low-concern functional group. In unique cases, based on production method and ingredients used, PTFE may have end groups that may contain O, and H, N, or S, depending on the initiator or chain transfer agent used in polymerization. Fluoropolymers have a very high MW, which yields an FGEW on the order of 10^5 or more, well beyond the FGEW threshold of concern.

Low MW leachables

Fluoropolymers satisfy the PLC criterion of low MW leachables. Concentration of leachables from fluoropolymers, particularly PTFE "fine powder" (ASTM [2015] 4895-16 Type I fine powder definition), are typically very low (<1 ppm) (see Supplemental Data). This finding can be explained by the sensitivity of the PTFE polymerization reaction to contamination and is due to the postpolymerization processing steps aggressively exercised to wash out residuals and drive off volatiles. In order to achieve high MW polymerization of TFE, all traces of telogenic H- or Cl-bearing impurities must be removed (Ebnesajjad 2011; Supplemental Data).

In the analysis done on PTFE (see Supplemental Data, p 32), residual TFE monomer was not detected in PTFE resin by headspace GC-MS with a limit of detection of 1 ppm. In addition, publicly available analytical data from independent industry authorities demonstrate that TFE is not detected in finished articles made from fluoropolymers at detection limits down to about 0.01 ppm wt/wt (SPI 2005). Table 3 compares the molecular weight and the 8-h time weighted average (TWA) (American Conference of Governmental Industrial Hygienists [ACGIH], threshold limit value [TLV]), for monomers used to make fluoropolymers (ACGIH 2010). The TWAs are the exposure levels to which a worker could be exposed in an 8-h shift without adverse effects. The monomers have significantly lower MW, have lower TWAs, and are reactive. Note that the fluoropolymers are high MW, have no TWAs, and are inert. Table 3 illustrates that polymers do not have the same health hazards or MWs as their monomers.

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Table 3. Fluoropolymer and monomer molecular weight and TLV data

Substance	CAS Nr	Molecular weight	ACGIH TLV 8-h TWA
Monomer: TFE	116-14-3	100	2 ppm
Monomer: Ethylene	74-85-1	28	200 ppm
Monomer: HFP	116-15-4	150	0.1 ppm
Monomer: PPVE	1623-05-8	266	200 ppm (vendor limit)
Polymer: PTFE	9002-84-0	389 000–45 000 000	None
Polymer: ETFE	25038-71-5, 68258-85-5	530 000–1 200 000	None
Polymer: FEP	25067-11-2	241 000–575 000	None
Polymer: PFA	26655-00-5, 31784-04-0	200 000–450 000	None

ACGIH = American Conference of Governmental Industrial Hygienists (ACGIH 2010); CAS = Chemical Abstracts Service; ETFE = ethylene tetrafluoroethylene; FEP = fluorinated ethylene propylene; HFP = hexafluoropropene; PFA = perfluoroalkoxy polymer; PPVE = perfluoropropylvinyl ether; PTFE = polytetrafluoroethylene; TFE = tetrafluoroethylene; TLV= threshold limit value; TWA = time weighted average.

Elemental composition

Fluoropolymers meet the widely accepted elemental composition criterion (BIO by Deloitte 2015). The USEPA, in updating its Polymer Exemption Rule, which applies to new polymers only, changed some review procedures to address certain side-chain fluorinated polymers that may degrade into small, mobile, and persistent substances (USFR 2010). This has contributed to confusion regarding the assessment of fluoropolymers. The exclusion of polymers under this step is not a conclusion of hazard, but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process.

When USEPA updated the polymer exemption rule in 2010, the agency excluded polymers containing $–CF_3$ or larger chains that are covalently bound to C. The agency's rationale for the change was "...because the Agency has receiving information which suggests that polymers containing PFAS (perfluoroalkyl sulfonates) or PFAC (perfluoroalkyl carboxylates) may degrade and release fluorochemical residual compounds in the environment. Once released, PFAS or PFAC are expected to persist in the environment, may bioaccumulate, and may be highly toxic..." (USFR 2006).

Although USEPA recognized that PFAS and PFAC chemicals with longer C chain lengths (C7 and longer) may be of greater concern, it stated that there is insufficient evidence at this time, however, to definitively establish a lower C chain length limit to meet the "will not present an unreasonable risk" finding, which is the determination necessary to support an exemption under section 5(h)(4) of TSCA. The USEPA believes that it is possible for polymers containing these other types of perfluoroalkyl moieties to also degrade over time in the environment, thereby releasing the perfluoroalkyl moiety (USFR 2006).

The updated USEPA polymer exemption definition in 2010, summarized in the Objective and Rationale section for the Final Rule, may imply that new fluoropolymers with pendant or terminal –CF3 groups, such as FEP, do not meet the polymer exemption eligibility for reduced PMN reporting (USFR 2010). However, the summary definition in USFR (2010) lacks critical context found in the preamble to the Final Rule, which elaborates the conditions that would be necessary to exclude a perfluoro chemical from the polymer exemption:

- The first condition is cited above, "...polymers containing PFAS (perfluoroalkyl sulfonates) or PFAC (perfluoroalkyl carboxylates)..." where the C or S atom is an integral part of the polymer molecule; and
- the second condition notes that, polymers containing fluorotelomers or "...perfluoroalkyl moieties that are covalently bound to either a carbon or sulfur atom where the carbon or sulfur atom is an integral part of the polymer molecule can be attached to the polymers using conventional chemical reactions."

For the PFAS and PFAC as described by USEPA, the agency offers a clarification about the nature of the linkage, stating "How these materials are incorporated into the polymer is immaterial (they may be counter ions, terminal/end capping agents, or part of the polymer backbone)" (USFR 2010). The key characteristic is the presence of a –CF3 group that is attached to, or forms part of, the polymer backbone and "this link (between the polymer backbone and the –CF3 group) is susceptible to degradation and cleavage." (USFR 2010). Thus, in USEPA's review, the presence of –CF3 group is important because it is a structural alert to consider potential degradation products. The USEPA will make a determination whether the potential degradation of the polymer in question presents an unreasonable risk to health and the environment under TSCA. As shown in Table 2, these fluoropolymers are not subject to degradation.

Water and lipid solubility and the octanol–water partition coefficient

Fluoropolymers, such as PTFE, are not soluble in octanol or water. Therefore, it is not possible to measure or calculate a

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K_{OW}. Because solubility in octanol is predictive of lipid solubility, PTFE cannot dissolve in cell membrane lipids to gain access to cellular contents, nor is it small enough to enter the cell due to its very high MW. Because PTFE cannot enter the cells, it is not capable of bioaccumulation or bioconcentration in aquatic life.

Stability

Under normal, foreseeable uses, fluoropolymers are stable. Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. Molecules with M_n <1000 Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment. Fluoropolymers, in general, have exceptional chemical and thermal stability; that is why they are so unique and useful. This is due to very strong C–F bonds that are stable under even extreme conditions (Gangal and Brothers 2015). Polytetrafluoroethylene is inert and chemically resistant to all solvents except molten alkali metals, chlorine trifluoride, and oxygen difluoride. Polytetrafluoroethylene, as a representative fluoropolymer, has the best chemical resistance of all currently known polymers and is insoluble in all known solvents, including water (Drobny 2006).

Abiotic stability

Polymers are stable; monomers are not. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Although PTFE will rapidly degrade in ionizing radiation (e.g., gamma radiation or high energy electron-beam radiation), it is resistant to photolysis (Drobny 2006). Photoinduced reactions with fluoropolymers do not occur. In addition, hydrolysis is a reaction involving the breaking of a bond in a molecule using water. The fluorine envelope surrounding the C backbone of PTFE is very hydrophobic. Fluoropolymers, such as PTFE, are hydrolytically stable, water resistant, and are not subject to hydrolysis catalyzed degradation (Arkles 1973). Finally, chemical oxidation is a reaction involving the loss of electrons from one atom to another. Because the C–F bond is one of the strongest known, and F is the most electronegative element, the C–F bond is thermodynamically stable, unfavorable to lose electrons (i.e., to oxidize) (Arkles 1973).

Biotic stability: aerobic, anaerobic and in vivo

Fluoropolymers like PTFE are biologically inert and not degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic conditions); in vitro and in vivo studies demonstrate this. In vivo degradation involves the breaking of the polymer bonds due to bacteria and other enzymes and oxidants. For example, PTFE hernia patches explanted from patients and examined by scanning electron microscopy, attenuated total reflectance Fourier transform infrared spectroscopy, modulated differential scanning calorimetry, and optical microscope showed no degradation in vivo (King et al. 2013).

Thermal stability

Fluoropolymers, when used as intended under normal, foreseeable use conditions as specified in Table 2 (or "continuous processing temperature") are thermally stable (Puts et al. 2014). The fluoropolymer industry has provided significant information on appropriate use of fluoropolymers (SPI 2005). Thermal gravimetric analysis determines mass loss over time and temperature of a test substance. Polytetrafluoroethylene is one of the most thermally stable polymers. Polytetrafluoroethylene's continuous processing temperature is 260 °C (SPI 2005). This means that PTFE could remain for decades at 260 °C and not decompose (SPI 2005 see percent mass lost per hour at maximum continuous processing temperature).

Outside of normal, foreseeable use conditions (also known as "misuse"), when fluoropolymers are held at temperatures above their recommended processing temperatures, they degrade. Upon decomposition, fluoropolymers generate volatile degradation products (SPI 2005). At 450 °C, the decomposition of PTFE "only proceeds at a rate on the order of one percent per hour. It is not until considerably above the polymer first-order transition temperature (329 °C) that substantial decomposition is observed" (Arkles and Bonnett 1974). As the temperatures increase above recommended processing temperatures, the rate of generation rises and may sufficiently degrade the polymer to produce hazardous gaseous byproducts and polymer (particulate) fume fever (SPI 2005). Temperature, availability of O, the physical form of the polymer article, and the residence time at elevated temperature factor into the ultimate nature of the decomposition products (SPI 2005), mainly fluoroalkenes, hydrogen fluoride, oxides of C, and lower molecular weight fluoropolymer particulates. For PTFE, TFE is the principle gaseous product observed at temperatures near 330 °C. See Supplemental Data for additional information regarding overheating PTFE.

PRODUCT-SPECIFIC REGULATORY REQUIREMENTS

Certain product-specific regulations, such as those for medical devices and food contact for the United States and the EU, require the development of additional data beyond what is required to conduct a PLC evaluation. The following text will discuss food contact requirements for the United States and the EU, and medical device requirements.

Data requirements for food, pharmaceutical, and medical device applications

There are country-specific data requirements for fluoropolymer use in food, pharmaceutical, and medical device applications because the intended use of these products has the potential to directly or indirectly introduce the product into the human body. An extensive fluoropolymer data set has been developed by W.L. Gore for these uses. The clinical history of the safe implantation of more than 40 million PTFE medical devices over 40 y, extensive toxicity data, preclinical

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data, and chemical extractables and migration testing confirmed that fluoropolymers are not bioavailable. Although the data requirements have evolved over time for contacting food, pharmaceuticals, or use in medical devices, the data (some of which are provided in the present article, the Supplemental Data for the present paper, regulatory submissions, and product literature) confirm the conclusion that fluoropolymers are safe for these intended uses and support the conclusion that fluoropolymers should be considered PLCs.

Polymer of low concern data and US and European Union food contact requirements

In general, the data required to support a PLC determination are helpful, but insufficient to qualify a material for food contact use. Submissions to the US Food and Drug Administration (USFDA) to support new food contact substances require extensive data submissions, including, for example, the nature and amount of nonvolatile extractives (USFDA 2017). Fluoropolymers, however, are not new substances in applications where they come in contact with food and have longstanding acceptance by regulators. In the United States, the USFDA is responsible for regulation of materials that come in contact with food and are considered "indirect food additives," specifically polymers (USFR 2016a). Food storage or food packaging materials, such as the fluoropolymers PTFE, FEP, and PFA, are "perfluorocarbon resins" acceptable for use by application and material type, provided they meet the extractable limits specified in the regulation (USFR 2016b).

Similarly, the European Food Safety Agency (EFSA) provides recommendations to the European Commission (EC) within the EU for the regulation of food contact materials, requirements for their evaluation, and authorization of acceptable uses (EC 2004). Polymer clearance is based in part upon the fact that polymers will not migrate into food due to their high molecular weight. The EU focuses on potential low molecular weight moieties, such as residual monomers and leachables, rather than on the polymer itself. The EU food contact regulation requires that monomers, other starting substances, and additives used to produce food contact polymers should be risk assessed and authorized (EU 2011). The regulation lists authorized substances that are permitted to have food contact (EU 2011). This regulation also sets the specific migration limit (SML), which is the maximum permitted amount of substance in food that has been determined not to pose a risk to human health, specifically for individual chemicals (e.g., monomer) (EU 2011). Note that these limits exist whether or not the substance is present in the food contact material (FCM). The monomers, other starting substances, and additives used to produce fluoropolymers for food contact (e.g., PTFE, FEP, and PFA) have been authorized for food contact uses. Representative SMLs for these monomers, additives, and starting substances relevant for fluoropolymers are given in the Supplemental Data (p 14).

Polymer of low concern data and medical device regulatory requirements

Satisfaction of the PLC criteria is insufficient to satisfy medical device requirements. Formal biocompatibility evaluations are required by the USFDA and other global regulatory authorities to support submissions for approval of medical devices and pharmaceuticals (e.g., combination products, such as drug-eluting stents or prefilled single-dose syringes). The International Organization for Standardization (ISO) 10993 Biocompatibility of Medical Devices standards describe a broad array of biocompatibility tests that require consideration for each new device or significant changes to existing devices (ISO 2009). Over the years, medical devices containing PTFE (or expanded PTFE) have been evaluated using ISO 10993 and US Pharmacopeia (USP) Class VI standards (USP 2011) and have been determined to be biocompatible in their intended uses.

The ISO 10993 standards provide guidance for evaluation of the biological response to a medical device. The USFDA, as well as most international regulatory agencies, recognizes and uses ISO 10993 standards to guide safety evaluations of medical devices submitted for their approval. Requirements to demonstrate the biocompatibility of medical devices are set forth in ISO 10993-1, and regulatory authority–specific requirements (e.g., PMDA 2003; USFDA 2016). In addition, country pharmacopeial organizations also specify testing required for biological reactivity of drugs (e.g., US Pharmacopiea, EU Pharmacopiea, Japan Pharmacopiea). The ISO requirements are categorized by the nature of body contact (e.g., mucosal membrane, circulating blood, tissue, bone, dentin) and duration of contact ($<$24 h, $\geq$1 d $\leq$30 d, $>$30 d). Depending on the nature and duration of contact, requirements include cytotoxicity, irritation, sensitization, implantation, acute–subchronic–chronic systemic toxicity, material-mediated pyrogenicity, hemocompatibility (e.g., hemolysis, thrombogenicity, and complement activation), genotoxicity (in vitro and in vivo), carcinogenicity, and developmental toxicity. (See Supplemental Data p 15 for a list of ISO 10993 biocompatibility tests.)

MEETING PLC CRITERIA PRECLUDES A FINDING THAT A CHEMICAL IS OF HIGH CONCERN

Just as regulatory frameworks have mechanisms to identify materials of low concern such as PLCs, they also have mechanisms to identify chemicals of high concern. For example, under REACH, a mechanism exists to identify substances of very high concern (SVHCs). Having demonstrated that fluoropolymers like PTFE should be considered PLCs, we will also demonstrate that these fluoropolymers cannot be SVHCs under REACH, do not meet the PM and PMT criteria proposed by UBA, and do not meet the criteria for listing as a POP under the Stockholm Convention.

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Fluoropolymers and EU REACH SVHC, CMR, PBT, vPvB, and endocrine disrupting chemical (EDC) criteria

According to the European Chemicals Agency (ECHA), SVHCs are defined in Article 57 of Regulation (EC) Nr 1907/2006 ("the REACH Regulation") (EC 2006) and include substances that are

- "Carcinogenic, mutagenic or toxic to reproduction (CMR), meeting the criteria for classification in category 1 or 2 in accordance with Directive 67/548/EEC. This directive was replaced in beginning of 2009 by the new EU regulation (EC) No 1272/2008 on classification, labeling and packaging of chemical substances and mixtures, the so-called CLP Regulation. According to the new CLP Regulation these substances shall be classified as 1a or 1b."
- "Persistent, Bioaccumulative and Toxic (PBT) or very Persistent and very Bioaccumulative (vPvB) according to the criteria in Annex XIII of the REACH Regulation."
- "Identified, on a case-by-case basis, from scientific evidence as causing probable serious effects to human health or the environment of an equivalent level of concern as those above (e.g., EDCs)."

Under REACH, polymer substances are not registered, but the monomers they are composed of are registered, and the registration must be supported by data submissions that are tiered on the basis of tonnage (see EC 2006, Annex VII). The REACH definition of polymer includes materials with as few as 3 repeating units. But such a small molecule would not meet common industry standard definitions for fluoropolymers (ASTM 2015). It is highly unlikely that fluoropolymers meeting the PLC criteria would exhibit the criteria of an SVHC under REACH. Fluoropolymer data developed for other regulatory needs support the predictive value of the PLC assessment criteria and demonstrate the low hazard potential of this class of PFAS. Due to their physical–chemical properties, PLCs are not bioavailable to cause toxicity or to bioaccumulate. Toxicity study data on PTFE in the Supplemental Data (p 15–27), for example, demonstrate a lack of toxicity, including genotoxicity. Although fluoropolymers are persistent, they are not bioaccumulative or toxic and therefore do not meet the PBT criteria.

Fluoropolymers and German UBA–proposed PMT criteria

As regulatory frameworks continue to evolve, more work is needed in the area of PFAS classification to ensure that regulations are appropriate in scope and proportionality. Although some well-known PFAS would qualify as PM or PMT substances as proposed by the UBA (2017), fluoropolymers do not possess these characteristics. Although fluoropolymers are highly stable (persistent), they do not meet the criteria to be mobile or toxic. To demonstrate this point, PTFE, a high molecular weight fluoropolymer and a member of the PFAS group, is assessed (in the last 4 paragraphs of this section) according to the proposed UBA criteria (UBA 2017).

Briefly, the changes to PM and/or PMT assessment proposed by UBA address applicability, persistence, mobility, and toxicity. The UBA proposes an initial step involving assessment of the chemical composition of a substance to determine if the substance is within the applicability domain of the proposed new assessment criteria. The UBA notes that currently only identifiable organic and organometallic chemicals are considered, and purely inorganic substances or substances of unknown or variable compositions, complex reaction products, or biological material are excluded (UBA 2017).

With respect to persistence, UBA proposes that the criterion for persistence be the same as in Annex XIII of REACH, which considers degradation half-lives in marine water, fresh- or estuarine water, marine sediment, and soil as part of the PBT/very persistent, very bioaccumulative (vPvB) assessment criteria; these degradation half-life criteria range from 40 to 180 d. The UBA proposes that a substance meets the persistent criterion if the degradation half-life in marine water at pH 6 to 8 and 12 °C is higher than 60 d, the half-life in fresh- or estuarine water at pH 6 to 8 and 12 °C is higher than 40 d, the half-life in marine sediment at pH 6 to 8 and 12 °C is higher than 180 d, the half-life in fresh- or estuarine water sediment at pH 6 to 8 and 12 °C is higher than 120 d, or the half-life in soil at pH 6 to 8 and 12 °C is higher than 120 d.

The UBA proposes that the mobility criterion for a persistent chemical should be determined on the basis of 2 considerations. First, the water solubility of a substance at pH 6 to 8 and 12 °C must be greater than or equal to 150 μg/L, and the log K_{OC} at pH 6 to 8 and 12 °C must be less than or equal to 4.5. The UBA notes that the mobility criterion should be applied only to substances that have fulfilled the criterion for persistence.

Lastly, with respect to toxicity, UBA proposes a 5-part test for involving data to understand if the substance is carcinogenic, germ cell mutagenic, or toxic for reproduction; if there is other evidence of chronic toxicity; and if there is evidence for effects on or via lactation. The derived no adverse effect level (DNEL) must be less than or equal to 9 $\mu g \cdot kg^{-1}d^{-1}$. The UBA notes that the first 2 considerations are the same criteria defined in Annex XIII of REACH as part of the PBT/vPvB assessment criteria regarding human health. The next 2 criteria specifically address concerns for drinking water exposure and are based on Regulation EC No 1272/2008 (EC 2008) and Cramer class II (Cramer et al. 1978) for substances exhibiting moderate or low biological activity, respectively. The DNEL criterion is based on Kalberlah et al. (2014).

Regardless of the arguments concerning the scientific foundation and credibility of the changes proposed by UBA to REACH PM and PMT assessment criteria, the central question with respect to PTFE is whether chemical-specific assessment would lead to an outcome different from that assuming PTFE behaved similarly to other PFAS substances. Polymers, including fluoropolymers, are different from non-polymeric chemicals and may be regulated differently. Because of these differences, it is recognized that some data requirements may not be applicable to polymers (EU 2011) For example, as we have shown, the physical–chemical criteria of PLC are predictive of lack of hazard.

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With respect to applicability, PTFE is not a substance currently registered under REACH because it meets the REACH definition of a polymer substance: "a molecule that contains a sequence of at least 3 monomer units, which are covalently bound to at least one other monomer unit or other reactant" (EC 2006). However, because PTFE is an identifiable organic substance, the proposed UBA framework for assessment using the proposed PMT criteria would be applicable. Further, PTFE is highly stable and persistent in the environment. It is resistant to thermal degradation, being stable for decades at temperatures up to 260 °C (SPI 2005); is stable in terms of hydrolysis, oxidation, and light (Brydson 1999); and is stable in terms of anaerobic and aerobic degradation (King et al. 2013). Therefore, PTFE would fulfill the UBA's proposed persistence criterion.

In contrast, PTFE is practically insoluble in water and, therefore, is not mobile in the environment. Using the descriptive solubility table for the USP (2011), the water solubility of PTFE would be classified as practically insoluble (1×10^{-5} mg/L or 0.01 μg/L) to very slightly soluble (1×10^{-4} mg/L or 0.1 μg/L) (USP 2011). The mobility of PFTE is 1000 to 10 000× lower than UBA's proposed mobility criterion. Therefore, PTFE does not fulfill UBA's proposed mobility criterion and would not be classified as a PM or PMT substance.

A similar negative finding for PTFE pertains to toxicity. The average molecular weight of PTFE is too large for the polymer to cross a cell membrane, which means it is not bioavailable or toxic. Polytetrafluoroethylene has been tested extensively in the United States and European Union to assess commercial applications for food contact and global medical device regulations (see Supplemental Data for additional details). Results demonstrate the absence of toxicity. Therefore, PTFE does not fulfill UBA's proposed toxicity criterion and would not be classified as a PM or PMT substance (Table 4).

Fluoropolymers and the Stockholm Convention POP criteria

In addition to country and regional regulations, there are global legally binding instruments, such as the United Nations Environment Programme–administered conventions on chemicals and waste (UNEP 2001), such as the Stockholm Convention on Persistent Organic Pollutants. The Convention aims to eliminate POPs by eliminating their production, reducing their use, or limiting their use through a cradle-to-grave approach. For the listing of new chemicals into the Convention, numeric or other criteria have been set for the screening of proposed compounds. Stockholm Convention Criteria (annex D) are compared to those of the USEPA, EU REACH, and the UBA-proposed PMT (Table 4). Fluoropolymers meet the persistence criterion only, not the bioaccumulative, toxic, or mobile criteria.

Fluoropolymers satisfy widely accepted criteria to be considered PLCs. Their physical–chemical properties prevent bioavailability, bioaccumulation, toxicity, and degradation. They have negligible monomer, oligomer, and leachable content and no reactive functional groups with high toxicity. These comparisons of PLC and various regulatory assessment criteria demonstrate that, in the realm of PFAS, high molecular weight fluoropolymers like PTFE have vastly different properties than do other PFAS, and therefore, they are truly a separate class of materials that must be assessed on their own merits as has been done here. They also underscore the value of a global regulatory definition of a polymer.

FUTURE WORK

It is important to acknowledge that the manufacture and end-of-life phases of the fluoropolymer life cycle are not the subject of the present paper. The following reflections are provided on how these may be explored in future work. Fluoropolymer manufacture includes fluoromonomers and a wide array of initiators, catalysts, et cetera, including polymer production aids, some of which are fluorosurfactants (non-polymer PFAS) (see Supplemental Data, p 8, for more information about them). Historically, perfluorocarboxylic acids such as PFOA and perfluorononanoic acid (PFNA) were used as polymer production aids in the manufacture of fluoropolymers. They are no longer used by leading global fluoropolymer manufacturers (USEPA 2017a), who are now using alternative substances such as fluorinated polyether carboxylates (see Supplemental Data Table S2). The toxicological and environmental properties (e.g., persistence, bioavailability, and mobility) of these alternatives are very important. Future work should delve into fluoropolymer manufacture and describe the safety, health, and environmental management practices and controls employed; should describe the applicable regulations; and should assess substances used in fluoropolymer manufacture, their human health and environmental attributes, and their mass balance.

At end-of-life when a fluoropolymer has fulfilled its intended use and will be disposed of, the fate of fluoropolymers should be investigated further. Although there are sufficient data to demonstrate that fluoropolymers such as PTFE do not degrade in the environment or release substances of toxicological or environmental concern (Hintzer and Schwertfeger 2014), the downstream, end-of-life process of incineration merits future work. For instance, at temperatures above 450 °C, PTFE begins to degrade, releasing hazardous substances such as hydrofluoric acid. There are published studies on the incineration of fluoropolymers under normal, foreseeable municipal waste incinerator conditions targeting specific analytes (Taylor 2009). Presently, most legislation addresses the release of hydrogen fluoride (HF) as the only critical parameter; limit values are for stack emissions (e.g., EU 2000). Future work should investigate incineration under a range of relevant foreseeable use conditions to determine more comprehensively the substances formed and their amounts. Such an incineration study is underway with results to be published upon completion (W.L. Gore 2017). In addition, the practice of the open burning of fluoropolymers, or for that matter of any polymer, is unacceptable and unsafe. Responsible incineration of fluoropolymers, adhering to regulatory guidelines, at the end of their life cycle is appropriate.

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Table 4. Comparison of United States, Stockholm Convention, EU REACH, and German Criteria

Criterion	United States[a]	Stockholm Convention[b]	REACH[c,d]	Germany[d,e]
Persistence (half-life)				
P	Water, soil, sediment > 60 d	Water >60 d	Marine water > 60 d	Same as REACH
		Soil, sediment >180 d	Estuarine water > 40 d	
			Fresh or estuarine sediment or soil > 120 d	
vP	Water, soil, sediment > 180 d		Marine, fresh, estuarine H_2O > 60 d	
			Marine, fresh, or estuarine sediment > 180 d	
			Soil > 180 d	
Bioaccumulation				
B	Aquatic BCF > 1000	Aquatic BCF or BAF > 5000	BCF > 2000	
		Log K_{OW} > 5		
vB	BCF > 5000		BCF > 5000	
Toxicity				
	Fish	Toxic or ecotoxic	Long-term aquatic NOEC or EC10 < 0.01	1) Carcinogenic, germ cell mutagenic, or toxic for reproduction[d];
	Low > 10 mg/L	(No numeric criteria)	Classified as carcinogen category 1A or 1B; mutagen 1A or 1B; reproductive toxin 1A, 1B, or 2[d]	2) other evidence of chronic toxicity[d]; and
	Moderate 0.1 mg/L–10 mg/L			3) evidence for effects on or via lactation[d].
	High < 0.1 mg/L			4) DNEL[f] ≤ 9 μg · $kg^{-1}d^{-1}$
			Specific target organ toxicity (STOT RE 1 or 2) upon repeated (chronic) exposure)[d]	
Long-range transport (potential for)		Long-range transport (potential for): Presence through monitoring or modeled data; $t_{1/2}$ (air): 2 d		
Mobility				Mobility: water solubility at pH 6–8, 12 °C, must be ≥150 μg/L, and the log K_{OC} at pH 6–8, 12 °C must be ≤4.5.

BAF = bioaccumulation factor; BCF = bioconcentration factor; DNEL = derived no adverse effect level; EU = European Union; M = mobile; P = persistent; REACH = Registration, Evaluation, Authorisation and Restriction of Chemicals; STOT RE = specific target organ of toxicity repeat exposure; T = toxic; v = very.
[a]USEPA 1999.
[b]UNEP 2001
[c]ECHA 2014
[d]EC 2008
[e]UBA 2017
[f]Barlow 2005; Kalberlah et al. 2014.

Recycling, reuse, and closed loop systems are alternative options at the end of life. Recent work has shown, on a small scale, the ability to convert fluoropolymers back to their monomers for capture (Schlipf 2014; Invertec 2017). This approach to a closed loop economy for fluoropolymers merits additional work and discussion, as does the recycling and reuse of melt-processable fluoropolymers, such as FEP.

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CONCLUSIONS

The present review has brought together fluoropolymer toxicity data, human clinical data, and physical–chemical characteristics, using PTFE as an example to show that fluoropolymers satisfy the widely accepted regulatory assessment criteria to be considered as PLCs. Fluoropolymers are high molecular weight, have narrow molecular weight distribution, and have negligible oligomer content and organic and inorganic leachables. Data show that fluoropolymers have thermal, chemical, photochemical, hydrolytic, and biological stability. Polytetrafluoroethylene has been extensively tested to comply with US and EU food contact and global medical device regulations (e.g., USFDA, CFDA, Korea MFDS, Japan PMDA), including ISO 10993 biocompatibility testing and preclinical animal testing. Toxicology studies on PTFE demonstrate the absence of acute or subchronic systemic toxicity, irritation, sensitization, local toxicity on implantation, in vitro and in vivo genotoxicity, hemolysis, complement activation, or thrombogenicity. The data presented demonstrate that the fluoropolymer class of PFAS is well defined, meets PLC criteria, and should be considered as distinctly different from other classes of PFAS. The grouping of all PFAS together is not supported by the scientific data.

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Data Accessibility—All data and information used in this manuscript have been made available in tabulated form (Tables 1–4) by the authors and are included in the paper and the Supplemental Data.

SUPPLEMENTAL DATA

The Supplemental Data contains descriptive and more detailed information as highlighted in the paper.

Figure S1. Where does polytetrafluoroethylene (PTFE) come from?

Figure S2. Fluoropolymer primer: polytetrafluoroethylene (PTFE) polymerization scheme.

Figure S3. Fluoropolymer primer: polytetrafluoroethylene (PTFE) finishing scheme.

Figure S2. A fluorinated ethylene propylene (FEP) fluoropolymer molecular weight distribution from a rheological study.

Table S1. Polytetrafluoroethylene (PTFE) polymerization and post polymerization aids

Table S2. Alterative fluoropolymer processing aids: Sources of data

Table S3. Solubility table from USP 34 NF 29 General Notices, Section 5.3.0, p 6

Table S4. European Union (EU) specific migration limits (SMLs) for monomers in representative fluoropolymers

Table S5. Biocompatibility tests, conditions, and acceptance criteria results for expanded polytetrafluoroethylene patch

Table S6. US Environmental Protection Agency's (USEPA's) chemical categories of concern, 2010

REFERENCES

[ACGIH] American Conference of Governmental Industrial Hygienists. 2010. TLVs and BEIs: Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati (OH): American Conference of Governmental Industrial Hygienists.

Arkles B. 1973. Recycling polytetrafluoroethylene in polymer science and technology. In: Guillet J, editor. Polymers and ecological problems, Vol. 3. New York (NY): Plenum. p 122.

Arkles B, Bonnett R. 1974. Method for the depolymerization of polytetrafluoroethylene, US 3832411A.

[ASTM] American Society for Testing and Materials. 2015a. ASTM D3159-15, Standard specification for modified ETFE fluoropolymer molding and extrusion materials.

[ASTM] American Society for Testing and Materials. 2015b. ASTM D4894, Standard specification for polytetrafluoroethylene (PTFE) granular molding and ram extrusion materials.

[ASTM] American Society for Testing and Materials. 2016a. ASTM D2116-16, Standard specification for FEP-fluorocarbon molding and extrusion materials.

[ASTM] American Society for Testing and Materials. 2016b. ASTM D3307-16, Standard specification for perfluoroalkoxy (PFA) resin molding and extrusion materials.

[ASTM] American Society for Testing and Materials. 2016c. ASTM D4895–16, Standard specification for polytetrafluoroethylene (PTFE) resin produced from dispersion.

Auer CM, Nabholz JV, Baetcke KP. 1990. Mode of action and the assessment of chemical hazards in the presence of limited data: Use of structure-activity relationships (SAR) under TSCA, Section 5. *Environ Health Perspect* 87:183–197.

Banks RE, Smart BE, Tatlow J. 1994. Organofluorine chemistry: Principles and commercial applications. New York (NY): Springer. 644 p.

Barlow S. 2005. Threshold of toxicological concern (TTC): A tool for assessing substances of unknown toxicity present at low levels in the diet. Brussels (BE): ILSI Europe. ILSI Europe Concise Monograph Series.

Berry KL, Peterson JH. 1951. Tracer studies of oxidation—Reduction polymerization and molecular weight of "Teflon" tetrafluoroethylene resin. *J Am Chem Soc* 73:5195–5197.

Beyer EC. 1993. Gap junctions. *Int Rev Cytol* 137:2.

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BIO by Deloitte. 2015. Technical assistance related to the review of REACH with regard to the registration requirements on polymers Final report prepared for the European Commission (DG ENV), in collaboration with PIEP.

Blum A, Balan SA, Scheringer M, Trier X, Goldenman G, Cousins IT, Diamond M, Fletcher T, Higgins C, Lindeman AE, et al. 2015. The Madrid statement on poly- and perfluoroalkyl substances (PFAS). *Environ Health Perspect* 123:A107–A111.

Brydson JA. 1999. Plastics materials. 7th ed. Oxford (UK): Butterworth Heinemann. 920 p.

Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, de Voogt P, Jensen AA, Kannan K, Mabury SA, van Leeuwen SPJ. 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integr Environ Assess Manag* 7(4):513–541.

ChemNews. 2016 Jul 7. Sweden's Kemi issues interim report on PFAS. Chemical Watch (Global Risk and Regulation News).

Chu B, Wu C, Buck W. 1989. Light scattering characterization of poly-(tetrafluoroethylene). PTFE in perfluorotetracosane: Molecular weight distribution and solution properties. *Macromolecules* 22:831–837.

Cramer GM, Ford RA, Hall RL. 1978. Estimation of toxic hazard—A decision tree approach. *Food Cosmet Toxicol* 16(3):255–276.

Dams R, Hintzer K. 2016. Industrial aspects of fluorinated oligomers and polymers. In: Ameduri B, Sawada H, editors. Fluorinated polymers, Vol 2: Applications. London (UK): Royal Society of Chemistry. p 1–31.

Doban RC, Knight AC, Peterson JH, Sperati CA. 1956. The molecular weight of polytetrafluoroethylene. Paper presented at 130th Meeting of American Chemical Society; 1956 Sep; Atlantic City, NJ. p 9S.

Drobny JG. 2006. Fluoroplastics. Shropshire (UK): Rapra Technology. p 12.

Ebnesajjad S. 2011. Introduction to fluoropolymers. In: Kutz M, editor. Applied plastics engineering handbook. New York (NY): Elsevier. p 49–60.

[EC] European Commission. 2004. Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC. [cited 2017 July 12]. http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02004R1935-20090807&from=EN

[EC] European Commission. 2006. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). [cited 2017 July 12]. https://echa.europa.eu/regulations/reach/legislation

[EC] European Commission. 2008. Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (Text with EEA relevance). [cited 2017 July 12]. http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32008R1272

[ECHA] European Chemicals Agency. 2014. Guidance on information requirements and chemical safety assessment. Chapter R.11: PBT/vPvB assessment version 2.0 November 2014. [cited 2017 July 12]. https://echa.europa.eu/documents/10162/13632/information_requirements_r11_en.pdf/a8cce23f-a65a-46d2-ac68-92fee1f9e54f

[ECHA] European Chemicals Agency. 2015. Opinion of the Committee for Risk Assessment and Opinion of the Committee for Socio-economic Analysis on an Annex XV dossier proposing restrictions of the manufacture, placing on the market or use of a substance within the EU. [cited 2017 July 12]. https://echa.europa.eu/documents/10162/13641/rest_pfoa_compiled_opinions_en.pdf/2f0dfce0-3dcf-4398-8d6b-2e59c86446be

[EU] European Union. 2000. Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste.

[EU] European Union. 2011. European Union Guidance on Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food as regards information in the supply chain available on the food safety part of the website of the European Commission, on the page concerning the legislation on Food Contact Materials. [cited 2017 July 12]. http://ec.europa.eu/food/safety/chemical_safety/food_contact_materials/legislation/index_en.htm

Frick A, Sich D, Heinrich G, Stern C, Schlipf M. 2012. Classification of new melt-processable PTFE: Comparison of emulsion- and suspension-polymerized materials. *Macromol Mater Eng* 297:329–341.

Gangal SV, Brothers PD. 2015. Perfluorinated polymers. In: Kirk-Othmer encyclopedia of chemical technology. New York (NY): Wiley. p 1–68.

Hintzer K, Schwertfeger W. 2014. Fluoropolymers – Environmental aspects. In: Smith Jr DW, Iacano ST, Iyer SS, editors. Handbook of fluoropolymer science and technology. New York (NY): Wiley. p 495–520.

Hougham G, Cassidy PE, Johns K, Davidson T. 1999. Topics in applied chemistry. Fluoropolymers 2: Properties. New York (NY): Springer. 408 p.

IHS Markit. 2016. Fluoropolymers chemical economics handbook. Freedonia Group.

Invertec. 2017. Pilot project: Recycling of fluoropolymers (PTFE). [cited 2017 July 12]. https://www.invertec-ev.de/en/projects/environmental-care/ptfe-recycling/

[ISO] International Organization for Standardization. 2006. ISO 12086-1:2006 Plastics – Fluoropolymer dispersions and moulding and extrusion materials. Part 1: Designation system and basis for specifications.

[ISO] International Organization for Standardization. 2009. ISO 10993-1: Biological evaluation of medical devices. Part 1: Evaluation and testing in the risk management process. Geneva (CH).

[ISO] International Organization for Standardization. 2011. ISO 1133-1:2011 Plastics — Determination of the melt mass-flow rate (MFR) and melt volume-flow rate (MVR) of thermoplastics. Part 1: Standard method.

Kalberlah F, Oltmanns J, Schwartz MA, Baumeister J, and Stiffler A. 2014. Guidance for the precautionary protection of raw water destined for drinking water extraction from contaminants regulated under REACH. Dessau-Roßlau (DE): Umweltbundesamt (UBA). Report FKZ 371265416.

Kemi Swedish Chemicals Agency. 2016. Strategy for reducing the use of highly fluorinated substances, PFASs: Interim report as part of a Government assignment. Report 11/16. [cited 2017 July 12]. https://www.kemi.se/global/rapporter/2016/report-11-16-strategy-for-reducing-the-use-of-higly-fluorinated-substances-pfas.pdf

King MW, Gupta BA, Guidoin R. 2013. Biotextiles as medical implants:15. Vascular prostheses for open surgery. Cambridge (UK): Woodhood. p 434–484.

LaGrega M D. Buckingham PL, Evans JC. 2010. Hazardous waste management. 2nd ed. Long Grove (IL): Waveland. 1232 p.

Liu J, Mejia-Avendaño S. 2013. Microbial degradation of polyfluoroalkyl chemicals in the environment: A review. *Environ Int* 61:98–114.

[NICNAS] National Industrial Chemicals Notification and Assessment Scheme. 2016. NICNAS Handbook - Guide for importers and manufacturers of industrial chemicals in Australia. Sydney (AU). [cited 2017 July 12]. http://webarchive.nla.gov.au/gov/20161017033100/https://www.nicnas.gov.au/regulation-and-compliance/nicnas-handbook

[OECD] Organisation for Economic Co-operation and Development. 1993. OECD Expert Group on Polymers. Third Meeting of the Experts on Polymers: Chairman's Report [ENV/MC/CHEM/RD(93)4]; 1993 Apr; Paris (FR).

[OECD] Organisation for Economic Co-operation and Development. 2009. Data analysis of the identification of correlations between polymer characteristics and potential for health or ecotoxicological concern. OECD Task Force on New Chemicals Notification and Assessment, Expert Group Meeting on Polymers; 2007 Mar; Tokyo, Japan. Paris (FR).

[OECD] Organisation for Economic Co-operation and Development. 2017. OECD portal on per and poly fluorinated chemicals. Country Information section. Paris (FR). [cited 2017 July 12]. http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/

Olabisi O, Adewale K. 2015. Handbook of thermoplastics. 2nd ed. Boca Raton (FL): CRC.

Pianca M, Barchiesi E, Esposto G, Radice S. 1999. End groups in fluoropolymers. *J Fluorine Chem* 95:71–84.

Plunkett RJ. 1987. The history of polytetrafluoroethylene: Discovery and development. In: Seymour RB, Kirshenbaum GS, editors. High performance polymers: Their origin and development. New York (NY): Elsevier. p 261–266.

[PMDA] Japan Pharmaceutical and Medical Device Agency, Ministry of Health, Labour and Welfare. 2003. Basic principles of biological safety evaluation required for application for approval to manufacture (import) medical

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devices. Tokyo (JP). PFBS/ELD (Iyakushin) Notification No. 0213001. 2003 Feb 13.
Putnam RE. 1986. Development of thermoplastic fluoropolymers. In: Seymour RB, Kirshenbaum GS, editors. High performance polymers: Their origin and development. New York (NY): Elsevier. p 279–286.
Puts G, Crouse P, Ameduri B. 2014. Thermal degradation and pyrolysis of polytetrafluoroethylene. In: Smith DW, Iacano TS, Iyer SS, editors Handbook of fluoropolymer science and technology. New York (NY): Wiley. p 81–104.
Scheringer M, Trier X, Cousins IT, de Voogt P, Fletcher T, Wang, Z, Webster TF. 2014. Helsingor statement on poly- and perfluorinated alkyl substances (PFAS). *Chemosphere* 114:337–339.
Schlipf M, Schwalm T. 2014. Closing the recyling loop. *Kunststoffe Intl* 2014/06. [cited 2017 July 12]. https://www.kunststoffe.de/en/journal/archive/article/up-cycling-of-end-of-life-fluoroplastics-841786.html
[SPI] Society of the Plastics Industry. 2005. SPIs guide to safe handling of fluoropolymers. Washington (DC).
Starkweather Jr HW, Wu S. 1989. Molecular weight distribution in polymers of tetrafluoroethylene. *Polymer* 30:1669–1674.
Suwa T, Takehisa M, Machi S. 1973. Melting and crystallization behavior of poly(tetrafluoroethylene). New method for molecular weight measurement of poly(tetrafluoroethylene) using a differential scanning calorimeter. *J Appl Polym Sci* 17:3253–3257.
Taylor PH, 2009. ECA incineration testing program: Laboratory-scale incineration testing of fluoropolymers. Dayton (OH): USEPA. USEPA Docket No. OPPT-2003-0071.
Tuminello WH. 1989. Molecular weight distributions of tetrafluoroethylene-hexafluoropropylene copolymers. *Polym Eng Sci* 29:645–653.
Tuminello WH, Buck WH, Kerbow DL. 1993. Rheological molecular weight distribution determination of ethylene/ tetrafluoroethylene copolymers: Implications for long-chain branching. *Macromolecules* 26:499–503.
[UBA] Umweltbundesamt. 2017. Protecting the sources of our drinking water from mobile chemicals. A proposal for implementing criteria and an assessment procedure to identify persistent, mobile and toxic (PM or PMT) substances registered under REACH. Dessau-Roßlau (DE). [cited 2017 July 12]. https://www.umweltbundesamt.de/en/publikationen/protecting-the-sources-of-our-drinking-water-from
[UNEP] United Nations Environment Programme. 2001. Conference of Plenipotentiaries on the Stockholm Convention. UNEP/POPS/CONF/2. [cited 2017 July 12]. http://www.wipo.int/edocs/trtdocs/en/unep-pop/trt_unep_pop_2.pdf
[UNEP] United Nations Environment Programme. 2009: Decision SC-4/17. Geneva (CH). [cited 2017 July 12]. http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP.4-SC-4-17.English.pdf; also accessible from table of new POPs: http://www.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx
[UNEP] United Nations Environment Programme. 2011. UNEP-POPS-POPRC.11-POPRC-11-4.English.docx. Geneva (CH). [cited 2017 July 12]. http://www.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC11/Overview/tabid/4558/mctl/ViewDetails/EventModID/871/EventID/553/xmid/13837/Default.aspx
[UNEP] United Nations Environment Programme. 2017a. Proposal for listing PFHxS (UNEP/POPS/POPRC.13/4). Geneva (CH). [cited 2017 July 12]. http://chm.pops.int/Convention/POPsReviewCommittee/Chemicals/tabid/243/Default.aspx
[UNEP] United Nations Environment Programme. 2017b. Risk management profile for PFOA, (UNEP/POPS/POPRC.13/7/Add.2). Geneva (CH). [cited 2017 July 12]. http://chm.pops.int/Convention/POPsReviewCommittee/Chemicals/tabid/243/Default.aspx
[USC] US Congress. 1976. The Toxic Substance Control Act. 15 U.S.C. 2601-2671. Public Law 94–469.
[USEPA] US Environmental Protection Agency. 1997a. Chemistry assistance manual for premanufacture notification submitters. Washington (DC). EPA 774-R-97-003. March 1997.
[USEPA] US Environmental Protection Agency. 1997b. Polymer exemption guidance manual. Washington (DC). EPA-744-B-97-001. June 1997.
[USEPA] US Environmental Protection Agency. 1999. Category for persistent, bioaccumulative, and toxic new chemical substances. *Fed Regis* 4(213). 1999 Nov 4.
[USEPA] US Environmental Protection Agency. 2010. Reviewing new chemicals under the Toxic Substances Control Act (TSCA) – EPA's Review Process - Chemical categories used to review new chemicals under TSCA: TSCA New Chemicals Program (NCP) Chemical Categories. Washington (DC): USEPA Office of Pollution Prevention and Toxics. [cited 2017 July 12]. http://www.epa.gov/oppt/newchems/pubs/npcchemicalcategories.pdf
[USEPA] US Environmental Protection Agency. 2012. Sustainable futures/P2 framework manual.
[USEPA] US Environmental Protection Agency. 2017a. US Environmental Protection Agency, PFOA Stewardship Program. Washington (DC). [cited 2017 July 12]. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfass#tab-3
[USEPA] US Environmental Protection Agency. 2017b. Using predictive methods to assess hazard under TSCA. Washington (DC). [cited 2017 July 12]. https://www.epa.gov/tsca-screening-tools/using-predictive-methods-assess-hazard-under-tsca
[USFDA] US Food and Drug Administration. 2017. Guidance for industry: Preparation of premarket submissions for food contact substances: Chemistry recommendations. College Park (MD). [cited 2017 July 12]. https://www.fda.gov/Food/GuidanceRegulation/GuidanceDocumentsRegulatoryInformation/ucm081818.htm#iid2
[USFDA] US Food and Drug Administration Center for Drug Safety and Radiological Health. 2016. Use of International Standard ISO 10993-1, "Biological evaluation of medical devices – Part 1: Evaluation and testing within a risk management process" Guidance for Industry and Food and Drug Administration Staff Document. Silver Spring (MD). [cited 2017 July 12]. https://www.fda.gov/ucm/groups/fdagov-public/@fdagov-meddev-gen/documents/document/ucm348890.pdf
[USFR] US Federal Register. 1984. Premanufacture Notification Exemptions for polymers; Final rule 49 FR 46066, 1984 Nov 21. FRL-2439-1.
[USFR] US Federal Register. 1995. Premanufacture notification exemptions; Revisions of exemptions for polymers; Final rule. *Fed Regist* 60(60): 16316–16336. Environmental Protection Agency. 60 FR 16316. 1995 Mar 29. FRL–4929–8.
[USFR] US Federal Register. 2006. Premanufacture notification exemption for polymers; Amendment of polymer exemption rule to exclude certain perfluorinated polymers. 40 CFR Part 723. 2006 Mar 7. Fed Reg No 06-02152.
[USFR] US Federal Register. 2010. Premanufacture notification exemption for polymers; Amendment of polymer exemption rule to exclude certain perfluorinated polymers. 40 CFR Part 723. 2010 Jan 27. EPA-HQ-OPPT-2002-0051; FRL-8805-5. RIN 2070-AD58.
[USFR] US Federal Register. 2012. Polymers (b). 40 CFR Sect 723.250.
[USFR] US Federal Register. 2016a. Indirect food additives. 21 CFR, Sect 174–178.
[USFR] US Federal Register. 2016b. Perfluorocarbon resins. 21 CFR, Sect 177.1550.
[USP] US Pharmacopeia 40. 2018. National Formulary 35 (USP), General Chapter 88, Biological Reactivity Tests, In Vivo.
[USP] US Pharmacopeial Convention. 2011. US Pharmacopeia National Formulary 2011: USP 34 NF 29. Rockville (MD). General Notices, Section 5.3.0, p 6.
Wagner PM, Nabholz JV, Kent RJ. 1995. The new chemicals process at the Environmental Protection Agency (EPA): Structure-activity relationships for hazard identification and risk assessment. *Toxicol Lett* 79:67–73.
Williams DF. 1987. Definitions in biomaterials. Amsterdam (NL): Elsevier. 72 p.
W.L. Gore. 2017. Fabrics goal for eliminating PFCs of environmental concern. [cited 2017 July 12]. https://www.gore-tex.com/pfcgoal

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Critical Review

A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers

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Abstract

Fluoropolymers are a distinct class of per- and polyfluoroalkyl substances (PFAS), high molecular weight (MW) polymers with fluorine attached to their carbon-only backbone. Fluoropolymers possess a unique combination of properties and unmatched functional performance critical to the products and manufacturing processes they enable and are irreplaceable in many uses. Fluoropolymers have documented safety profiles; are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic. Although fluoropolymers fit the PFAS structural definition, they have very different physical, chemical, environmental, and toxicological properties when compared with other PFAS. This study describes the composition, uses, performance properties, and functionalities of 14 fluoropolymers, including fluoroplastics and fluoroelastomers, and presents data to demonstrate that they satisfy the widely accepted polymer hazard assessment criteria to be considered polymers of low concern (PLC). The PLC criteria include physicochemical properties, such as molecular weight, which determine bioavailability and warn of potential hazard. Fluoropolymers are insoluble (e.g., water, octanol) solids too large to migrate into the cell membrane making them nonbioavailable, and therefore, of low concern from a human and environmental health standpoint. Further, the study results demonstrate that fluoropolymers are a distinct and different group of PFAS and should not be grouped with other PFAS for hazard assessment or regulatory purposes. When combined with an earlier publication by Henry et al., this study demonstrates that commercial fluoropolymers are available from the seven participating companies that meet the criteria to be considered PLC, which represent approximately 96% of the global commercial fluoropolymer market. *Integr Environ Assess Manag* 2022;00:1–29. © 2022 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Applications, Fluoropolymers, Low concern, PFAS, Property Combinations

This article contains online-only Supporting Information.

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INTRODUCTION

"Fluoropolymers are high MW polymers with fluorine atoms directly attached to their carbon-only backbone" (Ebnesajjad, 2017). The carbon–fluorine (C–F) bond is the strongest bond between carbon and another atom and imparts unique, outstanding, and beneficial properties and extraordinary functional performance to fluoropolymers (Ameduri, 2020; Ameduri & Sawada, 2017a, 2017b; Banks et al., 1994; Fluoropolymer Products Group of Plastics Europe [FPG], 2021a; Scheirs, 2007). These properties

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include chemical, biological, and thermal stability, heat and chemical resistance, unique dielectric properties, and durability. Additional fluoropolymer properties include fire resistance, weather resistance, nonwetting, and nonstick. Fluoropolymers are regarded as irreplaceable in many applications because their unique combination of specific properties, which are critical to ensure optimal performance in many applications, cannot be achieved or guaranteed by alternative materials (FPG, 2021a, 2017; Henry et al., 2018; Performance Fluoropolymer Partnership of the American Chemistry Council [PFP], 2020).

Per- and polyfluoroalkyl substances (PFAS), a universe of substances with widely diverse properties that have been used in industrial and consumer applications since the 1950s, include fluoropolymers as a distinct class (Buck et al., 2011; Henry et al., 2018). A single, globally harmonized definition for PFAS has not yet been agreed upon. PFAS have been defined differently based on their structure and atomic composition (Buck et al., 2021; Wallington et al., 2021). For example, the USEPA's working PFAS structure definition is "a structure that contains the unit R-CF_2-CF(R′)(R″), where R, R′, and R″ do not equal "H" and the carbon–carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included" (USEPA, 2021a). The European Chemicals Agency (ECHA) employed a much broader PFAS structural definition (ECHA, 2020). A recent Organisation for Economic Cooperation and Development (OECD) report, which defined PFAS as fluorinated substances that contain in their structure at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), that is, with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF_3) or a perfluorinated methylene group (–CF_2–; OECD, 2021). This report acknowledges that the term "PFAS" is broad, general, and nonspecific, which does not inform whether a compound presents risk or not, but only communicates that the compounds under this term share the same structural trait of having a fully fluorinated methyl or methylene carbon moiety. Further, the report highlights that, among the substances defined as PFAS, there are distinct substances with very different properties: polymers and nonpolymers; solids, liquids and gases; persistent and nonpersistent substances; highly reactive and inert substances; mobile and insoluble (immobile) substances; and (eco) toxic and nontoxic chemicals. In addition, the report recognizes that PFAS have diverse molecular structures (e.g., neutral, anionic, cationic, or zwitterionic; with or without aromatic rings; nonpolymers or polymers; low or high molecular weight (MW), and thus diverse physical, chemical, and biological properties (e.g., involatile or volatile; water soluble or water insoluble; reactive vs. inert; bioaccumulative or nonbioaccumulative) and as such highly recommends that such diversity be properly recognized and communicated in a clear, specific, and descriptive manner when communicating about PFAS.

There is considerable media and public confusion and misunderstanding regarding PFAS, as the many different chemicals and groups are often not clearly differentiated under the broad term PFAS. Per- and polyfluoroalkyl substances, a large, diverse group of substances with vastly different properties, is too broad to allow effective, science-based assessment and regulation of chemical compounds as an entire group. This point has been raised in recent publications that suggest approaches to effectively group PFAS for regulatory assessment (American Chamber of Commerce in Europe [Amcham], 2020a; Buck et al., 2021; Bundesverband der Deutschen Industrie e.V. [BDI], 2021; Fiedler et al., 2020; Miller et al., 2020; Orgalim, 2021; Royal Society of Chemistry [RSC], 2021; Sha et al., 2019; Wallington et al., 2021). A clear understanding of the origin of PFAS found in the environment, the PFAS that are commercially relevant (Buck et al., 2021), and assessment of their properties are needed to be able to determine which classes of PFAS require management action. PFAS must be assessed based on their chemical, physical, thermal, and biological property differences and uses (Amcham, 2020a; BDI, 2021; Buck et al., 2021; RSC, 2021; Wallington et al., 2021). As regulatory frameworks, such as the EU REACH regulation, continue to evolve, more work is needed to distinguish clearly among PFAS based on their properties to assure that regulations are appropriate in scope, proportionate, and are science-based.

Per- and polyfluoroalkyl substances are divided into two primary categories: nonpolymers and polymers (Buck et al., 2011). Polymeric PFAS, generally known as "fluorinated polymers," include fluoropolymers (discussed here), perfluoropolyethers (PFPE), and side-chain fluorinated polymers (SCFP; Buck et al., 2011; Henry et al., 2018 and Supporting Information: Figure 6.1). This article deals strictly with fluoropolymers. Neither PFPE nor SCFP are discussed here.

The nonpolymer category includes perfluoroalkyl substances and polyfluoroalkyl substances. Certain nonpolymer PFAS substances, for example, short- and long-chain per- and polyfluoroalkyl carboxylic acids and sulfonic acids, received regulatory scrutiny recently due to their toxicity, as well as their persistence, potential to bioaccumulate, and/or mobility in the environment. Regulatory processes have been launched worldwide to address these concerns related to specific nonpolymer PFAS. These targeted regulatory measures have evolved increasingly into restrictions on the entire family of PFAS. For example, five Member States of the European Economic Area have initiated a procedure to prepare a joint restriction proposal under the EU REACH Regulation to limit the risks to human health and the environment from the manufacture and use of all substances in the PFAS family based on structure alone (ECHA, 2020). Although fluoropolymers fit the PFAS structural definition, they have vastly different physicochemical, environmental, and toxicological properties than other PFAS in addition to substantial societal benefits and importance (Fluoropolymer Products Group of Plastics Europe [FPG], 2017, 2021a). For

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these reasons, fluoropolymers should be considered separately and not aggregated with all other PFAS for regulatory action. Concurrently, the USEPA prepared a PFAS Strategic Roadmap laying out how it plans to evaluate and potentially regulate PFAS (USEPA, 2021a). Recognizing that there are many PFAS very diverse in their physical form, chemical structure and composition, functional characteristics, and toxicity profiles, USEPA "is conducting new research to better understand the similar and different characteristics of specific PFAS and whether and how to address groups and categories of PFAS."

Fluoropolymers have documented safety profiles, are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic (Henry et al., 2018). Some fluoropolymers have been demonstrated to meet the "polymers of low concern" (PLC) criteria, and as such do not present notable concern for human health or the environment (Henry et al., 2018). PLC criteria were developed over time within regulatory frameworks around the world as an outcome of chemical hazard assessment processes, which identified physical–chemical properties of polymers that determine polymer bioavailability and thereby report a polymer's potential hazard. For example, many of the physicochemical properties, such as MW, limit the ability of a polymer to cross the cell membrane and therefore limit its bioavailability (Kostal, 2016; Lipinski et al., 2001; USEPA, 2012). The USEPA built on this knowledge to adopt a polymer exemption rule to exempt low-hazard polymers from certain regulatory notification requirements under the Toxic Substances Control Act's (TSCA) new chemicals program (United States Federal Register [USFR], 1984). An OECD expert group on polymers reached consensus on these criteria and their respective metrics, documenting the data required for a polymer to qualify as a PLC to human health and the environment (OECD, 1993). Subsequently, an additional OECD work group concurred that PLC have "insignificant environmental health and human health impacts" (OECD, 2009). In addition, the European Commission commissioned a report (BIO by Deloitte, 2015) wherein several member countries agreed on the polymer properties predictive of adverse human health and environmental hazard. The report outlined eligibility criteria for a polymer to be considered a PLC. In 2019, the industry-led European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a "Conceptual Framework for Polymer Risk Assessment" ("CF4Polymers"; ECETOC, 2019). CF4Polymers provides guiding elements to be considered in assessing potential ecological and human health hazards and risks posed by polymer substances. CF4Polymers also considers specific life-cycle stages of polymer products and their associated routes of exposure. The authors of the CF4Polymers framework support the PLC approach as a means to accomplish polymer risk assessments. They specifically support the findings of Henry et al. (2018) and state that they are "…unaware of scientific evidence to justify generally assigning fluoropolymers the same level of regulatory concern as other PFAS" (ECETOC, 2019). In 2020, the European Commission contracted a study to propose criteria for the identification of polymers requiring registration (PRR) under REACH (Wood, 2020a). The Wood report states that the authors consider that fluoropolymers meet the criteria to be considered PLC, "following the recommendations of Henry et al." Considerable debate and comment on proposals have been put forward as the process and discussion advances (American Chamber of Commerce in Europe [Amcham], 2020b; FPG, 2021a; Hafer, 2021).

Four major fluoropolymers have previously been demonstrated to meet the criteria as PLC (Henry et al., 2018). This 2018 study raised interest in gathering similar data for additional commercial fluoropolymer products, both in scope and polymer type. In this study, seven global fluoropolymer manufacturers from the USA, Europe, and Asia collaborated to gather and present data for 14 additional fluoropolymers. In addition to information describing chemical composition, uses, performance properties, and functionalities of the 14 fluoropolymers, author company data for each of the PLC criteria are presented and discussed. The results demonstrate that each of the 14 commercially manufactured fluoropolymers in this study satisfy the widely accepted assessment criteria to be considered PLC and merit such designation. The study results add further evidence to demonstrate that fluoropolymers are demonstrably different and should not be grouped with other PFAS for hazard assessment or regulatory purposes.

USES, PERFORMANCE PROPERTIES, AND FUNCTIONALITY OF FLUOROPLASTICS AND FLUOROELASTOMERS IN THIS STUDY

The fluoropolymers described and evaluated in this study are high-performance materials used in commercial and industrial applications. Described herein are the industries and sectors (Table 1) and the performance properties and functionalities (Table 2) of the study fluoropolymers. The unparalleled combination of properties makes fluoropolymers critical materials for a broad range of applications and industrial sectors including automotive, aerospace, energy production and storage, and electronics (Table 1). Fluoropolymers are an important driver of the European Green Deal (FPG, 2021a) and UN Sustainability Development Goals (United Nations [UN], 2021), supporting smart mobility, clean energy, and sustainable industry. They are used in various components of renewable energy installations, such as hydrogen and photovoltaic panels and facilitate advanced energy storage and conversion technologies such as lithium-ion batteries (FPG, 2021a). Fluoropolymers are (i) durable, stable, and mechanically strong in harsh conditions; (ii) chemically inert, meeting the requirements for low levels of contaminants and particulates in manufacturing environments that are critical to the food and beverage, pharmaceutical, medical, and semiconductor industries; and (iii) biocompatible, nonwetting, nonstick, and highly resistant to

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TABLE 1 Fluoropolymer end uses and industries

	Transportation		Health care		Chemical		Consumer			Telecommunications			Infra-structure	Renewable energy		
Industries End uses	Automotive	Aerospace	Pharma-ceuticals	Medical devices	Oil and gas	Chemical process industry (CPI)	Production of goods	Protection and packaging	Filtration	Electronics and semicon-ductors	Internet and wireless communica-tions	Textiles Technical textiles	Construc-tion and archi-tecture	Energy production	Hydrogen production	Energy storage
Fluoroplastics																
PVDF homopolymer	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
PVDF copolymer	•	•	•	•		•	•	•	•	•	•	•	•		•	•
ECTFE copolymer	•	•	•		•	•				•	•		•			
ECTFE terpolymer			•		•	•										
PCTFE		•	•							•						
FEVE	•	•								•			•			
EFEP	•			•		•				•						
CPT	•									•						
THV	•	•	•			•	•	•	•	•			•	•		•
Fluoroelastomers																
FEPM	•	•	•	•	•	•	•			•			•	•		
FKM	•	•	•	•	•	•	•	•		•		•	•	•	•	•
FFKM		•	•	•	•	•	•			•						
Specialty																
Amorphous		•	•	•		•				•	•				•	•
Ionomer	•			•		•			•	•				•	•	•

Note: See also Chapter 5 in the Supporting Information.
Abbreviations: CPT, chlorotrifluoroethylene-tetrafluoroethylene; ECTFE, ethylene-chlorotrifluoroethylene; EFEP, ethylene-tetrafluoroethylene-hexafluoropropylene; FEPM, trifluoroethylene-propylene copolymer; FEVE, fluoroethylene-vinyl ether; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMVE perfluoroelastomer; PCTFE, polychlorotrifluoroethylene; PVDF, polyvinylidene fluoride; THV, TFE-HFP-VF2.

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TABLE 2 Fluoropolymer properties and functionality

See Supporting Information: Chapter 2 for property descriptions	Durable				Inert—Stable				
	Mechanical strength	Wear resistance	Flexibility	Low coefficient of friction	Resistance to chemicals	Weatherability	Cryogenic properties (lower than −50 °C)	High operating temperature range	High limiting oxygen index
Fluoroplastics									
PVDF Homopolymer	•	•		•	•	•		•	•
PVDF Copolymer	•	•		•	•	•		•	•
ECTFE Copolymer	•	•		•	•	•	•	•	•
ECTFE Terpolymer		•		•	•	•		•	•
PCTFE	•	•		•	•	•	•	•	•
FEVE	•	•	•	•	•	•		•	•
EFEP	•	•		•	•	•	•	•	•
CPT				•	•	•	•	•	•
THV			•		•	•		•	•
Fluoroelastomers									
FEPM	•	•	•		•	•		•	•
FKM	•	•	•		•	•		•	•
FFKM	•	•	•		•			•	•
Specialty									
Amorphous			•	•	•			•	•
Ionomer			•		•				•

See Supporting Information: Chapter 2 for property descriptions	Functional								
	Electrical insulator—high data transmission rate	Ionic conductivity	Piezo-electrical properties	Barrier properties	Nonstick properties	Ultra high purity grades for clean applications	Optical clarity	Low refractive index—used for optical effects	Polymer processing additive (PPA)[a]
Fluoroplastics									
PVDF Homopolymer			•	•		•		•	•
PVDF Copolymer			•	•				•	•

(*Continued*)

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TABLE 2 (*Continued*)

See Supporting Information: Chapter 2 for property descriptions	Functional								
	Electrical insulator—high data transmission rate	Ionic conductivity	Piezo-electrical properties	Barrier properties	Nonstick properties	Ultra high purity grades for clean applications	Optical clarity	Low refractive index—used for optical effects	Polymer processing additive (PPA)[a]
ECTFE Copolymer	•			•					
ECTFE Terpolymer				•					
PCTFE				•	•	•	•	•	
FEVE				•			•		
EFEP				•	•		•	•	•
CPT				•	•	•	•	•	
THV				•			•	•	•
Fluoroelastomers									
FEPM	•			•					
FKM				•	•				•
FFKM	•			•		•			
Specialty									
Amorphous	•	•		•	•	•	•	•	
Ionomer	•	•		•			•		

Note: See Chapter 5 in the Supporting Information.
Abbreviations: CPT, chlorotrifluoroethylene-tetrafluoroethylene; ECTFE, ethylene-chlorotrifluoroethylene; EFEP, ethylene-tetrafluoroethylene-hexafluoropropylene; FEPM, trifluoroethylene-propylene copolymer; FEVE, fluoroethylene-vinyl ether; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMVE perfluoroelastomer; PCTFE, polychlorotrifluoroethylene; PVDF, polyvinylidene fluoride; THV, TFE-HFP-VF2.
[a]Polymer Processing Additives (PPA): also known as Polymer Processing Aid, Extrusion Process Aids or Polymer Processing and Recycling Aids.

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emperature, fire, and weather (Table 2). Fluoropolymers are the preferred choice of material because of their unique combination of properties that are not achievable from other materials or via other functions. As a result, fluoropolymers have become a critical mainstay for our society providing vital, reliable functionality to a broad range of industrial and consumer products.

Three fluoropolymer types are included in this study: fluoroplastics, fluoroelastomers, and specialty fluoroplastics. Here, we describe briefly each included in this study. Additional details about each polymer are provided in the Supporting Information: Chapter 5.

Fluoroplastics

The fluoroplastics included in this study are: polyvinylidene fluoride (PVDF) homopolymer, PVDF copolymer, ethylene-chlorotrifluoroethylene (ECTFE) copolymer, ECTFE terpolymer, polychlorotrifluoroethylene (PCTFE), fluoroethylene-vinyl ether (FEVE), ethylene-tetrafluoroethylene-hexafluoropropylene (EFEP) terpolymer, chlorotrifluoroethylene-tetrafluoroethylene (CPT) terpolymer, and tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride (TFE-HFP-VF2 [THV]) terpolymer as well as the specialty fluoroplastics, amorphous fluoropolymers, and fluorinated ionomers. Typical monomers used in the manufacture of fluoroplastics include tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinylidene fluoride (VDF or VF2), chlorotrifluoroethylene (CTFE), vinyl fluoride (VF), trifluoroethylene (TrFE), and perfluoroalkyl vinyl ethers (PAVEs), which include trifluoromethyl trifluorovinyl ether (PMVE), pentafluoroethyl trifluorovinyl ether (PEVE), and heptafluoropropyl trifluorovinyl ether (PPVE). In some copolymers, monomers that do not contain fluorine attached to the olefinic carbons may be used. These include ethylene, propylene, perfluoroalkyl-substituted ethylenes, and others (Ebnesajjad, 2000, 2003; Grot, 2011).

Fluoroelastomers

The fluoroelastomers included in this study are: trifluoroethylene-propylene copolymer (FEPM), HFP-VF2 polymer and HFP-VF2-TFE polymers (FKM), and TFE-PMVE perfluoroelastomer (FFKM). Typical monomers used in the manufacture of fluoroelastomers include VDF, HFP, TFE, CTFE, PAVEs, as well as propylene, 1-hydropentafluoropropene (HPFP), and 2,3,3,3-tetrafluoropropene (HFO-1234yf; FPG, 2021a). Although fluoroelastomers are based on many of the monomers that are also used for the synthesis of fluoroplastics, they are different because of the specific composition, flexibility with subambient glass transition temperatures, as well as their elastomeric properties, resulting from the cross-linking process. Cross-linking, known as curing or vulcanizing, is a hardening process to form chemical bonds between polymer chains that gives polymers their elasticity (Améduri et al., 2001; Drobny, 2016).

PVDF homo- and copolymers

Polyvinylidene fluoride fluoropolymers are specified by end users across the world for their outstanding combination of properties. Because they have high temperature resistance, low permeability, and high mechanical strength, and provide chemical resistance to a wide range of aggressive chemicals, PVDF fluoropolymers are used as a contact surface for the production, storage, and transfer of corrosive fluids (chemically resistant to halogens and acids) in the chemical processing industry, oil and gas transportation, and cables industry (Arkema, 2021a; Gujarat Fluorochemicals Limited, 2018, 2022; Solvay, 2021a). The outstanding resistance to sunlight/UV exposure make PVDF suitable for architectural coatings. The outdoor aging and weathering properties of PVDF resin led to its use in long-lasting paints for coating metal sheet for the past 50 years. PVDF resins can also be used to protect thermoplastics through coextrusion or film lamination techniques to obtain antigrime and antigraffiti surfaces with exceptional weathering properties. PVDF fluoropolymers also exhibit radiation resistance, desirable burn characteristics, flame, and smoke properties, easy processing on industry-standard equipment, and easy postprocessing steps, such as welding and fabrication. PVDF is used as a binder in lithium-ion batteries as well as PVDF film for solar power panels because of its high thermal and electrochemical stability, its stability under harsh environmental conditions, and its strong adhesion properties are critical to achieving environmental goals.

ECTFE (co- and terpolymers)

Ethylene chlorotrifluoroethylene (ECTFE) is a semicrystalline and melt-processable fluoropolymer obtained by the copolymerization of the two monomers, ethylene and chlorotrifluoroethylene, with an essentially 1:1 alternating structure (Ebnesajjad, 2017). Due to its chemical structure, ECTFE offers a unique combination of properties including chemical resistance, high thermal rating, and very good mechanical properties (Solvay, 2021b). ECTFE terpolymer with added hexafluoroisobutylene monomer displays enhanced stress-cracking performances resulting from chain-structure modifications of the polymer. ECTFE is used widely in anticorrosion applications such as coatings or in self-supporting construction (pipes) and architectural films (Solvay, 2021c). One of the principal advantages of ECTFE fluoropolymer is the ease with which it can be processed. It is a true thermoplastic that can be handled by conventional techniques of extrusion as well as by blow, compression, injection, rotational, and transfer molding. Powder coating methods are also applicable. ECTFE embodies an exemplary trade-off among general properties, offering high chemical and mechanical resistance combined with easy processing of the resin.

PCTFE

Polychlorotrifluoroethylene is a homopolymer of chlorotrifluoroethylene. PCTFE is melt processable and can be

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extruded or molded (Satokawa, 1990). PCTFE has outstanding mechanical properties, especially hardness, and chemical resistance compared with PTFE and PFA, although it is slightly inferior to PFA and FEP in heat resistance and chemical resistance (Daikin, 2021a; Satokawa, 1990). PCTFE has been applied widely in the semiconductor industries and aerospace industries (Curbell, 2021; Daikin, 2021a). In addition to distinguished thermal and chemical stability, it has very low moisture absorption and permeation; therefore, PCTFE is used in pharmaceutical packaging (Honeywell, 2021).

FEVE

Fluoroethylene-vinyl ether fluoropolymer resins are manufactured by copolymerization of fluoroethylene monomer and a vinyl ether monomer and consist of alternating fluoroethylene and alkyl vinyl ether segments (AGC Chemicals Company, 2021a; Parker & Blankenship, 2015). They were developed in 1982 as the first solvent-soluble fluoropolymers in the world (Darden & Parker, 2021; Kojima & Yamabe, 1984; Munekata, 1988; Yamabe et al., 1984). The alternating fluorinated segments provide outstanding UV stability, weather resistance, and chemical resistance, while the vinyl ether segments provide solvent compatibility and cross-linking sites (Parker & Blankenship, 2015; Scheirs, 2007). FEVE resins are used to make ultra-weatherable coatings for architectural, aerospace, automotive, bridge, and industrial maintenance markets (Hoshino & Morizawa, 2017).

EFEP

Ethylene-tetrafluoroethylene-hexafluoropropylene is a terpolymer of ethylene, tetrafluoroethylene, and hexafluoropropylene. It was designed to have many of the properties of ETFE. It has a lower processing temperature, which allows it to be coextruded with conventional thermoplastic polymers such as polyamide, ethylene vinyl alcohol (EVOH), and modified polyethylene. EFEP can be extruded, injection molded, and blow molded, and it is used in many applications such as those identified in Supporting Information: Chapter 4.7 (Daikin, 2011a). EFEP is a melt-processable resin with good processability because of its low melting point. It also has excellent mechanical properties, provides chemical resistance, low permeability, exceptional weatherability, and good heat resistance. Other prominent features include inherent flame retardancy as well as good optical properties given that EFEP is highly transparent and has both a low dielectric constant and loss tangent.

CPT

Chlorotrifluoroethylene-tetrafluoroethylene is a terpolymer of chlorotrifluoroethylene, tetrafluoroethylene, and perfluoroalkyl-vinyl-ether. It is a melt-processable polymer and resin, which is readily processed because of its lower melting point. It can be melt-molded as a thermoplastic resin by extrusion, injection, and compression molding. CPT is a modified perfluoroalkoxy fluoropolymer (PFA), which utilizes chlorotrifluoroethylene to provide low permeability to PFA, and it has many outstanding properties as a hybrid polymer of PFA and PCTFE as shown below. It has demonstrated permeation resistance to organic solvent, chemicals, water vapor, and gasoline (Daikin, 2011b). CPT offers superior permeation resistance against gasoline and flexible fuel and can be part of construction meeting the LEV III requirements (US environmental protection regulations in this automotive application). CPT also has notable barrier properties against many kinds of organic solvents and strong acids, especially HF, HCl, and HNO_3. This is very useful for semiconductor applications (Daikin, 2021b). In addition to the features noted above, CPT also provides heat resistance, excellent weatherability, flame retardancy, and good optical properties owing to its high transparency.

THV

THV fluoropolymers are a group of fluorinated thermoplastic polymers composed mainly of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and vinylidene fluoride (VDF; Dominghaus, 1998; Hintzer & Schwertfeger, 2014; Hull et al., 1997). The melting point of the different grades ranges from approximately 100 °C to nearly 250 °C. THV fluoropolymers are easy to process due to their broad processing windows. Different THV grades exhibit high flexibility, high transparency, bondability to fluorinated and nonfluorinated materials, and very good permeation resistance against fuels and other chemicals. The polymers are used as a barrier layer in fuel hoses, for transparent films and tubing, as matrix materials in composites, and the bonding layer in multilayer construction (Dams & Hintzer, 2017; Hull et al., 1997). The high transparency of the special film makes it an ideal adhesive film for laminated glass and the optimal protective film for surfaces. THV grades compete against other fluorothermoplastic materials for applications that require transparency and low refractive index as well as with fuel barrier materials. Commercial nonfluorinated materials cannot be used as substitutes for THV because of the unique combination of properties. Polymethylmethacrylate (PMMA) is used in conjunction with THV to provide differences in refractive index to create the total reflection needed for polymer optical fibers (Park et al., 2008). Transparent polymers, such as PMMA or polycarbonate, do not have the same chemical resistance or UV resistance to compete directly with THV.

FEPM

Trifluoroethylene-propylene copolymer elastomers, ASTM D1418, are high MW fluoropolymers with alternating tetrafluoroethylene and propylene segments (Kojima et al., 1977). They are also known as TFE-P copolymers. Various articles can be produced by means of compression molding, extrusion, injection molding, and calendering. FEPM elastomers are compounded and cured (cross-linked) to deliver unique and valuable properties by providing exceptional heat resistance with a continuous service temperature higher than

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200 °C, outstanding chemical resistance with little or no deterioration even in contact with strong acids, bases, and oxidants at high temperatures, steam resistance, and high electrical resistivity on the order of 10^{15}–10^{16} Ω/cm (bulk resistivity). Formulated FEPM components are now used worldwide in many critical industrial applications where they must function safely in harsh environments, thereby extending the life of critical components and reducing downtime and costly repairs. FEPM elastomers are used in a range of applications including thermal power plants, oil and gas industry, ocean development, chemical and nuclear plants, automotive, aerospace, heavy-duty diesel, electronics, machinery, renewable energy, food processing, and medical. Their noted heat and chemical resistance make them especially valuable in oil and gas extraction (downhole) applications, where reliability is essential to cost effective and environmentally responsible production (Hull, 1983). FEPM elastomers are also used in high-performance wire and cable applications as insulating materials with the highest heat resistance, for example, lightweight, high-voltage automotive cables and motor cables for Japanese high-speed bullet trains (AGC Chemicals Company, 2021b).

Fluoroelastomers (FKM)

FKM are a family of fluoroelastomer materials defined by ASTM international standard D1418 (ASTM, 2021). FKM fluoroelastomers contain vinylidene fluoride (VDF) as a monomer combined with a variety of other fluoromonomers to create a palette of polymers with properties tailored for specific uses (Dams & Hintzer, 2017; Drobny, 2016; Van Cleeff, 1997; Worm & Grootaert, 2001). Cross-linked FKM fluoroelastomers are amorphous polymers designed for demanding service applications in hostile environments characterized by broad operating temperature ranges in contact with industrial chemicals, oils, or fuels (Worm & Grootaert, 2001). FKM fluoroelastomers are used mainly in fabricated parts (e.g., o-rings, gaskets, seals) to provide barriers against a wide range of fluids under severe service conditions (Drobny, 2016). Their design allows stable extrusion and molding processes and fitting in a wide range of processing constraints, reducing the risk of failure and increasing productivity. FKM fluoroelastomers provide high temperature and aggressive fluids resistance and retention of properties over a wide and demanding range of operating use conditions (high and low temperatures) for sealing and fluid transport applications, offering far superior performance than hydrocarbon elastomers. Applications include aerospace, automotive, oil and gas, chemical processing, electrical, office equipment, food, pharmaceuticals, and consumer wearables. Additionally, uncured FKM fluoroelastomers are used as a polymer processing additive (PPA) or polymer extrusion aids in small amounts (50–2000 ppm) dispersed in polyolefins such as high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), significantly improving their film extrusion characteristics, reducing melt fracture and die build-up, as well as increasing productivity, minimizing energy and water footprint, and enabling the extrusion of thin films (Lavallée, 2020; Shell, 2020).

FFKM

Perfluoroelastomers, designated by ASTM D1418 as FFKM, are a fully fluorinated class of elastomers that are typically made up of tetrafluoroethylene (TFE), a perfluoro (alkyl vinyl ether; PAVE), and a cure site monomer(s) (Ohkura & Morizawa, 2017). FFKM elastomers offer superior chemical and temperature resistance, excellent resistance to gas and liquid permeation, and resistance to weather and ozone with operating temperatures ranging from −40 °C to 325 °C (Drobny, 2016; Greene-Tweed, 2021a, 2021b). These polymers can also be compounded to meet the special requirements of upstream, midstream, and downstream oil and gas exploration due to their superior properties (Barnwell, 2021; Daemar, 2021). Because of these properties, FFKM elastomers are used in a wide variety of applications such as critical sealing solutions for the aerospace, pharmaceutical, medical, chemical processing, semiconductor, and oilfield industries (Atkinson, 2018; Marshall, 2017).

Amorphous fluoropolymers

Amorphous fluoropolymers are copolymers of TFE and specialty monomers that yield linear, high molar mass noncrystalline polymers (AGC Chemicals Company, 2021c; Gangal & Brothers, 2010; Hintzer et al., 2013; Korinek, 1994; Resnick & Buck, 1997, 1999). Amorphous fluoropolymers have the outstanding chemical and thermal stability and surface properties of semicrystalline perfluoropolymers as well as the unique properties associated with amorphous materials such as optical clarity and high gas permeability. The optical properties are outstanding, with more than 90% transmission, and thereby low dissipation, over a wide range of wavelengths (e.g., 200–2000 nm). TFE/PDD (2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole) copolymers have the lowest refractive index known for a solid organic polymer (Groh & Zimmermann, 1991). This unique combination of properties makes amorphous fluoropolymers unmatched for uses in degassing, fiber optics, photolithography, antireflective coatings, passivation and protective coatings for medical, military, and aerospace devices, as well as electronic applications (Gangal & Brothers, 2010; Hintzer et al., 2013).

Fluorinated ionomers

Fluorinated ionomers are copolymers of TFE and a perfluorovinylether monomer containing an ionic group, typically a sulfonic acid or carboxylic acid (Grot, 2011, 2013). Fluorinated ionomers can be extruded or cast into film and converted into ion exchange materials (IXMs). IXMs come in a variety of useful forms offering a broad range of solutions for different applications (AGC Chemicals Company, 2021d; Asahi-Kasei, 2021; Chemours, 2021a). These forms include ion exchange membranes (IEMs), dispersions, and resins. IEMs must possess the required ion transport properties for the electrochemical cell in which they reside to perform well

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and work effectively. Some of these properties include high ionic conductivity, chemical resistance, high operating temperature range, low permeability, and balanced durability and performance (Chemours, 2021b).

Ion exchange membranes (IEMs) stand to play a noteworthy role in today's modern world (Chemours, 2021b) and as such, are utilized in a wide range of applications and end-use industries including electrochemical processing, energy production, and hydrogen production. IEMs revolutionized the chlor-alkali industry (Grot, 2013), the manufacture of primarily caustic soda and chlorine, by eliminating the use of hazardous materials such as mercury and asbestos (Asahi-Kasei, 2021) and, in doing so, reducing energy consumption. Water electrolysis, the process of converting water into hydrogen and oxygen, relies on IEM technology. Although this process requires electricity, renewable energy sources such as solar or wind power can be utilized, allowing the potential for hydrogen to be a "clean" energy source (Science Center, 2021). Hydrogen fuel cells, some of which use a type of IEM known as a proton exchange membrane, can then convert hydrogen to electricity, a crucial technology to reach the stated target of the EU New Green Deal (EC, 2021).

STUDY METHODOLOGY AND DATA

Seven global fluoropolymer manufacturers (AGC Chemicals Americas, Arkema, The Chemours Company, Daikin Industries, Gujarat Fluorochemicals Limited, Solvay Specialty Polymers, and 3M Company) participated in this study and contributed data, writing, critique, and analysis. The companies noted above are members of the US-based Performance Fluoropolymer Partnership (PFP) and/or EU-based Fluoropolymer Product Group (FPG).

This study provides data on 14 fluoropolymers, building on a prior study (Henry et al., 2018). The study was chartered within two global industry groups. Participants put forward candidate fluoropolymers of notable commercial importance for the study and provided company and published data that address the PLC criteria. Thirteen PLC criteria that relate to the polymer structure and properties, including three to physicochemical properties and five to stability, set forth in BIO by Deloitte (2015) and presented in prior work on four fluoropolymers (Henry et al., 2018), are addressed in this study (Figure 1). These criteria are briefly described in Table 3 with further description provided in Supporting Information: Chapter 3 and in the prior work (Henry et al., 2018). Participants provided company and published data and a description of methods and/or public references to demonstrate the origin of the data provided. These methods and references are provided in detail in Supporting Information: Chapter 4. The PLC criteria data were compiled and are presented in Tables 4 and 5.

The data assessment was done in two ways: Companies could self-assess the PLC data if they had the technical resources to do so or they could submit their PLC data to a third-party contractor for an independent technical review. The third-party consultant hired by PFP was GSI Environmental Inc. The objective was to be able to publish the references and methods behind the PLC data provided for each fluoropolymer in the study. In cases where the data and/or methods contained confidential business information, the third-party consultant independently evaluated the information supplied before it was shared in a blinded, aggregate form with the participating project companies. In several cases—FKM, PVDF, and ionomers—several companies submitted data for the same fluoropolymer. The data were combined and are presented in Tables 4 and 5. There is no intentional company attribution for the data presented.

The following describes further how the study data were generated and compiled.

- A third-party consulting company (GSI) was engaged to comment independently on data, methods, and references initially supplied by study participants for their respective fluoropolymers. Several study participants used this third-party consultant.
- Following the initial third-party assessment and assembly of the master data Tables 4 and 5 as well as the FKM data in Supporting Information: Table 4.11, a series of subsequent assessments were conducted (within PFP)

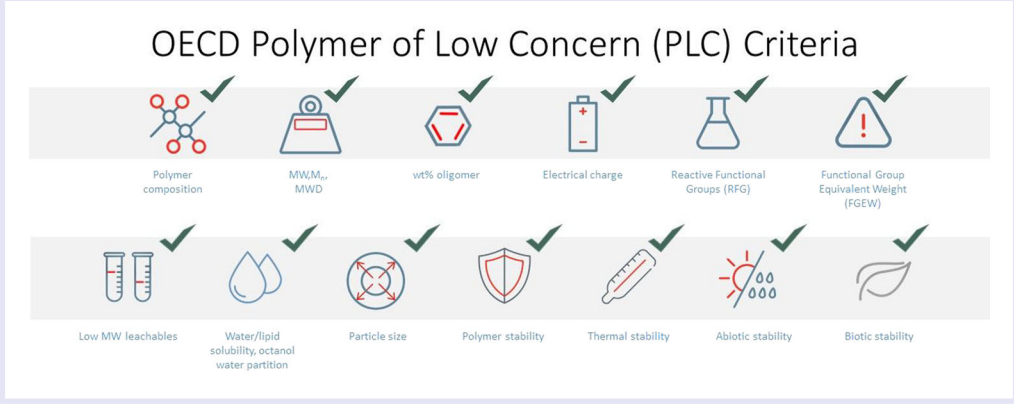


FIGURE 1 OECD polymer of low concern (PLC) criteria add (C) 2021 W.L.Gore & Associates

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TABLE 3 Polymer of low concern (PLC) criteria descriptions

(See Supporting Information: Chapter 3 for additional details) Criterion	Description
Polymer composition	The polymer composition criterion requires structure and elemental composition of the polymer be described and identified (e.g., by Chemical Abstracts Service [CAS] number).
Molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da	The number average molecular weight (Mn) and oligomer content are the most commonly used criteria for PLC assessment. The EU assessment report (BIO by Deloitte, 2015) states that the "most potential health concern polymers have a number average molecular weight, Mn, <1000 Da and oligomer content >1%." The higher the oligomeric content, the more likely a polymer is to be a health or ecotoxicological (OECD, 2009, p. 9).
	Molecular weight (MW) is an important predictor of biological effect because large molecules (>1000–10 000 Da) are too large to penetrate cell membranes (Supporting Information: in Beyer, 1993, p. 14). Because large molecular weight polymers cannot enter the cell, they cannot react with "target organs," such as the reproductive system, and are not bioavailable. "Therefore, as the Mn of a polymer increases, a reduced incidence of potential health concern effects might be expected" (OECD, 2009, p. 20).
	An additional PLC consideration is the weight percentage of oligomers that are <1000 Da. Oligomers may be composed of, for example, dimers, trimers, and tetramers, meaning they have 2- monomer, 3- monomer, and 4-monomer units, respectively. The EU report (BIO by Deloitte, 2015) concluded that most potential health concern polymers have Mn of <1000 Da and oligomer content of >1%: "…the distribution of potential health concern polymers exhibited an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content" (OECD, 2009, p. 24).
	Molecular weight distribution (MWD), also known as "polydispersity index," measures the heterogeneity of size of polymer molecules in a polymer. The MWD is an important parameter for predicting potential biological effects of polymers because, although Mn may be a large value, low MW oligomers <1000 Da may be present, which could penetrate the cell.
Ionic character	Electrical charge or ionic character can be anionic, cationic, amphoteric, or nonionic. Specifically, cationic polymers have been associated with aquatic toxicity (Auer et al., 1990; USEPA, 1997a).
Reactive functional groups and RFG ratio to MW	A "reactive functional group" (RFG) is defined as an atom or associated group of atoms in a chemical substance that is intended or can be reasonably expected to undergo facile chemical reaction (USFR, 2012). Some highly reactive functional groups (or a high ratio of RFGs per mole) have been associated with adverse human health and ecotoxicology (e.g., acrylates, methacrylates, isocyanates, anhydrides, aziridines; USEPA, 2010).
	The functional group equivalent weight (FGEW) is used to determine if the RFGs in a polymer are substantially diluted by polymeric material to allow the polymer to be a PLC (USEPA, 1997). The FGEW of a polymer is defined as the ratio of the Mn to the number of functional groups in the polymer. The FGEW is used as an indication of the degree of reactivity of the polymer; the lower the FGEW, the more reactive the polymer and the greater the potential for health and environmental impact (OECD, 2009, p. 10).
Low MW leachables	Low MW leachables are chemical molecules, either inorganic or organic, that migrate (i.e., leach) out of the polymer. These could be residual monomers or oligomers resulting from incomplete polymerization processes, surface residues, or other chemicals used in the manufacturing processes (e.g., initiators, catalysts, chain transfer agents, surfactants).
	Low MW leachables are critically important to the potential for a polymer to affect health and the environment, given that they may be able to migrate out of the polymer and cross cell membranes to potentially react with biomolecules. A report to the EU (BIO by Deloitte, 2015) concluded that "Polymers with <1% MW < 1000 Da and low water extractability are not able to cause systemic effects which are toxicologically or ecotoxicologically relevant."
	Monomers, by nature, are reactive. Unreacted monomers left in a polymer may migrate out of the polymer to react with biomolecules to cause potential adverse effects. Regulatory authorities (BIO by Deloitte, 2015) and the OECD Expert Group on Polymers (OECD, 2009) agree that the residual monomer content of a polymer is critical to determining if it qualifies as a PLC.

(*Continued*)

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TABLE 3 (*Continued*)

(See Supporting Information: Chapter 3 for additional details) Criterion	Description
Particle size	Particle size is also a PLC criterion. Particles that are small enough to reach the deep lung upon inhalation are often associated with adverse health effects. Therefore, to qualify as a PLC, median mass aerodynamic diameter (MMAD) of the polymer particle size should be >5 μm.
Structural and elemental composition	In the US, Chemical Categories of Concern are the result of the review of new chemicals by the USEPA under the TSCA (see https://www.epa.gov/reviewing-new-chemicals-under-toxic-substances-control-act-tsca/chemical-categories-used-review-new). The categories describe the molecular structure, boundary conditions such as MW, equivalent weight, the log of the octanol–water partition coefficient, log *P*, or water solubility, and standard hazard (mammalian and ecological) and (environmental) fate tests to address concerns.
Elemental composition	The elemental composition is a factor in the assessment of the eligibility of polymers for reduced notification requirements. The exclusion of polymers under this step is not a conclusion of hazard but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process. These elemental requirements differ across jurisdictions as covered in the report to the EU on global regulatory approaches to polymer assessment (BIO by Deloitte, 2015). For example, in the EU under REACH it is proposed that polymers composed from among these elements, covalently bound to C, have reduced hazard: H, N, O, Si, S, F, Cl, Br, or I (BIO by Deloitte, 2015). In contrast, the USEPA Polymer Exemption Rule states that a polymer is eligible for reduced agency review when it has at least two of the following elements: C, H, O, N, S, or Si (USFR, 1995).
Water and lipid solubility and the octanol–water partition coefficient	Water solubility is the extent to which a compound will dissolve in water. According to the OECD (2009) meeting of the Expert Group on Polymers, polymers with "negligible" water solubility, or those described as "hydrophobic" have been represented with a water solubility of 0.000001 mg/L (1×10^{-6} mg/L; assigned arbitrarily; OECD, 2009). That is equivalent to 1 ppt, a very conservative definition.
	Polymers with water solubility <10 mg/L showed generally low health concerns.
	The octanol–water partition coefficient (K_{ow}) is another criterion to assess chemicals and their environmental and health impact. The K_{ow} is a physical–chemical property at equilibrium to represent the lipophilic or hydrophilic nature of a chemical, the distribution of a compound in octanol, representing the lipophilic nature, to its solubility in water, representing the aqueous nature. The higher the K_{ow}, the more lipophilic the compound. Typically, a K_{ow} >5000 or a log K_{ow} >5 means high lipophilicity and, thus, a high potential to bioaccumulate or bioconcentrate. According to the Stockholm Convention, a bioconcentration factor of >5000 and a log K_{ow} >5 is used as a criterion for bioaccumulation.
Stability	Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. As was previously described in the Polymer of Low Concern section under the molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da heading, molecules with Mn <1000 Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment.
Abiotic stability	Polymers are stable; monomers are not. Abiotic degradation may involve sunlight, water, or oxygen. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Hydrolytic degradation of polymers is another potential way to break the polymer bonds, creating smaller oligomers that may be bioavailable. Chemical oxidation is a reaction involving the loss of electrons from one atom to another.
Biotic stability: aerobic, anaerobic, and in vivo	Biotic stability is assessed by whether the polymer is degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic) conditions; in vitro and in vivo stability studies demonstrate this. In vivo biodegradation involves the breaking of the polymer bonds by the action of bacteria, enzymes, and oxidants within the organism.
Thermal stability	Thermal stability of a polymer can be assessed when used as intended under normal, foreseeable use conditions or in extreme temperatures during disposal, such as by incineration. Thermal stability testing may involve Thermogravimetric Analysis (TGA), which determines mass loss over time and temperature of a test substance.

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TABLE 4 Fluoroplastics and PLC criteria

	Fluoroplastics				
Supporting Information Data: Chapter	**4.1 PVDF**	**4.2 PVDF-HFP copolymer**	**4.3 ECTFE**	**4.4 ECTFE**	**4.5 PCTFE**
	Polyvinylidene fluoride	Vinylidene fluoride, hexafluoropropene copolymer	Ethylene, chlorotrifluoroethylene copolymer	Ethylene, chlorotrifluorethylene, hexafluoroisobutylene terpolymer	Polychlorotrifluoroethylene
PLC assessment criterion[a]	CAS 24937-79-9	CAS 9011-17-0	CAS 25101-45-5	CAS 54302-04-04	CAS 9002-83-9
Structure	$–(CF_2–CH_2)_n–$	$–(CF_2–CH_2)_n–[CF(CF_3)–CF_2]_m–$	$–(CF_2–CFCl–CH_2–CH_2)_n–$	$–(C_4H_2F_6)_n–(C_2H_4)_m–(C_2ClF_3)_i–$	$–(CF_2–CFCl)_n–$
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes	Yes
Molecular weight (Mn)[b] (Mn >1000 Da and oligomer content <1%)	70 000–300 000	80 000–300 000	Mn >50 000	Mn >50 000	70 000–400 000 average based on grade type
Molecular weight distribution Mw[c] ÷ number average M_n	2–3	2–3	1.1	1.7	3
Wt% oligomer (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	Negligible	Negligible	Negligible
Ionic character	Neutral	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs)[d] **and functional group equivalent weight (FGEW)**	None and N/A	None and N/A	None and N/A	None and N/A	None and N/A
Low molecular weight leachables	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	Negligible
Residual monomers	<50 ppb	<50 ppb	<50 ppb	<50 ppb	<0.1 wt%
Ratio of residual monomers to molecular weight (typical value)	$\sim10^{-12}$–$\sim10^{-13}$	$\sim10^{-12}$–$\sim10^{-14}$	$\sim10^{-13}$	$\sim10^{-13}$	$<10^{-5}$
Structural similarities to RFG of concern	None	None	None	None	None
Reference standard	ASTM D3222-18a	ASTM D5513-18	ASTM D3275-81	ASTM D3275-81	

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TABLE 4 (*Continued*)

	Fluoroplastics				
Supporting Information Data: Chapter	**4.1 PVDF**	**4.2 PVDF-HFP copolymer**	**4.3 ECTFE**	**4.4 ECTFE**	**4.5 PCTFE**
Physical–chemical properties					
Water solubility and octanol/water partition coefficient, K_{ow}	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, MMAD, should be >5 μm)	Powders: 5–300 μm pellets: 2–4 mm	Powders: 5–300 μm pellets: 2–4 mm	D50%: 50–70 μm (typical)	D50%: 50–70 μm (typical)	Pellet: 2-4 μm, flake: 0.54 mm powder: 5–300 micron
Stability					
Hydrolysis, light (hν), Oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp. (°C)	150 °C	150 °C	150 °C	150 °C	120 °C
Meets [a]PLC criteria (Yes or No)	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**
Fluorinated polymerization aid (PA) used? (Yes or No)	No	No	No	No	No
Recommended processing/application (use) temperature (T°C)	Processing: 200 °C–250 °C Use max temp: 150 °C	Processing: 180 °C–250 °C Use max temp: 100 °C–140 °C depending on HFP content	Processing: 250 °C–280 °C Use max. Temp: 150 °C	Processing: 250 °C–280 °C Use max. Temp: 150 °C	Molding: 230 °C –330 °C and Use Max same as above at 120 °C

	Fluoroplastics			
Supporting Information Data: Chapter	**4.6 FEVE**	**4.7 EFEP**	**4.8 CPT**	**4.9 THV**
	Fluoroethylene-vinyl ether copolymer	1-Propene, 1,1,2,3,3,3-hexafluoro-, polymer with ethylene and 1,1,2,2-tetrafluoroethylene	1,1,1,2,2,3,3-Heptafluoro-3-[(trifluoroethenyl)oxy]propane polymer with chlorotrifluoroethylene and tetrafluoroethylene	1-Propene,1,1,2,3,3,3-hexafluoro-polymer with 1,1-difluoroethylene and tetrafluoroethylene
PLC assessment criterion[a]	cbi	35560-16-8	116018-07-6	25190-89-0

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TABLE 4 (*Continued*)

	Fluoroplastics			
Supporting Information Data: Chapter	**4.6 FEVE**	**4.7 EFEP**	**4.8 CPT**	**4.9 THV**
Structure	cbi	$-(CH_2-CH_2)_n-(CF_2-CF_2)_m-[CF_2-CF(CF_3)]_l-$	$-(CF_2-CF_2)_n-(CFCl-CF_2)_m-[CF_2-CF(OR_f)]_l-$	$-(CF_2CH_2)_x-(CF_2-CF-CF_3)_y-(CF_2-CF_2)_z$
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes
Molecular weight (Mn)[b] (Mn >1000 Da and oligomer content <1%)	7000–46 000	130 000	200 000–300 000	131 000
Molecular weight distribution Mw[c] ÷ number average M_n	2.0–4.0	4	2–5	1.8
Wt% oligomer (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Mn <1000 range of <3.5% and Mn <500 is <0.7%	Negligible; <0.1 wt% oligomer content	Negligible; <0.1 wt% oligomer content	wt.% <1000: None
Ionic character	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs)[d] **and functional group equivalent weight (FGEW)**	None and N/A	None and N/A	None and N/A	None and N/A
Low molecular weight leachables	Negligible; cross-linked as final product	Negligible	Negligible	No active leachables by USP class VI (121 °C)
Residual monomers	0.12%–1.43% non-fluorinated	Negligible	Negligible	None detected
Ratio of residual monomers to molecular weight (typical value)	10^{-7}–10^{-8}	$<10^{-5}$	$<10^{-5}$	$\sim10^{-13}$
Structural similarities to RFG of concern	None	None	None	None
Reference standard		ASTM D7472	ASTM D7471	

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TABLE 4 (*Continued*)

	Fluoroplastics			
Supporting Information Data: Chapter	**4.6 FEVE**	**4.7 EFEP**	**4.8 CPT**	**4.9 THV**
Physical–chemical properties				
Water solubility and octanol/water partition coefficient, K_{ow}	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, MMAD, should be >5 μm)	Solution or flake 150 nm for emulsion	2–4 mm (pellets)	2–4 mm (pellets)	Pellets ~400–750 μm
Stability				
Hydrolysis, light (hν), oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp. (°C)	220 °C	130 °C; low melting point 160 °C–190 °C and high decomposiiton temperature of 357 °C–380 °C	200 °C; low melting point 239 °C–251 °C and high decomposition temperature of >400 °C	Continuous use is expected ~room T. (<100 °C as host resin melts at 120 °C); No expected degradation; fluoropolymer degrades >350 °C by TGA
Meets [a]PLC criteria (Yes or No)	**Yes**	**Yes**	**Yes**	**Yes**
Fluorinated polymerization aid (PA) used? (Yes or No)	No	No	No	Yes and No
Recommended processing/application (use) temperature (T°C)	180 °C–200 °C	Molding temperature: 200 °C–280 °C; Use max as noted above	Molding temperature: 310 °C–330 °C; Use max as noted above	Melt processing: <350 °C Application: <100 °C (in LLDPE)

Abbreviations: ECTFE, ethylene-chlorotrifluoroethylene; HFP, hexafluoropropylene; PCTFE, polychlorotrifluoroethylene; PLC, polymer of low concern; PVDF, polyvinylidene fluoride.
[a]See OECD (2009) and BIO by Deloitte (2015) for details on characteristics of a "Polymer of Low Concern" and Supporting Information: Chapter 3.
[b]Molecular Weight is number average molecular weight which is defined as the total weight of the polymer divided by the total number of molecules. It is the mole fraction of molecules in a polymer sample.
[c]Molecular weight is weight average molecular weight which is determined by summing the weights of all the chians and then dividing by the total number of chains. It is the weight fraction of molecules in a polymer sample.
[d]For definition of reactive functional group, lists of low-, moderate-, and high-concern functional groups and FGEW limits, see USEPA polymer exemption guidance manual, BIO by Deloitte (2015, pp. 191–192), and USEPA (2010). See Supporting Information.

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TABLE 5 Fluoroelastomers and specialty fluoroplastics—PLC criteria

	Specialty fluoroplastics		Fluoroelastomers		
Supporting Information Data: Chapter	**4.13 Amorphous**	**4.14 Ionomer**	**4.10 FEPM**	**4.11 FKM**	**4.12 FFKM**
	Perfluoro(alkenyl vinyl) ether polymer	Sodium or potassium salts of perfluorosulfonic acid/TFE copolymer or perfluorocarboxylic acid/TFE copolymer	Tetrafluoroethylene-propylene copolymer	1-Propene,1,1,2,3,3,3-hexafluoro-polymer with 1,1-difluoroethylene copolymer and terpolymers	Tetrafluoroethylene-trifluoromethyl trifluorovinyl ether copolymer
PLC assessment criterion[a]	37626-13-4	9002-84-0, 1314-23-4, 409-21-2, 111173-25-2	27029-05-6	9011-17-0, 26425-79-6, 25190-89-0	26425-79-6
Structure	See Supporting Information	See Supporting Information	See Supporting Information	Supporting Information	-(CF2CF2)x -[CF2-CF(OCF3)]y-(Cure Site Monomer)z
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes	Yes
Molecular weight[b] (Mn >1000 Da and oligomer content <1%)	150 000–300 000	>100 000	Various grades vary between 146 000–275 000	30 000–340 000	10 000–1 000 000
Molecular weight distribution Mw[c] ÷ number average M_n	1.4–2.5	1.0–2.4	Various grades give various ratios from 1.4 to 3.3	1.2–2.4	1.2–3.5
Wt% oligomer (Figure MWD) (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	<0.01%	Negligible to <1%	Negligible
Ionic character	Neutral	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs)[d]	None and N/A	None and N/A	None and N/A	None and N/A	None and N/A
Functional group equivalent weight (FGEW; typical value)	$>10^5$	$>10^5$	$>10^5$	$>10^4$–10^5	$>10^4$

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TABLE 5 (*Continued*)

	Specialty fluoroplastics		Fluoroelastomers		
Supporting Information Data: Chapter	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
Low molecular weight leachables	<1 ppm	<1 ppm	No active leachables	<0.4 ppm to <1 ppm	No active leachables
Residual monomers	<1 ppm	<1 ppm	No residual monomers Only cross-linking agent at <1 ppm	<50 ppt to <5 ppm	<50 ppb
Ratio of residual monomers to molecular weight (typical value)	$>10^{-5}$	$>10^{-5}$	10^{-11}–10^{-12}	$>10^{-10}$–10^{-13}	0.25 ppt as Mn = 10^5 (for representative FKM)
Structural similarities to RFG of concern	None	None	None	None	None
Reference standard				ASTM D 1418	
Physical–chemical properties					
Water solubility and octanol/water partition coefficient, K_{ow}	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, aerodynamic diameter, MMAD, should be >5μm)	Solution, sheet or pellets	(1) Aqueous dispersion casting (as a film) followed by annealing or (2) Melt extrusion as a membrane (reinforced)	Sheet or crumb	Sheet or block; powders 300–350 μm stability increased/enhanced when cross-linked	Sheet or block; or "crumb"
Stability					
Hydrolysis, light (hν), oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable	Stable

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TABLE 5 (*Continued*)

	Specialty fluoroplastics		Fluoroelastomers		
Supporting Information Data: Chapter	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
Thermal stability at normal foreseeable use maximum continuous Temp (°C)	>250 °C	Sulfonic acid polymer: maximum operating temperature of 175 °C under anhydrous conditions, 220 °C –240 °C in aqueous systems carboxylic acid polymer: use below 120 °C	200 °C	180 °C	200 °C–300 °C
Meets[a] PLC criteria (Yes or No)	Yes	Yes	Yes	Yes	Yes
Fluorinated polymerization aid (PA) used? (Yes or No)	Yes and No	Yes and No	No	Yes and No	Yes and No
Recommended processing/ application (use) temperature (T°C)	<280 °C	Sulfonic acid polymer: maximum operating temperature of 175 °C under anhydrous conditions, 220 °C–240 °C in aqueous systems carboxylic acid polymer: use below 120 °C	–60 °C–204 °C (AFLAS Technical Document)	Melt processing: <300 °C 160 °C–320 °C (cross-linking temperature)	160 °C–320 °C (cross-linking temperature)

Abbreviations: FEPM, trifluoroethylene-propylene copolymer; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMVE perfluoroelastomer; PLC, polymer of low concern.
[a]See OECD (2009) and BIO by Deloitte (2015) for details on characteristics of a "Polymer of Low Concern."
[b]Molecular weight is *number* average molecular weight.
[c]Molecular weight is weight average molecular weight.
[d]For definition of reactive functional group, lists of low-, moderate-, and high-concern functional groups and FGEW limits, see USEPA polymer exemption guidance manual, BIO by Deloitte (2015, pp. 191–192), and USEPA (2010). See Supporting Information.

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until all data cells in the tables cited above were backed up with a narrative, a testing method, and/or references where publicly available.
- Where several companies have provided data on the same fluoropolymers, the table data presented provide a multicompany compilation and assessment along with appropriate methods and references.
- Individual companies supplying data are identified as authors, but there is no direct attribution regarding which company supplied which data for this study.

PLC ASSESSMENT RESULTS

This study was conducted on commercial fluoropolymer products using the PLC criteria to characterize their potential hazard. Figure 1 illustrates the PLC criteria used (BIO by Deloitte, 2015; Henry et al., 2018). The pictured criteria encompass structure, physicochemical property, and stability criteria evaluated in the study. Data informing structure criteria, MW, Mn, and MW distribution (MWD), physicochemical property criteria, water and lipid solubility and K_{ow}, and stability criteria are presented in Tables 4 and 5. The study also gathered structural data on (a) residual monomers, (b) ratio of residual monomers to MW, (c) structural similarities to reactive functional groups (RFGs) of concern, and (d) thermal stability at normal foreseeable maximum continuous use temperatures. Brief descriptions of PLC criteria are provided in Table 3 with additional details, including references for each criterion in Supporting Information: Chapter 3. An additional data point gathered was whether the fluoropolymer(s) presented utilized a fluorinated polymerization aid (PA) during manufacture. The study results are presented in Tables 4 and 5 and summarized below.

Polymer composition: Each of the fluoroplastics, specialty fluoroplastics, and fluoroelastomers assessed in this study met the criterion of polymer composition whereby either fluorine (F) and/or chlorine (Cl) must be covalently bound to the carbon-only polymer backbone.

MW and MWD: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the criteria for MW (Mn >1000 Da) and MWD (1–3). The data demonstrate the fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study are high-MW solid polymers with fairly narrow MWD and negligible to low wt% oligomer content. The MW for fluoroplastics in Table 4 and specialty fluoroplastics in Table 5 ranged from 50 000 to 300 000, and the MWD ranged from approximately 1.4 to 3. We note that FEVE was measured in its uncured state and that, upon curing, its MW increased significantly. The MW and MWD were determined in a variety of ways depending on the fluoropolymer and its solubility (or insolubility) in various solvents. The MW and MWD data for fluoroelastomers and specialty fluoroplastics in the study are presented in Table 5. The MW and MWD varied because of the various grades of fluoroelastomers ranging from 100 000 to 250 000 with some less than (down to 10 000) and greater than (up to 500 000). MWD was on the order of 1.4 to 3.5. Fluoroelastomer MW is lower for uncured fluoroelastomer versus cured fluoroelastomer. Cured fluoroelastomer is the form used in many formed-use applications (e.g., gaskets and o-rings). The methods and references for MW and MWD data are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. Methods included size exclusion chromatography (SEC), gel permeation chromatography (GPC) along with osmotic pressure, and parallel plate rheometry methods.

Weight % oligomer: The criteria for wt% oligomer are less than 5% oligomer content for Mn less than 1000 Da, and less than 2% oligomer content for Mn less than 500 Da (BIO by Deloitte, 2015; Henry et al., 2018; see also the Supporting Information). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the wt% oligomer criteria. Many polymers in the study were reported as "negligible" for oligomers based on analyses conducted. Polymers in the study not cited as negligible have reported numerical data presented in Tables 4 and 5. In addition to SEC and GPC, analytical methods employed included a weight loss upon heating method and the FDA 21 CFR 177.1380 method. The methods and references for wt% oligomer are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5.

Ionic character: The fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study are neutral polymers, either containing no ionic groups or may contain anionic at the terminus of their high MW polymer chains as noted in the prior study of fluoropolymers (Henry et al., 2018). Notably different are fluorinated ionomers, which have neutralized (salts) sulfonic acid or carboxylic acid groups pendant to the polymer backbone and as such are neutral and not ionically charged in their polymeric solid form and are low in toxicity and not dermally irritating on skin contact (USEPA, 1997). None of the evaluated polymers in the study have cationic nature. The methods and references for ionic character are presented in the Supporting Information: Chapter 4 with the specific subchapter noted in Tables 4 and 5.

RFG, functional group equivalent weight (FGEW) and structural similarities to RFG of concern: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the RFG and FGEW criteria. The polymers in this study do not contain the reactive functional groups set forth in the PLC criteria (e.g., acrylates, alkoxysilanes, amines, aziridines, carbodiimides, and so forth; see Supporting Information: Chapter 3). Given that the polymers in this study have no RFGs, the FGEW values in Tables 4 and 5 are very large numbers (such as $>10^4$–10^5) or the value given is not applicable due to the lack of RFGs altogether. Even the polymers with some functional groups present (e.g., fluorinated ionomers) are not reactive. For example, the FEVE polymerization process leads by design to a polymer with neutral and/or anionic end groups. FEVE resins do contain a small amount of hydroxyl and carboxyl functional groups. These functional groups are classified as low concern RFG

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by the USEPA (1997) and OECD (2009). There are no RFG structural similarities across the polymers in this study.

Low MW leachables (MW < 1000 Da): All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the low MW leachable PLC criteria, which has been widely discussed (see Supporting Information: Chapter 3 for references). Many of the study polymers report no active leachables, whereas the rest cite values less than 1 ppm (Tables 4 and 5). For FEVE, it is reported that some non-fluorinated polymer PA may well remain in the uncured polymer resin. The methods and references for low MW leachables are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. The data presented in Tables 4 and 5 were determined for each of the respective polymers in this study using techniques such SEC and GPC as the predominant analytical methods along with the use of USP Class VI testing. Additional methods included 21 CFR 177.2600 (USCFR, 2022) and the USEPA's toxicity characteristic leaching procedure (TCLP; SW-846 Test Method 1311; USEPA, 1992).

Residual monomers and ratio of residual monomers to typical MW: PLC criteria of equal interest to the low MW leachables are the residual monomers and the ratio of residual monomers to typical MW (see Supporting Information: Chapter 3 for references). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the residual monomers and ratio of residual monomers to typical MW PLC criteria. The study data presented in Tables 4 and 5 show the polymers in this study have residual monomers ranging from less than 50 ppb for several fluoropolymers and up to less than 0.1% for PCTFE based on the methods utilized. Fluoroelastomers in this study have residual monomers ranging from less than 50 ppb up to less than 5 ppm. Residual monomers were determined in several ways including dynamic and static headspace gas chromatography/mass spectrometry (GC/MS) at 150 °C. The monomers used in most cases have very low boiling points and are thus readily volatilized (and captured or destroyed) during polymer manufacture processing and drying steps. The methods and references for residual monomer determination are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. Given the very low residual monomer levels reported, the ratio of residual monomers to polymer MW range from 10^{-11} to 10^{-13} for the study polymers.

Water solubility and octanol/water partition coefficient (K_{ow}): The fluoroplastics, specialty fluoroplastics, and fluoroelastomers in this study are solids that are hydro- and oleophobic, practically insoluble in both water and n-octanol. Therefore, a K_{ow} cannot be computed and is not applicable to these substances. It is worth noting that the practical lack of solubility in water (<10 mg/L) and n-octanol indicate the inability for the study fluoropolymers to actively or passively cross cell membranes. This does mean there is no indication that these polymers can bioaccumulate or bioconcentrate in biota (Henry et al., 2018 and this study). The methods and references for solubility are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5.

Particle size: To meet the PLC assessment criteria for particle size, a powder must be 5 µm or greater in size (median mass aerodynamic diameter [MMAD]). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the particle size PLC criterion. As shown in Tables 4 and 5, the fluoroelastomers in this study are provided in sheets, blocks, pellets, or "crumb," and the fluoroplastics and specialty fluoropolymers in this study are provided in the form of powders, pellets, sheets, flake, or in dispersions. References and additional information regarding the form of the study polymers is provided in the Supporting Information: Chapter 4.

Stability: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the PLC criteria for hydrolysis, light stability, oxidative stability, and aerobic and anaerobic biodegradability (e.g., breakdown into species with Mn <1000 Da). Public literature has abundant thermal, chemical, and biological stability data for the polymers in this study as stability is a hallmark property for these polymers (Ebnesajjad, 2017). For biodegradation, the assessments were largely made based on property data of the study polymers demonstrating they are insoluble and stable in environmental media and thus are not expected to be bioavailable and therefore not biodegrade.

Additionally, published literature reports (Drobny, 2016; Ebnesajjad, 2017; Grot, 2013; Henry et al., 2018; Polymer Industry Association [PIA], 2019) that the study polymers are stable at foreseeable maximum continuous use temperatures presented in Tables 4 and 5. All polymers, including fluoropolymers can degrade when misused or when heated above their recommended use temperatures (Fluoropolymer Products Group of Plastics Europe [FPG], 2012; PIA, 2019). Of course, users are expected to follow guidance for use provided by manufacturers. Hence, the recommended temperatures for reasonably foreseeable use for the study substances are presented in Tables 4 and 5. References and additional information regarding the stability of the study polymers is provided in the Supporting Information: Chapter 4.

Fluorinated PA: If a fluorinated PA was used in the manufacture of the polymer, it was reported for each fluoropolymer in this study. Nine of the 14 fluoropolymers in the study were reported *not* to have used a fluorinated PA in their manufacture. It is industry practice to use fluorinated PAs when it is necessary to obtain specific end-use property or performance requirements generally related to very high-polymer MWs (see also Supporting Information: Chapter 7). For five study polymers, THV, FKM, FFKM, fluorinated ionomers, and amorphous fluoropolymers, a response of "Yes and No" was provided indicating that for some polymer grades a fluorinated PA is used, but not for others. See Supporting Information: Chapter 4 for additional information.

Results summary: This study examined three fluoroelastomers, nine fluoroplastics, and two specialty fluoroplastics:

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ionomers and amorphous. Data for each were gathered from the author companies and assessed by the PLC criteria applicable to the polymer itself "in use" (BIO by Deloitte, 2015; Henry et al., 2018; OECD, 2009). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the PLC criteria based on the data presented in Tables 4 and 5 with additional details provided describing methods and references in the Supporting Information: Chapter 4.

Including the four fluoroplastics in the prior study (Henry et al., 2018), data for 18 fluoropolymers have been provided for PLC assessment. These polymers have a wide range of compositions and structures and represent most of the global commercial fluoropolymer market (see additional text in the Discussion). These 18 fluoropolymers represent the major fluoropolymers manufactured and are used worldwide in innumerable critical end-use products and applications. Tables 1 and 2 highlight examples of the end-use markets as well as critical functionality and benefits these polymers provide.

Each of the assessed polymers in this study are insoluble in both water and n-octanol, and thus K_{ow} is not applicable. This lack of solubility in water and octanol confirms that fluoropolymers are not mobile in the environment and are not bioaccumulative and not able to bioconcentrate. The stability studies reported here on each of the study fluoropolymers reveal their stability in terms of light, hydrolysis, heat, oxidation, and biodegradation. When coupled with the lack of solubility, these fluoropolymers are most often characterized as relatively inert materials in the environment. Like any other chemical material or product, it is important to follow the fluoropolymer manufacturer's recommended use and temperature conditions. Tables 4 and 5 describe these recommendations for each fluoropolymer. As reported, the physical forms of the fluoropolymers are largely pellets, blocks, crumb, sheets, some powders (all with MMAD >5 μm). The solid fluoropolymers are not nanoparticles, and concerns related to nanoparticles do not apply during normal product use. Due to the properties described above for the assessed fluoropolymers—large molecules with no water solubility—the fluoropolymers are biologically inert without the practical ability to cross cell membranes.

During the evaluation of the study fluoropolymers, there was a conscious focus on several core PLC parameters: MW, low MW leachables, % oligomers, and residual monomers, which are direct outcomes related to fluoropolymer manufacturing. In addition to what is reported here in Tables 4 and 5 for the fluoropolymers themselves, industry efforts to manage emissions during manufacturing are discussed below.

DISCUSSION

Fluoropolymers have substantial, unique societal value: Fluoropolymers possess a remarkable combination of properties and functional characteristics, as shown in Tables 1 and 2, that make them valued materials of choice in a broad range of industries and applications critical to life and a sustainable environment in the 21st century. Their unparalleled combination of properties and performance characteristics deliver functionality to a wide variety of products and systems critical to achieving important societal goals (Amcham, 2020c; FPG, 2021a; Wood, 2020b). They are strategically important to innovation in vital sectors of the global economy requiring high-speed, high-volume data transmission, miniaturization, or operations in extreme temperatures. Moreover, they are crucial to achieving important societal goals such as decarbonization, renewable energies, and/or competitiveness in the digital transition (FPG, 2021a). Fluoropolymers are indispensable for critical applications in the chemical, electronic, semiconductor, healthcare, and transport sectors and the deployment of 5G networks (FPG, 2021a). For many critical applications, fluoropolymers are the material of choice because alternatives are unable to provide the full complement of performance and functionality required. As such, there are currently no viable commercial alternatives to fluoropolymers in virtually every critical application in which they are used (FPG, 2021a, 2017; PFP, 2020).

Commercial fluoropolymers in this study meet the PLC criteria: Widely used by regulators, PLC criteria have been established around the world and documented by OECD expert groups as an appropriate hazard assessment methodology for polymers in-use and can effectively identify low risk fluoropolymers to help prioritize regulatory action (BIO by Deloitte, 2015; OECD, 1993, 2009). Here, we present PLC data, for hazard assessment, that define a group of fluoropolymers' "in-use" properties. PLC is not a comprehensive life-cycle assessment tool. Full life-cycle assessments consider all phases of product "life" including creation (manufacturing) and end-of-life (disposal). Information on manufacture and end-of-life is provided later in this study. Recently, polymers have been under increased regulatory scrutiny. In 2019, the industry-led European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a Conceptual Framework for Polymer Risk Assessment ("CF4Polymers"; ECETOC, 2019). CF4Polymers provides guiding elements to be considered in assessing potential ecological and human health hazards and risks posed by polymer substances. CF4Polymers also considers specific life-cycle stages of polymer products and their associated routes of exposure. The authors of the CF4Polymers framework support the PLC approach as a means to accomplish polymer risk assessment. They specifically support the findings of Henry et al. (2018) and state that they are "unaware of scientific evidence to justify generally assigning fluoropolymers the same level of regulatory concern as other PFAS" (ECETOC, 2019). In 2020, the European Commission contracted a study to propose criteria to identify PRR under REACH (Wood, 2020a). The report states that the authors consider fluoropolymers meeting the criteria to be considered PLC, "following the recommendations of Henry et al. (2018)."

The properties and characteristics of fluoropolymers are anchored in the strength of the carbon–fluorine bond, which

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render them highly stable (thermally, chemically, and biologically), inert, and durable—long lasting in use—under exacting and high-performance conditions. Physical, chemical, thermal, and biological stability are important criteria for a polymer to be considered a PLC. The data presented in Tables 4 and 5 demonstrate that commercial fluoropolymers from the author companies meet the criteria to be considered PLC. The PLC criteria for physicochemical properties reflect the state of the polymers in this study, solids, as well as their inertness and stability. None of the fluoropolymers assessed in this study were soluble in water or octanol. They are biologically inert, insoluble in water and octanol, and not expected to move in or between environmental media. Fluoropolymers are also twice as dense as water. These properties and water insolubility mean fluoropolymers are not mobile in the environment and therefore would not be expected to be found in sources of drinking water. Fluoropolymers are neither bioavailable nor bioaccumulative. These solid polymers cannot be absorbed through a cell membrane via passive or active transport and do not bind or interact with the cell surface (see also Supporting Information: Chapter 8). In addition, whereas aquatic and mammalian toxicology studies of fluoropolymers may be desirable for some, they are technically difficult for insoluble, solid, high-MW polymers. The OECD test guidelines reiterate this in many cases. This is confirmed for example in REACH Annex VII guidance, which repeatedly states toxicity is unlikely to occur "if a substance is highly insoluble in water or the substance is unlikely to cross biological membranes" (see Supporting Information: Chapter 9).

Finally, structure criteria including MW, MWD, residual monomer(s), oligomers, and other synthesis by-products, as represented by low MW extractables and leachables have been determined for the fluoropolymers presented and meet values established for the PLC criteria and regulated uses (e.g., USP). The concentrations in the fluoropolymer that have been evaluated are extremely low, reflective of effective manufacturing processes that minimize these compounds complemented by capture and/or destruction systems for such materials. For additional information, see the section below discussing responsible manufacturing. This study and prior work (Henry et al., 2018) provide a guide for other global fluoropolymer manufacturers to gather and present data on additional commercial fluoropolymers to determine if they too meet the PLC criteria.

Fluoropolymer stability, aka persistence, is not an intrinsic hazard: Fluoropolymers are stable, inert, solid materials. Fluoropolymers resist degradation by acids, bases, oxidants, reductants, photolytic processes, microbes, and metabolic processes; for this reason, they are thermally, chemically, and biologically highly inert. Fluoropolymer stability was presented in the introduction and is further considered in the Supporting Information: Chapters 4 and 5. Fluoropolymers are not expected to degrade under environmental conditions or normal use and processing conditions (Wood, 2020a). They are stable and remarkably durable and are therefore persistent. However, persistence alone does not imply that there is a present or future risk to human health or the environment (Rüdel et al., 2020). Persistence itself is not an intrinsic hazard, as it does not in itself imply or inform the potential for an adverse effect (aka toxicity). There is no language in REACH supporting the notion that persistence alone justifies risk-management measures. REACH has regulated persistence in combination with other properties that do inform potential hazards. In fact, REACH combines persistence with bioaccumulation and toxicity (or "very persistent" with "very bioaccumulative/very mobile" vPvB/vPvM) to justify designation as a substance of very high concern (SVHC) and consideration of potential risk-management measures for uses associated with unacceptable risk. Therefore, persistence on its own does not justify the need for specific risk-management measures. Fluoropolymers themselves are persistent, but they are not bioaccumulative, not mobile, and not toxic and therefore not SVHCs from a regulatory perspective (Ruwona and Henry, 2021).

PFAS grouping and segmentation—Scope of regulatory measures: The OECD definition of PFAS is based only on chemical structure (OECD, 2021). It describes a universe of fluorinated organic substances with vastly different physical, chemical, and biological properties, including polymers and nonpolymers; solids, liquids, and gases; highly reactive and inert substances; soluble and insoluble substances; and volatile and involatile substances and is too broad to allow effective, science-based assessment and regulation of chemical compounds as an entire group (Amcham 2020a; BDI, 2021; Buck et al., 2021; Orgalim, 2021; Wallington et al., 2021). A 2021 OECD report states: "it is highly recommended that such diversity be properly recognized and communicated in a clear, specific and descriptive manner" and "the term 'PFASs' does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene aliphatic carbon moiety" (OECD, 2021).

In this context, the available property data (Tables 4 and 5) reveal that fluoropolymers have distinctly different properties from nonpolymeric PFAS and from SCFPs that have a polymeric backbone that does not contain C–F bonds directly attached to it. The perfluoroalkyl moiety in SCFPs is found in a side-chain connected via a functional group to the polymer backbone and "can potentially lead to the formation of nonpolymer PFAS as a result of degradation" (Fluoropolymer Products Group of Plastics Europe [FPG], 2021b; Wood, 2020a; see Supporting Information: Chapter 6). Segmentation that clearly differentiates the broad PFAS family according to their properties, rather than using a structure-based classification alone (OECD, 2021), is needed for a scientifically sound, risk-based regulatory approach. Regulating all PFAS as one homogenous group (ECHA, 2020) absent consideration of their properties, particularly when the properties are so demonstrably different, neglects basic scientific consideration of these properties,

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which are the foundation of substance differentiation. The USEPA does not consider all PFAS to have similar risk profiles and therefore they are following a categorical grouping approach based on information about similarities in structure, physicochemical properties, and existing test data on the toxicity of PFAS (USEPA, 2021b). Therefore, segmentation based on properties should be conducted before performing any grouping-based risk assessment, placing stable, nonhazardous fluoropolymers that meet the criteria to be considered PLC in a separate category (see also Supporting Information: Chapter 6).

Fluoropolymer market perspective: The commercial fluoropolymer global market sales have been reported to be approximately 230 000 MT (Dams & Hintzer, 2017). Given the expected fluoropolymer market growth, ranging from approximately 4%–5% to 7%–8% (Allied Market Research [AMR], 2022; Future Market Insights [FMI], 2022; FPG, 2021a; Globe Newswire, 2021), a pro forma market table was created for 2021 using a 5% growth rate. Adding ionomers as well as updated amorphous market information (company data) to the above, the total commercial fluoropolymer market sales is estimated to be approximately 330 000 MT in 2021 (see Supporting Information: Chapter 10). Four fluoropolymers: PTFE, FEP, PFA, and ETFE, were the focus of the first fluoropolymer PLC paper (Henry et al., 2018) and account for approximately 64% of fluoropolymers sold globally in 2021 (pro forma basis). The sales volume of these four fluoropolymers is represented by the first four bars in Figure 10.1 in Supporting Information: Chapter 10. This study discusses 14 fluoropolymers representing an additional 32% (pro forma basis) of the global fluoropolymer market. Therefore, this study, in combination with Henry et al. (2018), presents PLC data from the cited manufacturers of commercial fluoropolymers representing approximately 96% of the global commercial fluoropolymer market that meet the criteria to be considered PLC. The projected 2021 sales volume of the major types of commercial fluoropolymers covered in this study (PVDF, FKM, FEPM, amorphous, ionomers, THV, ECTFE, PCTFE, and FFKM, EFEP, CTP, and FEVE) are also represented in Figure 10.1 in Supporting Information: Chapter 10. As noted, estimated market volumes were provided for the sum of FEPM, CPT, EFEP, and FEVE as well as a small "others" category. The fluoropolymer polyvinyl fluoride (PVF) was not covered by these two papers but is also shown in Figure 10.1 in Supporting Information: Chapter 10. Other fluorinated polymers, perfluoropolyethers, and SCFPs are not addressed in this study (see Supporting Information: Chapter 6).

FLUOROPOLYMER LIFE-CYCLE CONSIDERATIONS

This study focuses on the properties of the 14 selected commercial fluoropolymers themselves in-use providing data that demonstrate they meet the criteria to be considered PLC. Additionally, the life-cycle stages of fluoropolymer creation (manufacturing) and disposal at the end of industrial or consumer use (end-of-life) are important to consider. The primary focus in these life-cycle stages is generally nonpolymer PFAS from the manufacturing process or fluoropolymer degradation in end-of-life disposal (ECHA, 2020; FPG, 2021a; Guelfo et al., 2021; Lohmann et al., 2020).

The long-established life-cycle assessment approach to environmental protection and risk management first considers the extent of emissions, their toxicity, and their exposure potential (Guinee et al., 2011). When emissions are sufficiently large in scope, toxicity, and exposure potential, emission-management methods are then considered, including process input changes and emission controls to reduce or eliminate the risk of the emissions. Fluoropolymer manufacturing and disposal life-cycle stages were discussed in the paper that first presented fluoropolymer PLC data (Henry et al., 2018). Here we provide an update and current perspective.

Responsible manufacturing: As corroborated by the data presented here and in prior work (Henry et al., 2018), a large volume percentage and number of commercial fluoropolymers are manufactured that meet the criteria to be considered PLC. Emissions from fluoropolymer manufacture are a key product life-cycle focus. The main focus during the manufacturing phase is not directly related to fluoropolymers but from emissions. Emissions of concern may include nonpolymer PFAS such as fluorinated PAs, unreacted monomers, oligomers, or other unintended by-products formed during manufacturing. It is important to note that, although some high-MW fluoropolymers require use of a fluorinated PA in manufacturing (see also Supporting Information: Chapter 10), it has been reported that at least 50% of commercial fluoropolymers are made without one (Pro-K Fluoropolymer Group, 2021).

Recently, a group of fluoropolymer member companies of FPG voluntarily committed to responsible manufacturing principles through the commissioning of a Regulatory Management Option Analysis, developed by independent consulting firm Chemservices (FPG, 2021a). Member companies of this group are working on individual projects and joint projects at the trade association level with third-party experts. Specifically, companies have committed to continuously improving and/or developing the best available techniques in the manufacturing process, managing environmental emissions, developing R&D programs for the advancement of technologies allowing for the replacement of nonpolymer PFAS PAs and/or working with downstream users to increase the recyclability and reuse of its products in line with the objectives of circular economy (FPG, 2021a). Implementation of this voluntary industry initiative to address concerns relating to fluoropolymers will strengthen already ongoing efforts performed by the fluoropolymer industry promoting responsible manufacturing practices. In addition, member companies are committed to working with EU authorities to establish and implement technical actions to guarantee adequate control of the risks derived from the manufacture and use of fluoropolymers to mitigate such risks wherever possible. This will be done following

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transparency principles and agreements to monitor progress. For example, important emission reduction has been demonstrated by major fluoropolymer manufacturers including fluorinated PA recovery for reuse, 99% removal of fluorinated PA in wastewater treatment, and 99.99% capture and destruction efficiency of gaseous emissions routed to a thermal oxidizer (Chemours, 2021c), as well as 99–99.9 plant emission reductions (Daikin, 2021c, 2022). Four other companies have reported replacement of fluorinated PAs with nonfluorinated PAs (Arkema, 2008, 2021b; Chemours, 2022; Gujarat Fluorochemicals Limited, 2022; Solvay, 2022). These are substantial efforts toward mitigating emissions associated with fluoropolymer manufacturing being worked on by fluoropolymer manufacturers. This study and the prior study (Henry et al., 2018) provide a guide for other global fluoropolymer manufacturers to gather and present data on their commercial fluoropolymers in-use demonstrating that they meet the PLC criteria.

End-of-use: At the end of industrial or consumer use, fluoropolymers may be disposed via the following routes: landfill, incineration (e.g., waste-to-energy [WTE] facilities), or reuse/recycling. There is considerable data demonstrating that fluoropolymers such as PTFE do not degrade in the environment or release substances of toxicological or environmental concern (FPG, 2021a; Hintzer & Schwertfeger, 2014). FPG member companies are working with the industry and end users on this subject and are engaged in a research project aimed at identifying conditions required for proper disposal (incineration) of fluoropolymers (FPG, 2021a).

Fluoropolymers are chemically, thermally, and biologically stable (Henry et al., 2018; this study) and therefore are not expected to transform to dispersive nonpolymeric PFAS when disposed of in a landfill. A recent study presented results from OECD guideline biodegradation studies demonstrating that PTFE is stable and does not degrade under environmentally relevant conditions (Ruwona and Henry, 2021). Further, fluoropolymers that meet the criteria to be considered PLC, such as those in this study and prior work (Henry et al., 2018), have negligible leachables, unreacted monomers, and oligomers most likely destroyed in fluoropolymer use processing and would therefore not be expected to significantly contribute to landfill leachate (Ruwona and Henry, 2021).

Available data reveal that fluoropolymers are mineralized (i.e., all C–F bonds broken, hydrofluoric acid generated, and scrubbed to calcium fluoride) under commercial WTE incineration operating conditions (Aleksandrov et al., 2019; Bakker et al., 2021; DEC, 2021; Giraud et al., 2021a, 2021b). In recent pilot scale studies representative of full-scale WTE facilities, the most common form of end-of-life destruction conducted on PTFE found that combustion converted the fluorine into controllable hydrogen fluoride gas and that, of the 31 PFAS studied, no fluorine-containing products of incomplete combustion were produced above background levels (Aleksandrov et al., 2019). Further, a recent study investigating the presence of PFAS in waste incinerator flue gas stated: "based on a literature review, RIVM expects that most of the PFASs will largely degrade during the incineration process and then be removed when the flue gases are cleaned. The remaining PFASs are expected to be removed during the recovery of the carbon dioxide" (Bakker et al., 2021). The RIVM report affirmed that PTFE is the most stable fluorine-containing polymer. For PTFE, the RIVM report concluded that complete thermal decomposition is achieved at a temperature of approximately 800 °C. It was therefore assumed that other fluorine-containing polymers also thermally decompose completely at a temperature of 800 °C. Temperatures at the pyrolysis front and the combustion front in the waste-burning bed range from 900 °C to 1100 °C (Asthana et al., 2006; Ménard et al., 2006), which is well above 800 °C, the temperature at which the complete thermal decomposition of PTFE is achieved (Bakker et al., 2021). Studies for additional fluoropolymers and those with additional pilot and/or full-scale fluoropolymer studies would contribute to this body of data and further affirm their results. The PFP and FPG currently have joint projects working on these potential contributions.

Recycling of fluoropolymer products and articles containing fluoropolymers is difficult because separation of the fluoropolymer from the end products is not always possible (FPG, 2021a; Hintzer & Schwertfeger, 2014; Pro-K Fluoropolymer Group, 2018). This is because fluoropolymers are used predominantly in small components of larger finished articles involving a wide variety of materials. There are several options to recycle fluoropolymer products. In primary recycling, solid fluoropolymer waste is ground and later fed back into the manufacturing cycle of some fluoropolymer products. Recycled fluoropolymers may be used in high-end applications when correctly collected, cleaned, and reprocessed. In secondary recycling, solid fluoropolymer waste is ground, followed by degradation to approximately 1% of the original degree of polymerization by using electron beams, gamma rays, or thermomechanical degradation. The recovered material can be used in the manufacturing of new fluoropolymer products. Lastly, in tertiary recycling or upcycling, solid fluoropolymer is ground, then decomposed into the starting monomers at temperatures higher than 600 °C (pyrolysis) to obtain the same chemical components from which the fluoropolymer was manufactured; monomers, such as tetrafluoroethylene, are purified by distillation, and can then be reused to manufacture new fluoropolymer (3M, 2021; Schlipf & Schwalm, 2014). For the primary and secondary schemes, recycling treatments can be undertaken by the manufacturers of fluoropolymers themselves (onsite), or at a larger scale, mainly by specialist recycling companies. The upcycling needs to be colocated to a fluoropolymer manufacturing plant that can use tetrafluoroethylene.

Primary and secondary recycling is limited because of the presence of fillers, colorants, and other materials in the composition of their final articles. Further, recycling might not work for all end-of-life components, as they are used predominantly in small components of larger

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finished articles involving a wide variety of materials. Therefore, collecting and dismantling for recycling might not be feasible for all products (FPG, 2021a; Hintzer & Schwertfeger, 2014; Pro-K Fluoropolymer Group, 2018). However, it should be noted that upcycling treatment is applicable to some articles containing fluoropolymers, such as pipe liners in chemical plants, as well as other plant components such as pumps, tank liners, seals, hoses, compensators, and many other fluoropolymer components and systems. These are the products for which the high quantities of fluoropolymers are used offering significant recycling potential.

SUMMARY

This study has described the composition, uses, performance properties, and functionalities of 14 commercially available fluoropolymers, including fluoroplastics and fluoroelastomers. Fluoropolymers are the preferred material of choice because of their unique combination of properties, which are not achievable from other materials or via other functions. As a result, fluoropolymers have become a critical mainstay for society and are useful to modern living, as they provide vital, reliable functionality to a broad range of industrial and consumer products. Further, the study has presented data demonstrating the subject fluoropolymers satisfy the widely accepted polymer hazard assessment criteria to be considered PLC. The data presented demonstrate the fluoropolymers in the study are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic, and contain low levels of impurities. These results further demonstrate that the fluoropolymer class should be considered distinctly different and should not be grouped with other PFAS for hazard assessment or regulatory purposes. When combined with earlier work (Henry et al., 2018), the study demonstrates that commercial fluoropolymers are available that meet the criteria to be considered PLC, which represent approximately 96% of the global fluoropolymer market. Lastly, emissions from fluoropolymer manufacture and disposal at end-of-use are a product life-cycle focus. Emissions may include nonpolymer PFAS such as fluorinated PAs, unreacted monomers, oligomers, or other unintended by-products formed during manufacturing. Fluoropolymer manufacturers recently committed voluntarily to responsible manufacturing principles by continuously improving and/or developing the best available techniques in the manufacturing process, managing environmental emissions, developing R&D programs for the advancement of technologies allowing for the replacement of fluorinated PAs, and/or increasing recyclability and reusing fluoropolymers in line with the objectives of circular economy.

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CONFLICT OF INTEREST

The authors are employed by companies that commercially manufacture fluoropolymers. SHK is an independent fluorotechnology consultant working on behalf of AGC Chemicals Americas Inc. and principal of BeachEdge Consulting LLC.

DATA AVAILABILITY STATEMENT

Data gathered for this paper is presented in the paper itself and the Supporting Information: Data file provided. Additional data are available upon request from the corresponding author Stephen Korzeniowski ([redacted]@gmail.com).

SUPPORTING INFORMATION

The Supplement contains a glossary of terms as well as additional information on the study of fluoropolymers properties and functionalities, polymer of low concern (PLC) background and criteria, references and methods for the PLC data for the study of fluoropolymers, benefits, features and alternatives assessment for the study of fluoropolymers, the differences between fluoropolymers and side-chain fluorinated polymers, fluoropolymer bioavailability and toxicity studies, fluoropolymer global market information, fluoropolymer socioeconomic analyses and risk-management options analysis (RMOA).

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REFERENCES

3M. (2021). *Up-cycling. Closing the loop.* https://multimedia.3m.com/mws/media/907323O/up-cycling-fluoropolymers-brochure.pdf?fn=Up-Cycling_Brochure_EN.pdf

AGC Chemicals Company. (2021a). *FEVE LUMIFLONbrochure®*. https://www.agcchem.com/wp-admin/admin-ajax.php?juwpfisadmin=false&action=wpfd&task=file.download&wpfd_category_id=170&wpfd_file_id=1927&preview=1&embedded=true

AGC Chemicals Company. (2021b). *Cytop® amorphous fluoropolymers.* https://www.agc-chemicals.com/jp/en/fluorine/products/detail/index.html?pCode=JP-EN-F019

AGC Chemicals Company. (2021c). *Forblue™ Flemion™ fluorinated ion-exchange membranes.* https://www.agc-chemicals.com/jp/en/fluorine/products/category/result.html?c_id=11

AGC Chemicals Company. (2021d). *AFLAS fluoroelastomers.* https://www.agcchem.com/wp-admin/admin-ajax.php?juwpfisadmin=false&action=wpfd&task=file.download&wpfd_category_id=172&wpfd_file_id=1901&preview=1&embedded=true

Aleksandrov, K., Gehrmann, H. J., Hauser, M., Matzing, H., Pigeon, D., Stapf, D., & Wexler, M. (2019). Waste incineration of polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and poly-fluorinated alkyl substances (PFAS) in flue gas. *Chemosphere, 226*, 898–906. https://doi.org/10.1016/j.chemosphere.2019.03.191

Allied Market Research (AMR). (2022). *Fluoropolymers market by product type.* https://www.alliedmarketresearch.com/fluoropolymers-market

American Chamber of Commerce in Europe (Amcham). (2020a). *Grouping of PFAS: Regulation by distinct PFAS classes is scientifically superior to*

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classification by a broad PFAS group. https://www.amchameu.eu/position-papers/grouping-pfas-regulation-distinct-pfas-classes-scientifically-superior

American Chamber of Commerce in Europe (Amcham). (2020b). *A narrow regulatory focus on persistence-only is not justifiable and can undermine innovation to produce materials that support societal sustainability goals*. https://www.amchameu.eu/position-papers/use-persistency-and-mobility-criteria-chemicals-regulation-amcham-eu-comments

American Chamber of Commerce in Europe (Amcham). (2020c). *REACH Restriction: Essential use criteria in the context of socio-economic impact analysis when unacceptable risk is demonstrated*. https://www.amchameu.eu/position-papers/reach-restriction-essential-use-criteria-context-socio-economic-impact-analysis-when

Ameduri, B. (2020). The promising future of fluoropolymers. *Macromolecular Chemistry and Physics*, *221*, 1900573. https://doi.org/10.1002/macp.201900573

Améduri, B., Boutevin, B., & Kostov, G. (2001). Fluoroelastomers: Synthesis, properties and applications. *Progress in Polymer Science (Oxford)*, *26*(1), 105–187. https://doi.org/10.1016/S0079-6700(00)00044-7

Ameduri, B., & Sawada, H. (2017a). *Fluorinated polymers. Volume 1: Synthesis, properties, processing and simulation*. Royal Society of Chemistry.

Ameduri, B., & Sawada, H. (2017b). *Fluorinated polymers. Volume 2: Applications*. Royal Society of Chemistry. https://doi.org/10.1039/9781782629368

Arkema. (2008). *Arkema eliminates fluorosurfactants from Kynar 500PVDF®*. https://www.pcimag.com/articles/88876-arkema-eliminates-fluorosurfactants-from-kynar-500-pvdf

Arkema. (2021a). *KynarPVDF family®*. https://www.extrememateriels-arkema.com/en/product-families/kynar-pvdf-family/chemical-resistance-fuel-resista/download-kynar-pvdf-chemical-res/

Arkema. (2021b). *Fluorosurfactant free KynarPVDF resin®*. https://kynar500.arkema.com/en/product-information/fluorosurfactant-free/

Asahi-Kasei. (2021). *Aciplexion exchange membranes®*. https://www.asahi-kasei.co.jp/salt-electrolysis/en/?_ga=2.192307178.1574253781.1637252713-425530764.1637252713

Asthana, A., Ménard, Y., & Patisson, F. (2006). A 2-D mathematical model of on-grate municipal solid waste combustion. In F. Kongoli & R. G. Reddy (Eds.), *Sohn International Symposium Advanced Processing of Metals and Materials, Volume I—Thermo and physicochemical principles: non-ferrous high-temperature processing* (pp. 465–474). The Minerals, Metals & Materials Society (TMS).

ASTM. (2021). *Standard practice for rubber and rubber latices—Nomenclature* (pp. D1418–D1421). ASTM International. https://doi.org/10.1520/D1418-21

Atkinson, S. (2018). Essential high-purity sealing materials for semiconductor manufacturing. *Sealing Technology*, *7*, 5–7. https://doi.org/10.1016/S1350-4789(18)30284-8

Auer, C. M., Nabholz, J. V., & Baetcke, K. P. (1990). Mode of action and the assessment of chemical hazards in the presence of limited data: Use of structure-activity relationships (SAR) under TSCA, Section 5. *Environ Health Perspect*, *87*, 183–197.

Bakker, J., Bokkers, B., & Broekman, M. (2021). *Per- and polyfluorinated substances in waste incinerator flue gases* (RIVM Report 2021-0143). https://www.rivm.nl/bibliotheek/rapporten/2021-0143.pdf

Banks, R. E., Smart, B. E., & Tatlow, J. C. (1994). *Organofluorine chemistry: Principles and commercial applications*. Plenum.

Barnwell. (2021). *Perfluoroelastomer O rings (FFKM)*. https://www.barnwell.co.uk/products/perfluoroelastomer-ffkm-o-rings/

Beyer, E. C. (1993). Gap junctions. *International Review of Cytology*, *137*, 2.

BIO by Deloitte. (2015). *Technical assistance related to the review of REACH with regard to the registration requirements on polymers* (Final Report). Prepared for the European Commission (DG ENV) in collaboration with PIEP.

Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Jensen, A. A., Kannan, K., Mabury, S. A., & van Leeuwen, S. P. J. (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management*, *7*(4), 513–541. https://doi.org/10.1002/ieam.258

Buck, R. C., Korzeniowski, S. H., Laganis, E., & Adamsky, F. (2021). Identification and classification of commercially relevant per- and polyfluoroalkyl substances (PFAS). *Integrated Environmental Assessment and Management*, *17*(5), 1045–1055. https://doi.org/10.1002/ieam.4450

Bundesverband der Deutschen Industrie e.V. (BDI). (2021). *EU chemicals Legislation: Restriction of PFAS (EN)*. english.bdi.eu/publication/news/eu-chemicals-strategy-restriction-of-pfas/

Chemours. (2021a). *Nafion™ ion exchange materials*. https://www.nafion.com/en

Chemours. (2021b). *Economic and environmental improvements with versatile membranes*. https://www.nafion.com/en/support/white-papers/versatility-of-ion-exchange-membranes-white-paper

Chemours. (2021c). *Thermal oxidizer destroying PFAS at greater than 99.99% efficiency*. https://www.chemours.com/en/-/media/files/corporate/fayetteville-works/2020-0320-thermal-oxidizer-efficiency-results-announced.pdf?rev=87dbfd0ebb9c45aeaa475fddd2a899b4&hash=05916EC2AC2B5A3C41135773A3FCDED0

Chemours. (2022). *Chemours announces process innovation with New Viton™ fluoroelastomers advanced polymer architecture (APA) offering*. https://www.chemours.com/en/news-media-center/all-news/press-releases/2022/chemours-announces-process-innovation-with-new-viton-fluoroelastomers-advanced-polymer-architecture

Curbell. (2021). *PCTFE*. https://www.curbellplastics.com/Research-Solutions/Materials/PCTFE

Daemar. (2021). *DuPont Kalrez—Oil and gas product selector guide®*. https://daemar.com/wp-content/uploads/2017/11/OilGasProduct-SelectorGuide_KZE-A40042-00-A0217.pdf

Daikin. (2011a). *EFEP. Fluoropolymer handbook* (pp. 84–93). Daikin Industries.

Daikin. (2011b). *CPT. Fluoropolymer handbook* (pp. 58–62). Daikin Industries.

Daikin. (2021a). *NeoflonPCTFE®*. https://www.daikinchemicals.com/solutions/products/fluoropolymers/neoflon-pctfe.html?_ga=2.84898265.1754525417.1636603879-520575968.1622167042

Daikin. (2021b). *Neoflon CPT*. https://www.daikinchemicals.com/solutions/products/fluoropolymers/neoflon-cpt.html?_ga=2.257391307.1754525417.1636603879-520575968.1622167042

Daikin. (2021c). *Daikin–A responsible steward for PFAS emission reductions and safe alternatives*. https://www.daikinchem.de/sites/default/files/pdf/News/Daikin_Responsible_Steward_PFAS_Emission_Reduction_210601.pdf

Daikin. (2022). *Measures concerning environment emission of PFAS*. https://www.daikinchemicals.com/company/sustainability/pfas.html?_ga=2.233775006.1492271271.1653437409-1591380784.1653437409

Dams, R., & Hintzer, K. (2017). Chapter 1: Industrial aspects of fluorinated oligomers and polymers. In B. Ameduri & H. Sawada (Eds.), *Fluorinated polymers Volume 2: Applications* (pp. 3–31). Royal Society of Chemistry, Cambridge.

Darden, W., & Parker, R. (2021). *Fluoropolymer coatings for plastics*. AGC Chemicals. https://lumiflonusa.com/wp-content/uploads/FluoropolymerCoatingsForPlastics.pdf

Domininghaus, H. (1998). Chapter 2.1.7.4: Tetrafluorethylen/hexafluorpropylen/vinylidenfluorid-terpolymer. In *Kunststoffe, Eigenschaften und Anwendungen* (5th ed., 564f, pp. 525–598). Springer. https://books.google.com/books?id=Ar-oBgAAQBAJ&printsec=frontcover#v=onepage&q&f=false

Drobny, J. G. (2016). *Fluoroelastomers handbook* (2nd ed.). Elsevier. https://www.elsevier.com/books/fluoroelastomers-handbook/drobny/978-0-323-39480-2

Ebnesajjad, S. (2000). *Fluoroplastics Volume 1. Non-melt processible fluoroplastics*. PDL Handbook Series. Plastics Design Laboratory.

Ebnesajjad, S. (2003). *Fluoroplastics Volume 2. Melt processible fluoropolymers*. PDL Handbook Series. Plastics Design Laboratory.

Ebnesajjad, S. (2017). Introduction to fluoropolymers. In *Applied plastics engineering handbook: Processing, materials, and applications* (2nd ed., pp. 55–71). Elsevier. https://doi.org/10.1016/B978-0-323-39040-8.00003-1

ECETOC. (2019). *The ECETOC conceptual framework for polymer risk assessment (CF4POLYMERS)* (Technical Report No. 133-1). May. https://www.ecetoc.org/publication/tr-133-the-ecetoc-conceptual-framework-for-polymer-risk-assessment-cf4polymers/

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ECHA. (2020). *The national authorities of Germany, the Netherlands, Norway, Sweden and Denmark invite interested parties to send in evidence and information on the use of per- and polyfluoroalkyl substances (PFAS)*. https://echa.europa.eu/-/five-european-states-call-for-evidence-on-broad-pfas-restriction

Environment & Infrastructure Solutions UK Limited (Wood). (2020a). *Scientific and technical support for the development of criteria to identify and group polymers for Registration/Evaluation under REACH and their impact assessment* (European Commission Report). Brussels. https://circabc.europa.eu/ui/group/a0b483a2-4c05-4058-addf2a4de71b9a98/library/4acda744-777f-473e-b084-76e125430565/details

Environment & Infrastructure Solutions UK Limited (Wood). (2020b). *Socio-economic assessment (SEA) of the US fluoropolymer industry* (Final Report 2020_0225). https://fluoropolymerpartnership.com/wp-content/uploads/2020/03/Socio-Economic-Assessment-of-the-US-Fluoropolymer-Industry-Executive-Summary.pdf

European Commission (EC). (2021). *A European green deal*. https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en

Fiedler, H., Kennedy, T., & Henry, B. J. (2020). A critical review of a recommended analytical and classification approach for organic fluorinated compounds with an emphasis on per- and polyfluoroalkyl substances (PFAS). *Integrated Environmental Assessment and Management*, *17*(2), 331–351. https://doi.org/10.1002/ieam.4352

Fluoropolymer Products Group of Plastics Europe (FPG). (2012). *Guide for the safe handling of fluoropolymer resins*. https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/tfe-safe-handling-guide

Fluoropolymer Products Group of Plastics Europe (FPG). (2017). *Socio-economic analysis of the European fluoropolymer industry*. https://fluoropolymers.plasticseurope.org/application/files/7816/1167/4026/Final_SEA_Fluoropolymers_summary2017_3.pdf

Fluoropolymer Products Group of Plastics Europe (FPG). (2021a). *Risk management options analysis (RMOA)*. https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/rmoa

Fluoropolymer Products Group of Plastics Europe (FPG). (2021b). *Fluoropolyers vs. side-chain fluorinated polymers*. https://fluoropolymers.plasticseurope.org/application/files/3516/3913/1778/Fluorpolymers_vs._side_chain_fluorinated_polymers_final.pdf

Future Market Insights (FMI). (2022). *Fluoropolymer market overview*. https://www.futuremarketinsights.com/reports/fluoropolymers-market

Gangal, S. V., & Brothers, P. D. (2010). Perfluorinated polymers, Tetrafluoroethylene-perfluorodioxole copolymers. In *Encyclopedia of polymer science and technology*. John Wiley & Sons Inc. https://doi.org/10.1002/0471440264.pst420.pub2

Giraud, R. J. (2021b). *Municipal waste-to-energy combustion of fluorinated polymers as a potential source of PFOA in the environment*. PhD thesis, University of Delaware.

Giraud, R. J., Taylor, P. H., & Huang, C.-P. (2021a). Combustion operating conditions for municipal waste-to-energy facilities in the U.S. *Waste Management*, *132*, 124–132. https://doi.org/10.1016/j.wasman.2021.07.015

Globe Newswire. (2021). *Global fluoropolymers market is forecasted to grow at a CAGR of 4.3% during the forecast period 2017–2027*. https://www.globenewswire.com/news-release/2021/08/31/2289045/28124/en/Global-Fluoropolymers-Market-is-Forecasted-to-Grow-at-a-CAGR-of-4-3-During-the-Forecast-Period-2017-2027.html

Greene-Tweed. (2021a). *FKM versus FFKM–A comparison of properties*. https://live-greene-tweed.pantheonsite.io/wp-content/uploads/2020/04/FKM-vs-FFKM-Properties-Comparison-R3.pdf

Green-Tweed. (2021b). *FKM vs. FFKM*. https://www.gtweed.com/materials/fkm-vs-ffkm/

Groh, W., & Zimmermann, A. (1991). What is the lowest refractive index of an organic polymer? *Macromolecules*, *24*(25), 6660–6663. https://doi.org/10.1021/ma00025a016

Grot, W. (2011). *Fluorinated ionomers*. PDL Handbook Series. Elsevier Inc. https://doi.org/10.1016/C2010-0-65926-8

Grot, W. (2013). Chapter 12: Fluorinated ionomers: History, properties and applications. In S. Ebenesajjad (Ed.), *Introduction to fluoropolymers* (pp. 277–291). Elsevier. https://doi.org/10.1016/B978-0-323-39040-8.00003-1

Guelfo, J. L., Korzeniowski, S., Mills, M. A., Anderson, J., Anderson, R. H., Arblaster, J. A., Conder, J. M., Cousins, I. T., Dasu, K., Henry, B. J., Lee, L. S., Liu, J., McKenzie, E. R., & Willey, J. (2021). Environmental sources, chemistry, fate and transport of per- and polyfluoroalkyl substances: State of the Science, key knowledge gaps, and recommendations presented at the August 2019 SETAC Focus Topic Meeting. *Environmental Toxicology and Chemistry*, *40*, 3234–3260. https://doi.org/10.1002/etc.5182

Guinee, J. B., Heijungs, R., Huppes, G., Zamagni, A., Masoni, P., Buonamici, R., Ekvall, T., & Rydberg, T. (2011). Life cycle assessment: past, present, and future. *Environmental Science and Technology*, *45*(1), 90–96. https://doi.org/10.1021/es101316v

Gujarat Fluorochemicals Limited. (2018). *InoflarPVDF resins™*. https://www.inoflar.com/

Gujarat Fluorochemicals Limited. (2022). *Company announcement on the development of a non-fluorinated polymerization aid*. https://gfl.co.in/upload/pages/ebce5fed9030753d0ee651bf1f48d0a0.pdf

Hafer, J. (2021). REACH registration of polymers: Identifying polymers of low concern. *ICRL*, *1*(2021), 21–25. https://chemservice-group.com/wp-content/uploads/2021/03/icrl_2021_01.pdf

Henry, B., Carlin, J., Hammerschmidt, J., Buck, R. C., Buxton, L., Fiedler, H., Seed, J., & Hernandez, O. (2018). A critical review of the application of polymers of low concern and regulatory criteria to fluoropolymers. *Integrated Environmental Assessment and Management*, *14*(3), 316–334. https://doi.org/10.1002/ieam.4035

Hintzer, K., & Schwertfeger, W. (2014). Fluoropolymers—Environmental aspects. In D. W. Smith, S. T. Iacono, & S. S. Iyer (Eds.), *Handbook of fluoropolymer science and technology* (pp. 495–520). https://onlinelibrary.wiley.com/doi/10.1002/9781118850220.ch21

Hintzer, K., Zipplies, T., Carlson, D. P., & Schmiegel, W. (2013). Fluoropolymers, Organic. In *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley. https://doi.org/10.1002/14356007.a11_393.pub2

Honeywell. (2021). *Blister packaging*. https://lifesciences.honeywell.com/us/en/applications/healthcare-packaging/blister-packaging

Hoshino, T., & Morizawa, Y. (2017). Chapter 5: Fluorinated specialty chemicals–Fluorinated copolymers for paints and perfluoropolyethers for coatings. In B. Ameduri & H. Sawada (Eds.), *Fluorinated polymers: Volume 2: Applications* (pp. 110–126). The Royal Society of Chemistry. https://pubs.rsc.org.en/content/ebook/978-1-78262-916-0

Hull, D. E. (1983). *Tetrafluoroethylene-propylene copolymer (Aflas): New technology, new uses*. Xenox Inc. http://www.allsealsinc.com/pdf2/Aflas1.pdf

Hull, D. E., Johnson, B. V., Rodricks, I. P., & Staley, J. B. (1997). THV fluoroplastic. In J. Scheirs (Ed.), *Modern fluoropolymers* (257ff.). Wiley & Sons.

Kojima, G., Kojima, H., & Tabata, Y. (1977). A new fluoroelastomer derived from tetrafluoroethylene and propylene. *Rubber Chemistry and Technology*, *50*(2), 403–412. https://doi.org/10.5254/1.3535154

Kojima, G., & Yamabe, M. (1984). A solvent soluble fluororesin for paint. *Journal of Synthetic Organic Chemistry, Japan*, *42*, 841–849.

Korinek, P. M. (1994). Amorphous fluoropolymers—A new generation of products. *Macromolecular Symposia*, *82*(1), 61–65. https://doi.org/10.1002/masy.19940820108

Kostal, J. (2016). Chapter 4: Computational chemistry in predictive toxicology: Status quo et quo vadis? In J. C. Fishbein & J. M. Heilman (Eds.), *Advances in molecular toxicology* (Vol. 10, pp. 136–186). Elsevier. https://doi.org/10.1016/B978-0-12-804700-2.00004-0

Lavallée, C. (2020). Section 4.16 Polymer processing additives (PPA). In J. Macnamara (Ed.), *Film extrusion manual—Process, materials, properties* (3rd ed., pp. 291–302). TAPPI Press. https://imisrise.tappi.org/TAPPI/Products/01/R/0101R360.aspx

Lipinski, C., Lombardo, F., Dominy, B., & Feeny, P. (2001). Experimental and computational approaches to estimate solubility and permeability in drug discovery and development settings. *Advanced Drug Delivery Reviews*, *46*(1–3), 3–26. https://doi.org/10.1016/s0169-409x(00)00129-0

Lohmann, R., Cousins, I., DeWitt, J., Glüge, J., Goldenman, G., Herzke, D., Lindstrom, A., Miller, M., Ng, C., Patton, S., Scheringer, M., Trier, X., & Wang, Z. (2020). Are fluoropolymers really of low concern for human and environmental health and separate from other PFAS? *Environmental*

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Science and Technology, *54*(20), 12820–12828. https://doi.org/10.1021/acs.est.0c03244

Marshall, J. 2017. Kalrez®-type perfluoroelastomers—Synthesis, properties and applications. In J. Scheir (Ed.), *Modern fluoropolymers* (pp. 349–358). John Wiley and Sons.

Ménard, Y., Ashtana, A., Patisson, F., Sesiecq, P., & Ablitzer, D. (2006). Thermodynamic study of heavy metals behaviour during municipal waste incineration. *Process Safety and Environmental Protection*, *84*(B4), 290–296.

Miller, M., Pelch, K., Reade, A., Soehl, A., Trier, X., Venier, M., Wagner, C., Wang, Z., & Blum, A. (2020). Scientific basis for managing PFAS as a chemical class. *Environmental Science & Technology Letters*, *7*(8), 532–543. https://doi.org/10.1021/acs.estlett.0c00255

Munekata, S. (1988). Fluoropolymers as coating materials. *Progress in Organic Coatings*, *16*, 113–134. https://www.sciencedirect.com/science/article/pii/0033065588800104

NY State Department of Environmental Conservation (DEC). (2021). *Norlite environmental sampling report*. https://www.dec.ny.gov/chemical/121118.html

Organisation for Economic Co-operation and Development (OECD). (1993). *OECD expert group on polymers. Third Meeting of the Experts on Polymers: Chairman's Report* (ENV/MC/CHEM/RD(93)4). April.

Organisation for Economic Co-operation and Development (OECD). (2009). *Data analysis of the identification of correlations between polymer characteristics and potential for health or ecotoxicological concern*. OECD Task Force on New Chemicals Notification and Assessment, Expert Group Meeting on polymers, March, 2007, Tokyo, Japan. https://www.oecd.org/env/ehs/risk-assessment/42081261.pdf

Organisation for Economic Co-operation and Development (OECD). (2021). *Reconciling terminology of the universe of per- and polyfluoroalkyl substances: recommendations and practical guidance*. Series on Risk Management No. 61. https://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV/CBC/MONO(2021)25&docLanguage=en

Ohkura, M., & Morizawa, Y. (2017). Fluoroplastics and fluoroelastomers–Basic chemistry and high-performance applications. In B. Ameduri & H. Sawada (Eds.), *Fluorinated polymers Volume 2: Applications*. RSC Polymer Chemistry Series No. 24. RSC. https://doi.org/10.1039/9781782629368

Orgalim. (2021). *Orgalim Position Paper on the restriction of PFAS*. https://orgalim.eu/position-papers/environment-orgalim-position-paper-restriction-pfas?&utm_campaign=Policy%20Brunch%20for%20FPP4EU%207%20February&utm_medium=email&utm_source=Mailjet

Park, E.-J., Park, I.-C., Lee, M. S., & Park, M. (2008). Preparation of cladding polymers for plastical optical fibers—Miscibility and interfacial adhesion of PMMA/THV blends. *Textile Science & Engineering*, *45*(6), 364–369. https://www.koreascience.or.kr/article/JAKO200806135610008.pa1ff8ge

Parker, R., & Blankenship, K. (2015). Fluoroethylene vinyl ether resins for high-performance coatings. In K. B. Tator (Ed.), *ASM handbook Volume 5B, Protective organic coatings*. ASM International. https://doi.org/10.31399/asm.hb.v05b.9781627081726

Performance Fluoropolymer Partnership of the American Chemistry Council (PFP). (2020). *Socio-economic assessment of the US fluoropolymer industry*. https://fluoropolymerpartnership.com/fluoropolymer-facts/socioeconomic-importance/

Polymer Industry Association (PIA). (2019). *Guide to the safe handling of fluoropolymer resins* (5th ed.). https://www.plasticsindustry.org/supply-chain/material-suppliers/fluoropolymers-division-fpd

Pro-K Fluoropolymer Group. (2018). *Recycling of fluoropolymers*. https://www.pro-kunststoff.de/assets/Merkbl%C3%A4tter%20und%20Co/FP%20TM-10-Recycling-of-fluoropolymers.pdf

Pro-K Fluoropolymer Group. (2021). *PFAS restriction—Proposal & request for exemption of fluoropolymers*. https://www.pro-kunststoff.de/fachwissen/pfas-restriction-proposal-und-request-for-exemtion-of-fluoropolymers.html

Resnick, P. R., & Buck, W. (1997). Teflon® AF amorphous fluoropolymers. In J. Scheirs (Ed.), *High performance polymers for diverse applications* (pp. 397–419). John Wiley & Sons.

Resnick, P. R., & Buck, W. H. (1999). Teflon® AF: A family of amorphous fluoeopolymers with extraordinary properties. In W. H. Properties, G. Hougham, P. E. Cassidy, K. Johns, & T. Davidson (Eds.), *Topics in applied chemistry, fluoropolymers* (pp. 25–33). Springer, New York, NY. https://doi.org/10.1007/b114560

Royal Society of Chemistry (RSC). (2021). *Risk-based regulation for per- and poly-fluoroalkyl substances (PFAS)*. https://www.rsc.org/globalassets/22-new-perspectives/sustainability/a-chemicals-strategy-for-a-sustainable-chemicals-revolution/pfas-policy-position-dec-2021.pdf

Rüdel, H., Körner, W., Letzel, T., Neumann, N., Nödler, K., & Reemtsa, T. (2020). Persistent, mobile and toxic substances in the environment: A spotlight on current research and regulatory activities. *Environmental Sciences Europe*, *32*, 5. https://doi.org/10.1186/s12302-019-0286-x

Ruwona and Henry. (2021). *PTFE: Persistence without hazard at environmentally relevant temperatures and durable by design*. Fluoros 2021, Providence, RI.

Satokawa, T. (Ed.) (1990). *Fluoropolymer handbook: PCTFE* (pp. 337–357). Nikkan-Kogyo-Shimbun.

Scheirs, J. (2007). *Modern fluoropolymers—High performance polymers for diverse applications*. John Wiley & Sons.

Schlipf, M., & Schwalm, T. (2014). *Closing the recycling loop, Up-cycling of end-of-life fluoroplastics*. Kunststoffe International. June. https://www.kunststoffe.de/en/journal/archive/article/up-cycling-of-end-of-life-fluoroplastics-841786.html

Science Center. (2021). *Energetic electrolysis: The potentials of hydrogen power*. http://www.sciencenter.org/climatechange/d/cart_activity_guide_energetic_electrolysis.pdf

Sha, B., Schymanski, E., Ruttkies, C., Cousins, I., & Wang, Z. (2019). Exploring open cheminformatics approach for categorizing per- and polyfluoroalkyl substances (PFAS). *Environmental Science: Processes & Impacts*, *21*, 1835–1851. https://doi.org/10.1039/C9EM00321E

Shell. (2020). *Leveraging maximum value from polymer processing aids in polyethylene blown film* [Educational White Paper]. https://www.shell.us/business-customers/shell-polymers/polyethylene-film.html

Solvay. (2021a). *PVDF design and processing guide*. https://www.solvay.com/sites/g/files/srpend221/files/2018-08/Solef-PVDF-Design-and-Processing-Guide_EN-v2.7_0.pdf)

Solvay. (2021b). *HalarECTFE design and processing guide®*. https://www.solvay.com/sites/g/files/srpend221/files/2018-07/halar-ectfe-design-and-processing-guide-en.pdf)

Solvay. (2021c). *HalarECTFE®*. https://www.solvay.com/en/brands/halar-ectfe

Solvay. (2022). *Innovating with non-fluorosurfactant technologies*. https://www.solvay.com/en/innovation/science-solutions/pfas

United Nations (UN). (2021). *United Nations sustainable development goals*. https://sdgs.un.org/goals

US Code of Federal Regulations (USCFR). (2022). *21 CFR 177.2600 Rubber articles intended for repeated use*. https://www.ecfr.gov/current/title-21/chapter-I/subchapter-B/part-177/subpart-C/section-177.2600

USEPA. (1992). *TCLP toxicity characteristic leaching procedure* (SW-846 Test Method 131). https://www.epa.gov/sites/default/files/2015-12/documents/1311.pdf

USEPA. (1997). *Polymer exemption guidance manual* (EPA-744-B-97-001). June.

USEPA. (2010). *Reviewing new chemicals under the Toxic Substances Control Act (TSCA) EPA's Review Process - Chemical categories used to review new chemicals under TSCA: TSCA New Chemicals Program (NCP) Chemical Categories*. Washington (DC): USEPA Office of Pollution Prevention and Toxics. [cited 2017 July 12]. http://www.epa.gov/oppt/newchems/pubs/npcchemicalcategories.pdf

USEPA. (2012). *Sustainable futures/P2 framework manual*. https://www.epa.gov/sustainable-futures/sustainable-futures-p2-framework-manual

USEPA. (2021a). *PFAS strategic roadmap: EPA's commitments to action 2021—2024*. https://www.epa.gov/system/files/documents/2021-10/pfas-roadmap_final-508.pdf

USEPA. (2021b). *PFAS national testing strategy*. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/national-pfas-testing-strategy#:%7E:text=To%20protect%20human%20health%20and,PFAS%20chemicals%20to%20inform%20future

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United States Federal Register (USFR). (1984). *Premanufacture notification for polymers* (Final Rule 49 FR 46066, 1984 Nov 21. FR-2439-1).

United States Federal Register (USFR). (1995). *Premanufacture notification exemptions; Revisions of exemptions for polymers* (Final rule 60 FR 16316. 1995 Mar 29. FRL-4929-8). Fed Regist *60*(60), 16316–16336. Environmental Protection Agency.

United States Federal Register (USFR). (2012). Polymers (b). 40 CFR Sect 723.250.

Van Cleeff, A. (1997). Fluoroelastomers. In J. Schiers (Ed.), *Modern fluoropolymers* (pp. 507–614). John Wiley & Sons.

Wallington, T. J., Andersen, M. P. S., & Nielsen, O. J. (2021). The case for a more precise definition of regulated PFAS. *Environmental Science: Processes & Impacts*, *23*(12), 1834–1838. https://doi.org/10.1039/D1EM00296A

Worm, A. T., & Grootaert, W. (2001). Fluorocarbon elastomers. *Encyclopedia of Polymer Science & Engineering*. Wiley. https://doi.org/10.1002/0471440264.pst137

Yamabe, M., Higaki, H., & Kojima, G. (1984). New fluoropolymer coatings. In G. D. Parfitt & A. V. Pastis (Eds.), *Organic coatings science and technology* (Vol. 7, pp. 25–39). Marcel Dekker.

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Assessment of PFAS Emissions during the Lifecycle of PTFE: A Case Study

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Assessment of PFAS Emissions during the Lifecycle of PTFE: A Case Study

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*PFAS emissions refer to non-polymeric low molecular weight PFAS that are of concern

Glossary

AOF/EOF	Analysis of Extractable (EOF) and adsorbable (AOF) organically bound fluorine analysis
DSAP	Disodium succinic acid peroxide
EOL	End-of-life
FKM	Class of fluorinated, carbon-based synthetic rubber, known as fluoroelastomer
FP	Fluoropolymer
FPA	Fluorinated polymerization aid
GAC	Granular Activated Carbon
GFL	Gujarat Fluorochemicals Limited
HFP	Hexafluoropropylene
kg	kilogram
LC-MS/MS	Liquid chromatography–mass spectrometry/ mass spectrometry
NFPA	Non-fluorinated polymerization aid
PFA	Perfluoroalkoxy alkane
PFAS	Per- and polyfluoroalkyl substances
PFOA	Per fluoro octanoic acid
ppb	Parts per billion
ppm	Parts per million
PFCA	Perfluoroalkyl carboxylic acid
PFSA	Perfluoroalkyl sulfonic acid
PPVE	perfluoro(propylvinylether)
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
TDL	Tunable Diode Laser
TFE	Tetrafluoroethylene

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1. Executive Summary

Fluoropolymers are used for many critical industrial applications and are important for the functioning of modern society. They are covered in the recent EU REACH PFAS restriction proposal due to their high persistence in the environment and the potential release of PFAS of concern to the environment during production, processing, use and end-of-life (EOL) stages of fluoropolymers. These PFAS of concern include non-polymeric, low molecular weight compounds that are mobile, bio-accumulative and/or soluble in water.

Out of all the fluoropolymers, Polytetrafluoroethylene (PTFE) has been selected for this report because it is the most-widely used, consumed and well documented fluoropolymer in the world. This case study examines the PTFE production technologies implemented at one major global industrial site to illustrate potential PFAS emissions during the lifecycle of PTFE.

PTFE may be manufactured by means of suspension polymerization or emulsion polymerization. The latter uses either fluorinated polymerization aids (FPA) – which are PFAS – or non-fluorinated polymerization aids (NFPA). Historically, the ammonium salts of perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) were the most commonly used FPAs. In recent years, many PTFE producers have transitioned to the use of shorter-chain FPAs, such as per- and polyfluoroalkylether carboxylic acids like HFPO-DA (Gen-X), ADONA and PFHxS. Regulators and environmentalists consider this transition of C8 PFOA by C6 PFAS as a regrettable substitution of one PFAS of concern by another and have started demanding to stop the use of any PFAS as polymerization aid in fluoropolymer manufacturing.

This report addresses quantification of PFAS emissions associated with both intentional use of PFAS as fluorinated polymerization aids (FPA) and unintentional generation of PFAS by-products during the manufacturing process of PTFE, to provide an estimate of potential total PFAS emissions during the lifecycle of PTFE. The results of the case study reveal a substantial reduction in potential PFAS emissions related to manufacturing of PTFE at the site of this case study when non-fluorinated polymerization aids (NFPA) are substituted for FPA. Besides, the case study considers potential emissions from processing, use and EOL stages of PTFE lifecycle.

In this case study, the main source of PFAS emissions is associated with the intentional use of PFAS surfactants or FPA during the production of emulsion PTFE. Currently, approximately 70% of the estimated annual production volume of PTFE in the European Economic Area [EEA] (i.e., 14,000 tons of approximately 20,000 tons in total) are manufactured using FPAs, requiring 2-10 kg FPA per ton PTFE. Thus, based on a worst-case approach, the related FPA emissions are max. 140 tons when no abatement technologies would be implemented. In contrast, based on information from one European manufacturing site which reports 3% releases of FPA from manufacturing and extrapolating these emissions to this entire European annual production volume, it is estimated that the potential PFAS emissions from use of the FPAs is 4.2 tons per year (best-case estimate). Furthermore, there is some evidence that these FPAs can break down to form lower molecular weight volatile PFAS (Bao, et al., 2018) that may be difficult to identify and to capture.

In quantifying potential PFAS releases related to PTFE manufacturing in this case study, the entire lifecycle of FPAs was considered. Firstly, some of the raw materials to produce FPAs are also PFAS and therefore manufacturing of FPAs may result in PFAS emissions. Secondly, the packaging, storage and transportation of FPAs is also likely to result in some PFAS emissions due to handling, filling and decanting process, cleaning of equipment and contaminated equipment. Due to the adsorptive behavior and persistent nature of these PFAS, they should not be released to the environment, but it is also not possible to completely clean the packaging materials from the FPAs. Thus, to completely avoid additional releases of FPAs, packaging materials have to be incinerated at high temperatures. During use phase of FPAs, they may break down largely to degradation

products which partly may be non-characterized chemicals without CAS numbers that are however PFAS as well.

PFAS emissions can become negligible if PTFE manufacturing moves away from the use of FPA to NFPA in the polymerization process or is able to avoid the use of polymerization aids where possible, i.e., suspension polymerization. As of today, technologies are established and commercially used to manufacture PTFE emulsion without the use of FPA (Ameduri, Sales, & Schlipf, 2023).

Unintentional generation of PFAS with subsequent potential releases to the environment can happen during the PTFE polymerization process itself, irrespective of the use of FPAs (Lohman, et al., 2020). However, using standard abatement techniques like ion exchange resin, ultrafiltration and foam fractionation which are commonly used techniques by most manufacturers, emissions of unintentionally-generated PFAS can significantly be reduced (Lanxess, 29 October 2021) (Lee, 2022) (Smith, 2023).

Based on PFAS releases from actual production of PTFE without use of FPA by one producer and extrapolating the production conditions from this one producer to all European manufacturers, residual emissions of unintentional PFAS by-products are estimated at maximum 0.002 ton of PFAS per year for the total amount 20,000 annual tons of PTFE produced in Europa. These emissions are much lower than the estimated annual PFAS emissions of 4.2-140 tons currently associated with the use of FPA in PTFE manufacturing.

Related to the substitution of FPAs by NFPAs it should be noted that the choice of the actual NFPA used in the polymerization process influences the potential for formation of PFAS by-products; i.e., the NFPA should be non-reactive with the monomers involved in the polymerization. Furthermore, the NFPA influences the amount of initiator used in the polymerization reaction that defines the amount of radicals present in the reaction. Higher amounts of radicals are associated to the formation of shorter polymer chains that are undesirable. Therefore, it is important to choose a NFPA that is suitable to achieve higher polymer molecular weights, and less amount of low molecular weight fractions which reduce the formation of PFAS by-products.

It is noted, however, that total annual PFAS emissions resulting from manufacturing and consumption as per RAC-64 Plenary meeting presentation submitted by the 5 PFAS restriction dossier submitters is estimated at 200,000 tons per year in the EEA (RAC-64 Plenary Meeting Presentation, 2023).

During thermomechanical processing of PTFE, PFAS emissions will solely originate from the impurities or modifiers that evaporate or decompose from the PTFE. In case PTFE is exempted from the restriction and considering the threshold of 250 ppb for the sum of PFAS as proposed in the EU PFAS REACH restriction proposal, a maximum of only 0.005 ton of PFAS per year could theoretically be released from total production of 20,000 annual tons of PTFE in the EU.

With the implementation of adequate abatement technologies at processing sites, potential PFAS emissions from the PTFE matrix can be significantly reduced. Quantitative information on potential emissions during processing of PTFE is, however, not presented in this report but should be made available by processing companies during the public consultation. PTFE is an inert fluoropolymer, that does not degrade under intended use conditions. The melting point of PTFE is around 370°C and the processing window temperature is 380-420°C while the Thermogravimetric analysis (TGA) onset temperature is 480°C. Therefore, degradation of PTFE is unlikely at the processing conditions.

At its end-of-life (EOL) stage (Conversio Market & Strategy GmbH, 2022), fluoropolymers are either incinerated (84%), landfilled (13%) or recycled (3%). For the purposes of this case study, it is assumed the same applies to the EOL stage for PTFE. The controlled and selective combustion of PTFE in standard European municipal and industrial waste incineration plants will lead to insignificant emissions of PFAS, i.e., below 0.00185 ton per year as per 2023 KIT study (Dr.

Gehrmann, Herremans, & Dr. Taylor, 2023). Due to inert nature, purity and non-degradation of PTFE, leaching of PFAS to ground water from landfilling of PTFE is considered negligible (Dr. Barbara Henry, 2022).

2. Introduction to Detailed study

Fluoropolymers (FPs) are covered under the current version of the REACH restriction proposal and only for very few, specific applications' derogations have been proposed by the submitters of the Annex XV dossier (ECHA - European Chemicals Agency, 2023). As documented in various papers, fluoropolymers only fulfill the persistence criteria, which is not a stand-alone hazard criterion under CLP (Classification, Labelling and Packaging of chemical substances). This is probably also the reason, why it is stated in the Annex XV dossier that the concern regarding fluoropolymers is more of an "indirect" character, as non-polymeric per- and polyfluoroalkyl substances (PFAS) compounds might be released to environment during the manufacturing and end-of-life stages.

Although fluoropolymers are used for many industrial applications, there is no publicly available study providing a holistic depiction of all possible PFAS emissions covering the full life cycle of fluoropolymers. However, this is a critical information for the regulators and constitutes a major data gap in the restriction proposal on PFAS which needs to be addressed.

The aim of this assessment is to close the existing data gaps and to facilitate sound and science-based decision-making by presenting a case study for the manufacture of PTFE with the specific technologies implemented with or without the use of fluorinated surfactants or polymerization aids (FPAs), as PTFE is the most widely manufactured fluoropolymer.

This report provides general information on possible PFAS emissions due to intentional use and unintentional generation of PFAS emissions during the manufacturing process of polytetrafluoroethylene (PTFE) as well as a quantitative overview of PFAS emissions during manufacture and end of life (EOL) of PTFE.

3. General information on PTFE

PTFE has been selected for this case study not only because PTFE accounts for the most-widely used and consumed fluoropolymer in the world (S&P Global Commodity Insights, 2022) but also because PTFE is the best documented fluoropolymer in the literature concerning its industrial manufacture, volumes produced in the EEA, downstream uses, and physical properties, etc. PTFE is expected to play a very important role in the sunrise sectors like semiconductors, decarbonization technologies, electrification of vehicles and so on. The sources, nature and quantities of emissions and relevant substances that are assessed in the below analysis will support the proportionality considerations of this report.



Figure 1: The lifecycle of PTFE

Tonnage information on PTFE:

Annex A (table A.6) of the restriction proposal on PFAS substances published on 22 March 2023 by ECHA (ECHA - European Chemicals Agency, 2023) provides an overview of PTFE volumes produced in the EEA. The table indicates 34,000 tons per year including processing of PTFE. However, this

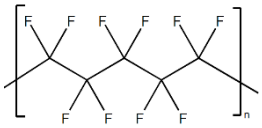
value will not be taken as reference for the calculation of emissions in this report as the actual production of fluoropolymers in the market is estimated to 50,000 tons per year and roughly **20,000 tons PTFE per year produced in the EU**. This amount is considered further in the report as total annual amount of PTFE produced in the EU.

Considerations about thermal & chemical stability, resilience and robustness toward the degradation or the decomposition of PTFE:

PTFE is a polymer known for its remarkable properties. A particular feature of this polymer is its inertness and stability. PTFE will not react with aggressive media such as corrosive acids and bases (e.g., boiling sulfuric, nitric, hydrofluoric and hydrochloric acid), oxidizers such as fluorine and oxygen. Therefore, PTFE cannot lead to PFAS emissions under intended use conditions.

Physical and chemical features of PTFE are summarized in Table 1.

Table 1: Product specific information

Property	Value
Name	polytetrafluoroethylene
Abbreviation	PTFE
CAS No.	9002-84-0
EC No.	618-337-2
Empirical formula	$-(CF_2-CF_2)_n-$
Colour	White and opaque
Molecular structure	
Molecular weight (Mw)	> 389.000 $g.mol^{-1}$
Melting point	335 °C
Glass transition	-103 °C
Crystallinity	50-70 %
Crystalline transition	19 °C
Decomposition	590 °C
Tensile strength	31 MPa (at 23°C)
Compressive strength	4.4 °C (at 23°C)
Specific gravity	2.13-2.20 g/cm^3
Solubility	hydrophobic and insoluble in organic solvents (except fluorinated ones)
Reactivity	Inert to all chemicals
Particle size d_{50} (emulsion)	0.12 to 0.35 µm
Particle size d_{50} (suspension)	1.5 mm

4. General information about PFAS emissions resulting from the manufacturing of PTFE

During manufacturing of PTFE, emissions of low molecular weight PFASs can be generated in two ways – by intentional use of PFAS and unintentional generation of PFAS.

4.1 Intentional use of PFAS

4.1.1 Use of PFAS monomers

The principal monomer used in the manufacturing of PTFE is Tetrafluoroethylene or TFE. TFE is neither soluble in water nor is a PFAS as per the OECD definition. Although at lower concentrations of up to a maximum of 0.1%, some other fluorinated substances that are used in the manufacturing of PTFE can be PFAS like Hexafluoropropylene (HFP) or Perfluoropropylvinylether (PPVE) etc. All of these are intermediate substances that react and transform to PTFE polymer matrix. Unreacted monomer substances are recovered, recycled and reused in the next batch of polymerization through a closed loop process. Basically, the unreacted monomer, TFE, is collected through a vent recovery process and sent to the monomer recycling unit where - after purification - the monomer is stored in storage tanks for reuse in the polymerization process. This is a continuous closed loop system that ensures that the monomer does not get released to the environment (see Figure 2). Being insoluble in water, TFE is not present in the polymer latex and also not released into the coagulation drain water. Therefore, the chance of monomer emissions is considered negligible.

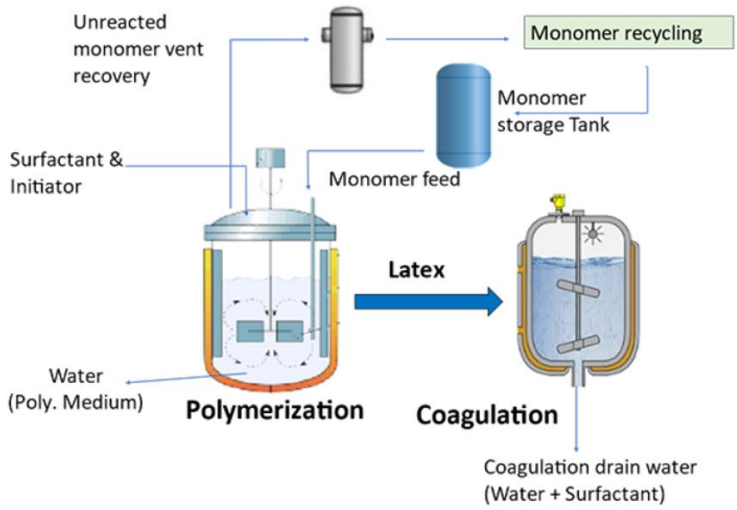


Figure 2: Overview of closed loop system and monomer recycling in the polymerization process

4.1.2 Use of PFAS surfactants or polymerization aids and alternative technologies

PTFE can be polymerized using two methods – Suspension polymerization and Emulsion polymerization. Suspension polymerization does not require the use of polymerization aids and therefore more than 50% of PTFE made globally using suspension process does not require the use of polymerization aids during manufacturing. However, emulsion polymerization process requires the use of polymerization aids (PFAS or non-PFAS).

4.1.2.1 Use of fluorinated polymerization aids (FPA) in PTFE manufacturing

Historically, PFOA (per fluoro octanoic acid) was used as a surfactant in the emulsion polymerisation of PTFE. After understanding its toxic nature and impact to the human health, its manufacturing and use has been restricted globally. At present, except for some producers in China, no one really uses PFOA in the manufacturing of PTFE. Since then, the producers outside China have shifted to C6 PFAS chemistry like HFPO-DA (Gen-X) or ADONA or PFHxS. Regulators and environmentalists consider this transition of C8 PFOA by C6 PFAS as a regrettable substitution of one PFAS of concern by another and have started demanding to stop the use of any PFAS as polymerization aid in fluoropolymer manufacturing.

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When fluorinated polymerization aids are used during the manufacturing of PTFE, PFAS emissions may get generated at several stages in the process such as during the pre-polymerization step all the way from:

a. manufacturing of FPA raw materials (some are also PFAS),
b. manufacture of FPAs,
c. storage, packaging and transportation of FPAs, and
d. the use (and emissions thereof) of FPAs in the manufacturing of PTFEs
e. release of FPAs during processing of PTFE product

FPAs are highly water soluble, volatile and may breakdown to other partly non-characterized and toxic low molecular weight and low temperature volatile PFASs in the environment which are partly chemicals without CAS numbers, very difficult to identify, and also to capture. Furthermore, the packaging of FPAs causes additional environmental burden as the packing units cannot be completely cleaned from the FPAs and need to be incinerated for a proper destruction of the FPAs. Any surface coming in contact with FPAs would eventually require high temperature incineration and it becomes practically unachievable without leaving a PFAS environmental footprint.

The manufacture, intentional use and disposal of FPAs has been considered to be the main source of PFAS emissions linked to PTFE (Prevedouros, Cousins, Buck, & Korzeniowski, 2006). These FPAs are not intermediates as they are not supposed to get consumed during polymerization. Practically, FPAs entering the reaction must therefore be recovered fully, which is difficult to achieve. First, not all manufacturers recover and reuse FPAs, burdening the environment with PFAS. Second, current recycling processes have varying recovery efficiencies ranging from 40% to 80%. The non-recoverable FPAs are partially captured by various abatement techniques such as ultrafiltration, nanofiltration, reverse osmosis, foam fractionation, drying, scrubbing, adsorption by ion exchange resin, granular activated carbon bed (GAC) and destroyed subsequently by thermal oxidation. GAC adsorbs the majority of PFAS, and the saturated carbon beds are incinerated at high temperatures for complete destruction of PFASs with an efficiency of more than 99% (For an overview of abatement technologies please refer to chapter 4.3.4)

Not only the FPAs need to be fully recovered or abated, their degradation products that could be low temperature highly volatile PFAS substances also need to be captured and destroyed (see Figure 3).

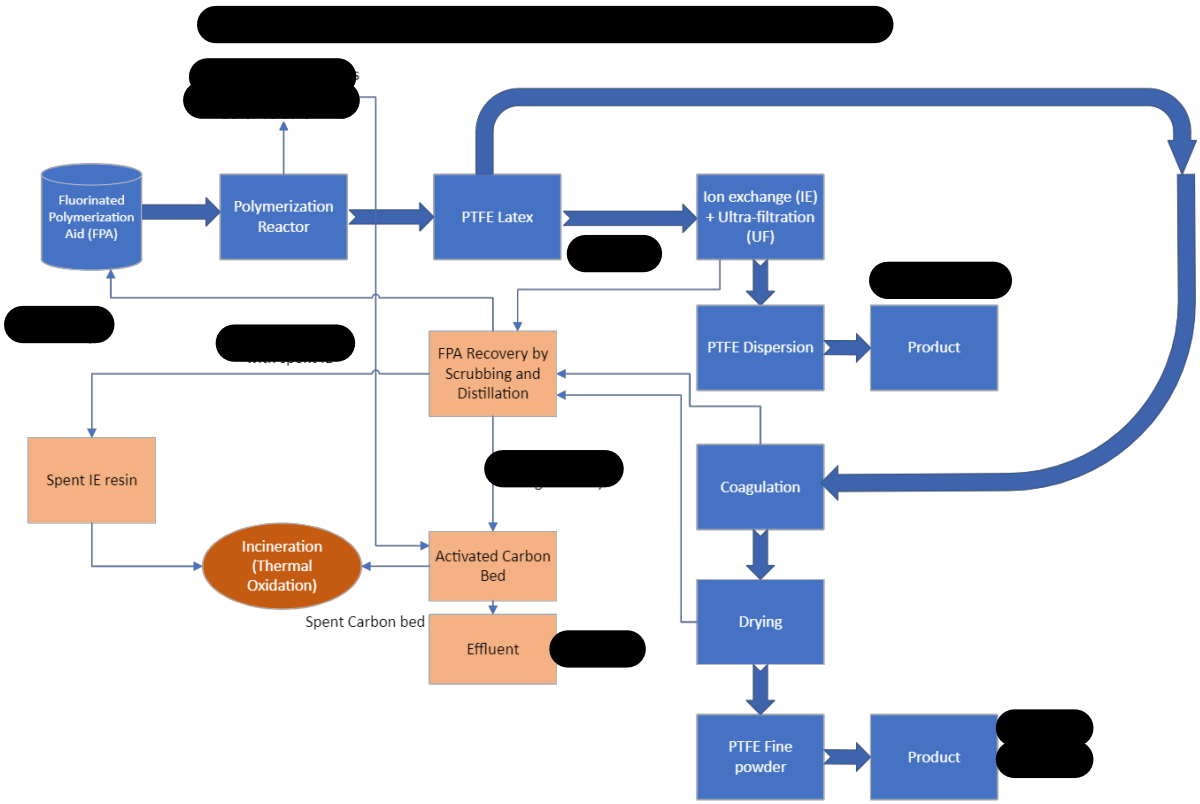


Figure 3: PTFE emulsion polymerization process with fluorinated polymerization aid

As verified by analytical measurements [redacted] may finally end up respectively in the product and wastewater effluent (see Figure 3).

PTFE products are sold as fine powders (also known as coagulated PTFE) and as aqueous dispersions containing typically 60% solids in water. Except for FPAs, there are no significant amounts of other PFAS by-products present in the PTFE products. Please note, the amount of fluorinated polymerization aids in the PTFE fine powder product is not detectable, [redacted] The main source of PFAS released via effluent is due to the use of FPA.

However, percentages of FPAs recovered, abated and released vary depending on individual manufacturing sites as per their respective inbuilt abatement facilities. For example, one European manufacturer claims to recover 40% of FPA with 57% FPA abated and 3% FPA emitted, while the manufacturer intends to further reduce the remaining emissions. Another major manufacturer in India, GFL, can recover 80 - 85% of FPAs from PTFE emulsion polymerization process.

The PFAS emissions due to the intentional use of FPAs can be quantified as follows:

- Approximately 2-10 kg of FPAs are used per ton of PTFE production. In EEA, the share of suspension to emulsion PTFE consumption is equal. However, the European production is focussed mainly on emulsion PTFE products whereas the imports into EEA are primarily suspension PTFE. Therefore, considering 70% of 20,000 tons of PTFE produced in EEA require the use of polymerization aids, we can estimate that max. 140 tons of FPAs are being used.

  ➔ 10 kg of FPA/1 ton PTFE · 14,000 tons of PTFE production = 140 tons of FPA/year

By implementation of recycling & abatement technologies like thermal oxidation[1] (see Figure 3), these FPA emissions can be reduced significantly.

- Some companies recover and recycle up to 40% FPA for reuse. The remaining unrecovered percentages are abated, or may end up in water, air or solid effluent, but can vary significantly depending on each specific manufacturing site, type of FPA used and product portfolio. A small part of this polymerization aid is also carried in the product itself.

  ➔ Actual FPA emissions to the environment due to its intentional use in PTFE polymerization can currently not be precisely quantified but have to be considered to be at least:
  3% of · 140 tons of FPA/year **≥ 4.2 tons of FPA/year.** Below diagram shows the mass balance of FPA.
  In an absolute worst case, from a manufacturing site not having any recovery, recycle or abatement process entire **140 tons of FPA/year** might get released.

Please note: In the "Report summary on PFAS and PFAS polymer production" resulting from the second call for evidence (REACH Competent Authorities, 2021), emission factors of fluoropolymers to air and water of 0.02% and 0.01%, respectively, were derived based on survey results from European manufacturers and processors[2] which have provided further information on both production volume and PFAS emissions. Based on an annual volume of 20,000 tons PTFE produced per year in the EU, **2 tons and 4 tons PFAS are annually released to water and air, respectively,** in relation to the PTFE production and processing.

4.1.2.2 Fluoropolymer manufacturing without the use of fluorinated polymerization aids

It is noteworthy to mention that not all fluoropolymers produced using emulsion technology are dependent upon fluorinated polymerization aids. According to publication by Chemservice Iberia in International Chemical Regulatory & Law Review 2023 (Ameduri, Sales, & Schlipf, 2023), many companies announced shifting to the use of non-FPAs by substituting FPAs in 2022. More than 30 patents from major fluoropolymer producers are cited in this report. Today, technologies exist to produce PTFE, PVDF, FKM & PFA that no longer require the use of FPAs. Major players like Arkema, Solvay, GFL & Honeywell have announced commitments to put a total stop on use of FPAs in the near future. Chemours has announced the development of non-FPA technology in the production of FKM. Hence, PFAS emissions from manufacturing of PFAS polymerization aids, its packaging and transportation and its use during polymerization can be eliminated. **Thus, by stopping the use of fluorinated polymerization aids for PTFE, a potential PFAS emissions between 4.2 and 140 tons can be prevented** plus an additional quantity if we take into account emissions during manufacturing of FPAs themselves as explained under 4.1.1.1. It is clear that the non-fluorinated polymerization aid technology to manufacture fluoropolymers is well researched and commercially established. A mandate from the regulators to stop the use of FPAs completely will expedite the transition from the use of FPA to non-FPA to manufacture fluoropolymers. Also, it is important to note that the transition from FPA to non-FPA does not require a significant change in the manufacturing equipment or plant setup.

However, in relation to the substitution of FPAs by NFPAs it should be noted that the choice of the actual NFPA used in the polymerization process influences the potential for formation of PFAS by-products; i.e., the NFPA should be non-reactive with the monomers involved in the polymerization. Furthermore, the NFPA influences the amount of initiator used in the polymerization reaction that defines the amount of radicals present in the reaction. Higher amounts of radicals are associated to the formation of shorter polymer chains that are undesirable. Therefore, it is important to choose

[1] Incineration of saturated carbon beds at high temperatures ensure complete destruction of PFASs with an efficiency > 99%.
[2] The scope of the project included fluoropolymers, F-gases and other PFAS. It also included PFAS processors (dryers, powder generators, mixers,extruders etc.).

a NFPA that is suitable to achieve higher polymer molecular weights, and less amount of low molecular weight fractions which reduce the formation of PFAS by-products.

4.2 Unintentional generation of PFAS during polymerization

There could be unintentional generation of PFAS during polymerization irrespective of the type of process, suspension or emulsion, with or without the use of FPA or non-FPA (Lohman, et al., 2020). This unintentional generation of PFAS by-products depends upon the choice of manufacturing process - mainly use and choice of surfactant; choice, type and quantity of initiators used in the process. When compared to PFAS emissions associated to the intentional manufacture & use of FPA (4.2 – 140 tons per year), the amount of unintentional PFAS generated in this manner is very minimal.

To quantify PFAS emissions associated to PTFE manufacturing using non-FPAs, PFAS concentrations in the wastewater and the product are analysed.

[redacted]. In a worst-case approach the release factor to water during emulsion polymerization [redacted], and the actual amount of wastewater produced during the manufacturing of 1 ton of PTFE at GFL. Thus, the amount of unintentional PFAS by-products released to the environment via wastewater [redacted]

Considering the 250 ppb sum of targeted PFAS concentration limit in the final product as proposed by regulators for the 20,000 tons[4] of PTFE produced per year, it can be estimated that the **future maximum potential of** PFAS contained in PTFE **is 5 kilograms per year** assuming a 100% release of PFAS by-products from PTFE during e.g., processing.

When measured in final products using liquid chromatography-mass spectrometry tandem mass spectrometry (LC-MS/MS) analytical method 537.1 suggested by US EPA, the sum of 45 targeted long-chain PFAS carboxylic and sulfonated compounds is less than 5 ppb. Determining the presence of other non-targeted PFAS in final products is difficult and inaccurate using the currently available analytical methods. In any case, using standard abatement techniques like ion exchange resin, ultrafiltration and foam fractionation etc., PFAS generated unintentionally can be reduced to below 1 ppm in all types of PTFE products.

Unintentional PFAS by-products generated in production are significantly reduced (captured and destroyed) using abatement techniques as mentioned in below process diagram (see Figure 4; example from GFL).

[3] Analytical verification according to US EPA 537.1; analytical method for targeted analysis for 45 PFAS on weekly basis using LC-MS/MS with an LOQ of <5 ppb for individual PFAS.

[4] 20,000 tons as estimated PTFE production in EEA

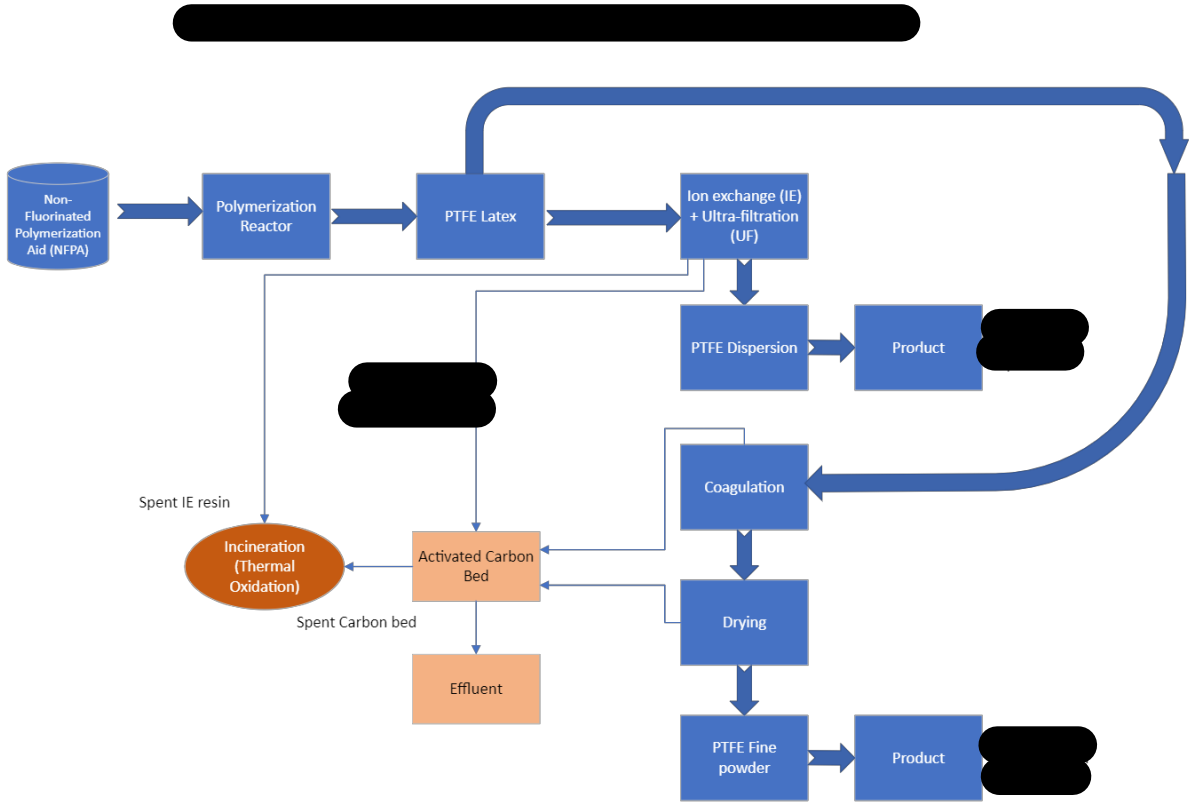


Figure 4: PTFE emulsion polymerization process with non-fluorinated polymerization aid

4.3 Details on the manufacture of PTFE

An overview of the manufacturing process of PTFE and potential sources of PFAS emissions during production is provided in Figure 5. Depending on the regional and technical know-how, supply and demand of final products with different quality requirements, the industrial set up might vary. Despite the fact that there is not only one way to produce PTFE, the industrial synthesis generally follows a four step procedure:

(1) Production of hydrofluoric acid: $CaF_{2\,(s)} + H_2SO_{4\,(l)} \rightarrow CaSO_{4\,(s)} + 2\ HF_{\,(g)}$

(2) Fluorination of chloroform: $CHCl_{3\,(l)} + 2\ HF_{\,(g)} \rightarrow CHClF_{2\,(g)} + 2\ HCl_{\,(g)}$

(3) Pyrolysis of chlorodifluoromethane: $2\ CHClF_{2\,(g)} \rightarrow C_2F_4$[5] $_{(g)} + 2\ HCl_{\,(g)}$

(4) Polymerization: $C_2F_{4\,(g)} \rightarrow -(CF_2\text{-}CF_2)_n-$

4.3.1 Step (1) Production of HF

HF is produced by the endothermic reaction of fluorspar and sulfuric acid. Depending on the grade of fluorspar (ranging from the ore grade (25-30 % purity) to crystalline grade (99 % purity)) various impurities might form during the reaction. The final product HF requires purification to remove these impurities that might affect the quality in the next steps. A flow chart on HF synthesis is available on the Eurofluor website (HF production - Eurofluor; (Eurofluor, 2023)). Regarding emissions aspects: the synthesis of HF is well understood and fluorinated impurities resulting from the reaction and from the purification step (e.g., SiF_4, H_2SiF_6) are documented. A report of the United States Environmental Protection Agency (EPA) on HF emissions is available (Environmental Protection

[5] C_2F_4 = TFE

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Agency, 1993). It can be concluded that undesired **PFAS side products are not produced** in the entire process of HF synthesis.

4.3.2 Step (2) Fluorination of chloroform

HF is then transferred to the plant where the production of the monomer tetrafluoroethylene (TFE) will be performed prior to polymerization. The production of TFE occurs in two steps (Step (2) and (3)). The most efficient industrial method is the so-called Route 22 (R-22) via pyrolysis of chlorodifluoromethane (Ameduri M. , 2019). In the step (2), chloroform is first reacted with HF at 80 °C in presence of SbF_3 to give $CHClF_2$. SbF_3 is a catalyst that specifically exchanges the chlorine ions with fluorine ions according to a multistep equilibrium. The kinetic of rate exchange between Cl and F as well as potential polyfluorinated side products (e.g., $CHCl_2F$, CHF_3, SbClxFy) are well documented (Serio, 1989). These polyfluorinated side products do not meet the definition of PFAS and the process is, therefore, **free from PFAS emissions**.

4.3.3 Step (3) Pyrolysis of $CHClF_2$

The step (3) is the pyrolysis of $CHClF_2$ at 800 °C to give TFE. Documentation on the formation of PFAS side products is available in kinetic studies and infers emissions of perfluoroisobutene (C_4F_8) (Ritter, 1988) , octafluorocyclobutane (C_4F_8) (Atkinson, 1957), hexafluoropropylene (HFP) and chlorofluorocarbon side products such as $H(CF_2)_2Cl$, $H(CF_2)_3Cl$ (Sunavala, 1987) and CF_4 (Ameduri M. , 2019). These sources of PFAS represent the first source of potential PFAS emissions in the synthetic route of PTFE.

When the pyrolysis reaction is finished, appropriate purification of TFE and elimination of fluorinated residues must be considered to avoid PFAS emissions in the environment. As TFE is highly reactive it cannot be stored and must be timely injected for polymerization which happens in a continuous process (i.e., TFE is known to be a biradical that can self-dimerize into C_4F_8 according to thermo-equilibrium (Ritter, 1988)). The most convenient setup is to generate TFE on site so that TFE is directly injected in the autoclave. Per se this lowers the risk of PFAS emissions as there is no storage stage.

Beside storage aspects, TFE can be synthesized with a high purity grade and residues of the TFE synthesis can be controlled in a safe way that allow a significant reduction of PFAS emissions in the later steps. At GFL, the TFE synthesis is a continuous process and TFE is circulated continuously as the monomer cannot be stored or transported. The purity of the monomer is determined every two hours by means of online GC analysis. According to GFL, the purity of TFE, which is achieved by means of distillation, is maintained to 99.99999%. Due to the closed continuous nature of the production process (3), **no emissions of potential PFAS are expected.** In addition, the distillation residues containing above said PFAS side products are incinerated at high temperatures.

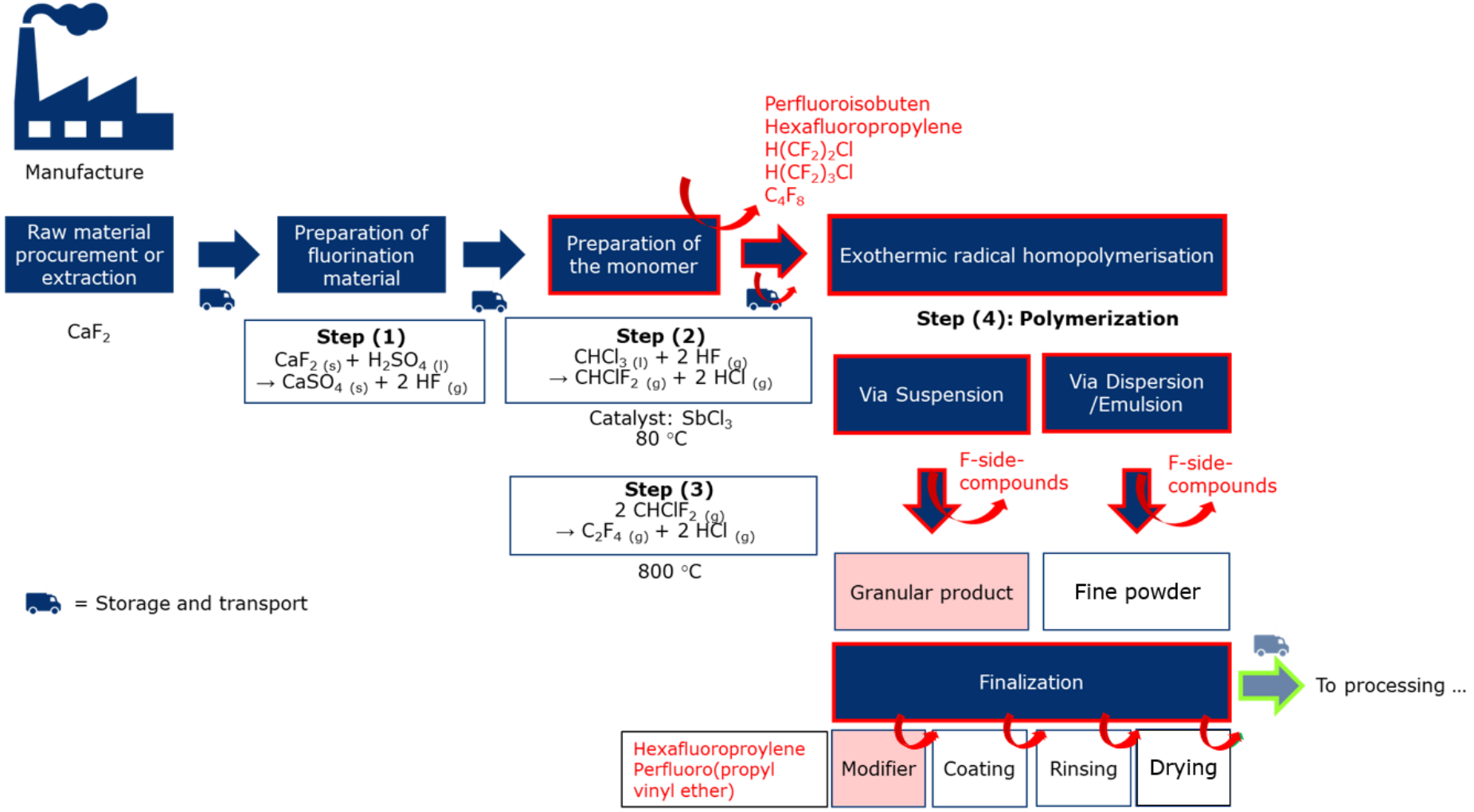


Figure 5: Potential sources of PFAS emissions during the manufacture of PTFE

4.3.4 Step (4) Polymerization

TFE is safely transferred to the plant where the polymerization into PTFE, step (4) will be performed. At industrial scale, the exothermic radical homopolymerization of TFE takes place in large, high-pressure, stirred-tank reactors. Depending on demand and the feature requirements of the polymer, two different polymerization methods can be applied. These two methods equally contribute to the global annual volumes of produced PTFE, ca 85,000 tons each, i.e., 170,000 tons in total (Noort, 2022). One polymerization method is performed via suspension and results in the formation of granular polymers, which are processed as molding powders (Ebnesajjad, 2000). The degree of clumping and the size of the granules depends on the vigorousness of the agitation in the reactor. This method does not use surfactants (neither FPA nor NFPA). The other polymerization method is performed via emulsion, which is possible by the introduction of surfactants. The surfactant will form droplets in which the polymerization will occur from where a fine PTFE powder can be synthesized. In both polymerization methods, the reaction vessel is closed during the polymerization process, and only opened when the remaining gaseous TFE has been consumed.

The polymerization of PTFE is a versatile reaction, where reagent types and quantities are adaptable and will play a critical role in the resulting properties of the final product. Wherever a reagent is identified as a PFAS, it can easily be replaced by a non-fluorinated functional equivalent. This constitutes a direct implementable abatement technology to minimize the introduction of PFAS in the manufacturing process. The reagents needed for the polymerization setup are:

- Initiators
- Monomers
- Solvent
- Additives/Modifiers
- Surfactants in case of emulsion polymerization

A list of initiators that generate the radicals in the polymerization of PTFE can be found in the literature (Ameduri M. , 2019). Among the 27 initiators listed, 16 are non-fluorinated peroxides such as DSAP and represent a significant PFAS abatement option.

A common solvent used for the polymerization of PTFE is water, which is a green solvent. The water that was used in the autoclave as solvent of the polymerization can be treated post-polymerization via a water treatment process that recovers potential surfactants and eliminates dissolved impurities. This process constitutes an example of an efficient abatement method already implemented by GFL.

In the case of emulsion polymerization where surfactants are needed, non-fluorinated surfactants can be used for the polymerization in place of conventionally used fluorinated surfactants.

Additives/modifiers can be added in the polymerization vessel and will result in the production of "modified PTFE", which displays better properties in respect to processability and end use performance.

The addition of a modifier (such as Perfluoropropylvinylether or Hexafluoroproylene) can be made at any time during the polymerization and will provide a more suitable coalescence temperature of the polymer allowing a better processing of PTFE. In counterpart it will increase the risk of PFAS emission. In the case of PTFE, a maximum of 0.1% PPVE or 0.5 % HFP is added. Approximately 25% of the total PTFE production involves the application of modifiers. The non-used modifiers are partly recovered and fed-back/re-used in the production process as the modifiers are extremely expensive. Around 70% of unreacted PPVE is recovered for reuse and the remaining amount is captured during distillation process as residue, which is then sent for thermal destruction. Unreacted HFP along with TFE is recycled where monomers

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are separated by distillation process. The purified monomers are recycled and reused in the next polymerization batch. Unreacted TFE, hexafluoropropylene (HFP) and perfluoro-propylvinylether (PPVE) are vented back to monomer plant and again purified by means of distillation. The unreacted monomers are then again mixed with fresh TFE/HFP for re-use. PPVE is separated out from TFE vent by condensation and recovered in liquid form and re-used with fresh PPVE.

Theoretical emissions of PFAS can result from the termination step of the polymerization of PTFE. There is a common understanding about the mechanistic of the homopolymerization of PTFE characterized by the linear addition of TFE to the growing macroradicals. The macroradicals are essentially immobile and extend until two macroradicals are in close enough proximity to terminate by coupling. In case this recombination does not occur, the macroradical reactive species will be entrapped in the polymer matrix and persist indefinitely under inert conditions. Polymer treatments can be made in order to cap these trapped radicals in PTFE. If no capping is made, the presence of the radical will likely alter the properties of PTFE (by possible reaction into peroxides via air exposure) and result in potential PFAS emissions. To avoid these potential PFAS emissions, chain termination agents - typically alcohols – are used which control and inactivate the radicals. Apart from that, the reaction can also be terminated by stopping the monomer feed to the polymerization reactor.

Additionally, at the end of the reaction, PTFE polymers with short chains, which are not in the targeted range of final PTFE product, need to be eliminated via purification steps as they might alter the functionality of the material.

In the finalization step, the polymer must be treated depending on the polymerization method that has been used and depending on the requirements that the final product has to meet. These proceedings are:

- A rinsing step
- A drying step

During suspension polymerization the rinsing step involves the washing of insoluble polymer with organic or aqueous solvent to remove impurities. The number of washes depends upon the purity required for various applications, e.g., products intended for semiconductor applications require a very high level of purity. All potential impurities contained in PTFE which are soluble in water or in organic solvent should be removed with this step. However, other volatile impurities trapped in the PTFE matrix will be removed during the sintering of the polymer. Water and/or organic solvent from the washing steps is cleaned by means of an activated carbon bed.

The subsequent drying step is a continuous or batch process which is in any case a closed process at 90-200°C. For PTFE, drying takes place around 200°C. During the drying step, remaining solvent molecules are evaporated. This operation should be made at temperatures where the solvent evaporates, but far below the operating temperatures of the sintering during which PFAS emissions in the air are possible (see section "Processing" below). The exhaust air from the drying step is treated by means of an activated carbon bed. The impurities that have been trapped in the adsorbent bed are incinerated to ensure their proper destruction.

While suspension products will have relatively negligible amounts of side products generated unintentionally according to GFL, trace amount of side products are generated in emulsion products at low ppm or ppb level. These are largely abated and destroyed at the manufacturing site (wastewater, exhaust air). These abatement technologies comprise of:

- Ion exchange resins which currently constitute the best available technique to capture these PFASs; even very low concentrations of 200 ppb of PFAS were removed as a result (Lanxess, 29 October 2021);

- Filtration methods, e.g., reverse osmosis and nano filtration (Lee, 2022); this technology separates short- and long-chain PFAS at excellent rejection efficiencies;
- Scrubbing and GAC adsorption followed by incineration at high temperature;
- Electrochemical oxidation and foam fractionation (Smith, 2023); foam fractionation recovery efficiency is excellent for long chain PFASs;
- Thermal oxidation with a combustion efficiency of more than 99.999% regarding destruction / oxidation of PFASs and related halogenated hydrocarbons.

Measured release values for the individual steps in this section are not available. However, based on release factors to water (0.01 %) and air (0.02 %) from the PTFE manufacturing and processing industry PFAS emissions are estimated at 6 tons PFAS per year when the production of fluoropolymers uses FPA (REACH Competent Authorities, 2021) (full range ≥ 4.2-140 tons FPA per year). With a future change to non-fluorinated polymerization aids, emissions can be reduced to 2 kg of unintentional PFAS by-products per year (see chapter 4)[6].

4.3.5 Conclusion

There are few potential sources of PFAS emissions resulting from the PTFE manufacture other than the use of FPA. Since these potential sources of PFAS emissions are relatively very small compared to use and emissions of FPAs, it is possible to control the emissions via implementation of abatement methods. The sources of PFAS and abatement methods can be summarized as follow:

- Impurities and side products formed during the PTFE polymerization.
- The finalization of the PTFE crude product before processing (caping/coating; addition of fluorinated modifiers; drying; rinsing).

Implemented abatement technologies include the use of:

- Non-fluorinated initiators, solvents and surfactants.
- An industrial setup to extract and eliminate residual impurities contained in the solvent and in the reaction vessel after reaction (cleaning step) by means of ion exchange resins, filtration methods (nano filtration, reverse osmosis, scrubbing and GAC adsorption followed by incineration at high temperature; electrochemical oxidation and foam fractionation; Thermal oxidation).
- An industrial setup to recycle the non-consumed monomers TFE, HFP and PPVE of the polymerization reaction. The monomers are fed back to the polymerization process.

5. Semi-quantitative assessment of PFAS emissions during the further life cycle of PTFE

5.1 Processing of PTFE

No detailed quantitative information on emissions from PTFE processing can be provided by PTFE producers as they do not process PTFE. This information has to be provided by PTFE processing companies or their association, *Pro-K (Industrieverband Halbzeuge und Konsumprodukte aus Kunststoff e.V.)*. Based on the proposed 250 ppb PFAS concentration limit, for the 20,000 tons of PTFE produced per year, it can be estimated that **maximum potential of** PFAS contained in fluoropolymers and subsequently released **is 5 kilograms per year**.

A high-level description of PTFE processing is provided in the following: Processing is the second stage of the PTFE lifecycle. Depending on the type of PTFE that needs to be processed e.g., in granular or fine powder or aqueous dispersion form, the processing will respectively be a compression or a paste extrusion or a coating, followed by sintering process. Therefore,

[6] Annual tonnage of PTFE of 50,000 tons used as basis for calculation.

the possibility for PFAS emissions will be different from one process to the other. The different steps allocated to the two different processes are represented in Figure 6 overleaf.

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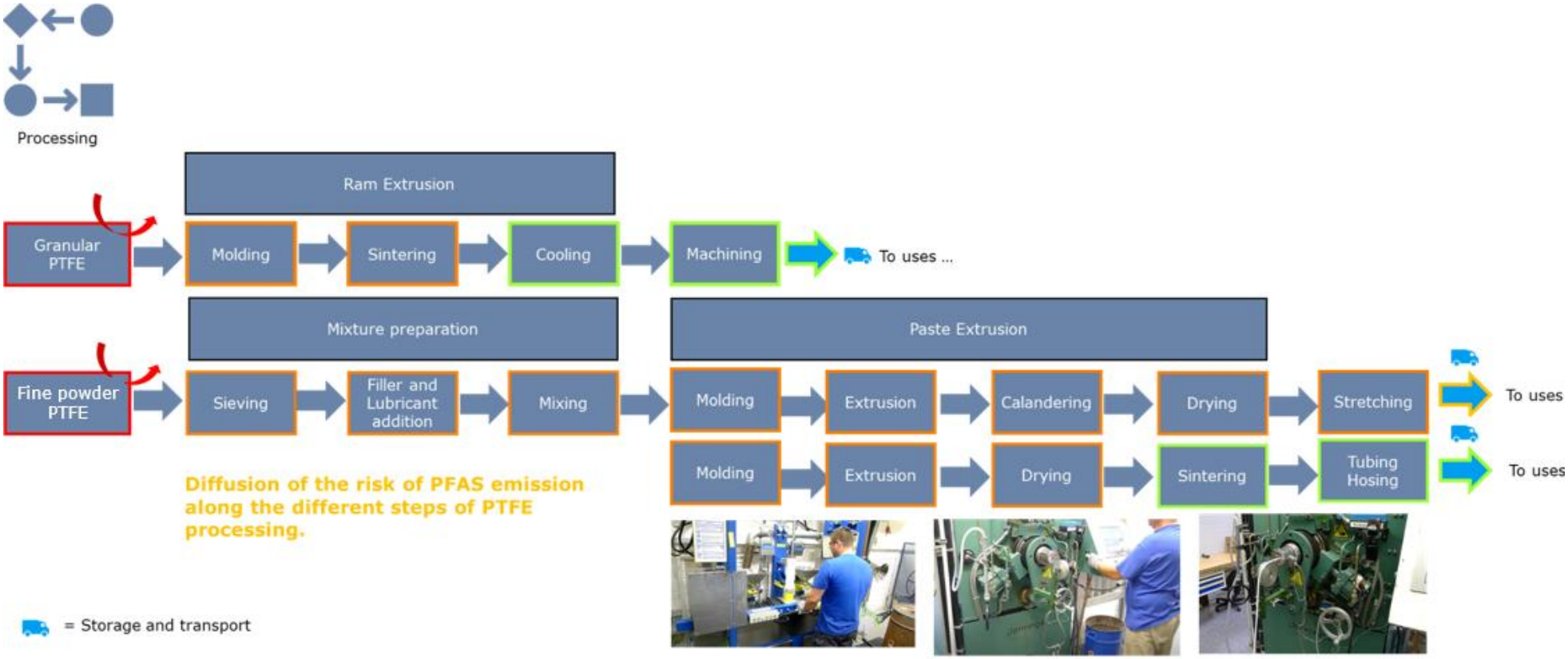


Figure 6: Representation of the different steps during the processing of PTFE.

5.1.1 Granular PTFE

The Granular PTFE processing starts with molding. The PTFE powder is charged to the mold and compressed (operating temperature 21 – 25 °C) and held for a dwell period via hydraulic press. After the preform is made, it is removed from the mold and allowed to rest for stress relaxation and degassing (Ebnesajjad, 2000).

The next step is the sintering of PTFE, which is a thermal treatment (operating temperatures from 360 to 380 °C) during which the polymer is melted and coalesced and where the polymer molecules rearrange in the lattice to provide the desired properties. The temperature range of 360-380 °C is much below the decomposition temperature of 590 °C, so no disintegration of PTFE occurs during its processing.

In the following cooling step, PTFE will recrystallize (operating temperature 260 °C). Alternatively, PTFE is extruded (ram extruder) to form tubes and rods. In the next step, PTFE shapes are given its final form during the machining step, where sawing, shearing, drilling, tapping, threading or skiving can be performed. If the process is performed in a closed machine, wastes of PTFE resulting from these processes are collected and the emissions to the environment are minimized. It should be reminded here that PTFE is a non-volatile, non-soluble, non-toxic inert polymer, which makes the elimination of residual PTFE from the processing convenient. Waste PTFE collected from machining is grinded and used in other applications e.g., as an additive in engineering polymers like polyamides to improve its wear resulting in longer life of final application further supporting the circularity objectives.

5.1.2 Fine powder PTFE or coagulated dispersion PTFE

The processing of fine powder PTFE requires three preparation sub-steps. The powder is sieved in order to homogenize the particle size. Non-fluorinated fillers and non-fluorinated lubricants are added in the powder and the resulting mixture is stirred. After this, the product will undergo a sequence of processing steps, which might differ, depending on the final shape that the product needs to have (e.g., films, tubes or hoses, etc.). In the two first common steps of the paste extrusion, the powder needs to be molded and later extruded. In the case of film fabrication, the product is then calendared, dried and stretched. In the case of tubes fabrication, the product resulting from the extrusion is dried, sintered and later given the desired shape. It is noteworthy that a controlled cooling step is not required after the sintering as the targeted product needs flexibility and a crystallization should be avoided.

5.1.3 Aqueous dispersion PTFE

Aqueous PTFE dispersions contain approximately 60% PTFE solids. The rest is mostly water along with approximately 5% of non-fluorinated secondary surfactant added in the polymer post polymerization to give stability to latex and avoid settlement. Few other non-fluorinated additives like a defoaming agent and a wetting agent may be added as per requirements. Aqueous PTFE dispersions are widely used as a coating on to glass fabrics for architectural use and on aluminum metal for non-stick frying pans besides other uses. Post coating (multiple) step(s), the surface is dried and sintered resulting in evaporation of water and other additives including secondary surfactant. Since aqueous dispersions can contain up to tens of ppm of fluorinated polymerization aids besides other non-fluorinated additives, the processors require the use of granulated active carbon beds to absorb all impurities avoiding any PFAS release in the environment. The spent activated carbon beds are incinerated. This abatement step will not be required should the processors switch to PTFE produced without the use of FPAs.

5.1.4 PFAS emissions

In the overall processing of PTFE, there is no subsequent addition of new PFAS substances and per se, the potential of PFAS emissions will solely rely on the impurities or modifiers that evaporate or

decompose from the PTFE by thermomechanical processing of PTFE. It should again be reminded that PTFE is a solid, non-volatile, non-soluble, inert polymer. All mechanical actions in the PTFE processing lead to solid wastes of PTFE (abrasion, machining, transport, packing, transfer, dust formation etc.) which should be captured, have high economic value and are reused.

Sintering is the emblematic processing step known to emit most volatile PFAS during the overall lifecycle of PTFE. However, when sintering is conducted safely with the right abatement measures in place, it is also a key step that allows elimination of residual PFAS impurities contained in the PTFE polymer. When the resulting emissions are trapped, it constitutes an essential abatement method. The operating temperatures of sintering (ca. 370 °C) allow lighter PTFE compounds or potential PFAS volatiles to evaporate or decompose. If the sintering is performed in a closed setup and adequately ventilated, "PTFE fumes"[7] (C.H., 1997) will not be released to the air and PFAS emissions are controlled. After the sintering step, the concentration of more volatile PFAS in the PTFE matrix is significantly reduced.

5.2 Use of PTFE at downstream users

The third lifecycle stage of PTFE corresponds to its usage. A general description of uses of PFAS can be found in the literature (Glüge, et al., 2020). The main usage categories of PTFE have been summarized in Figure 7. After the processing step of PTFE, the material shall be considered an article under the definition of REACH (Regulation (EC) No 1907/2006, Art.3 §3) and these components can directly be introduced into more sophisticated objects such as jets, cars, electronic devices, etc. from where PTFE is generally less directly accessible to handling. Given that PTFE is mostly used in inaccessible parts of functional devices, **emissions of PTFE or other PFAS from PTFE are considered negligible** and this is due to two reasons:

- The first one is the remarkable stability of PTFE, which will not decompose unless a device is misused (e.g., parts where PTFE is overheated over functional temperatures of 300 °C, no emissions of PFAS result from the use of PTFE. Even when PTFE is exposed to the harshest conditions (e.g., gasket used in aerospace, geomembranes (Tippett, 2023), or seals that come in contact of highly corrosive substances of the chemical industry), PTFE is not meant to decompose or to react.

- The second reason is the low concentration levels (ppb) of PFAS impurities demonstrated in the previous part of this report.

[7] Note that PTFE itself does not evaporate and any PTFE fume resulting from other compounds gets contained in the PTFE matrix.

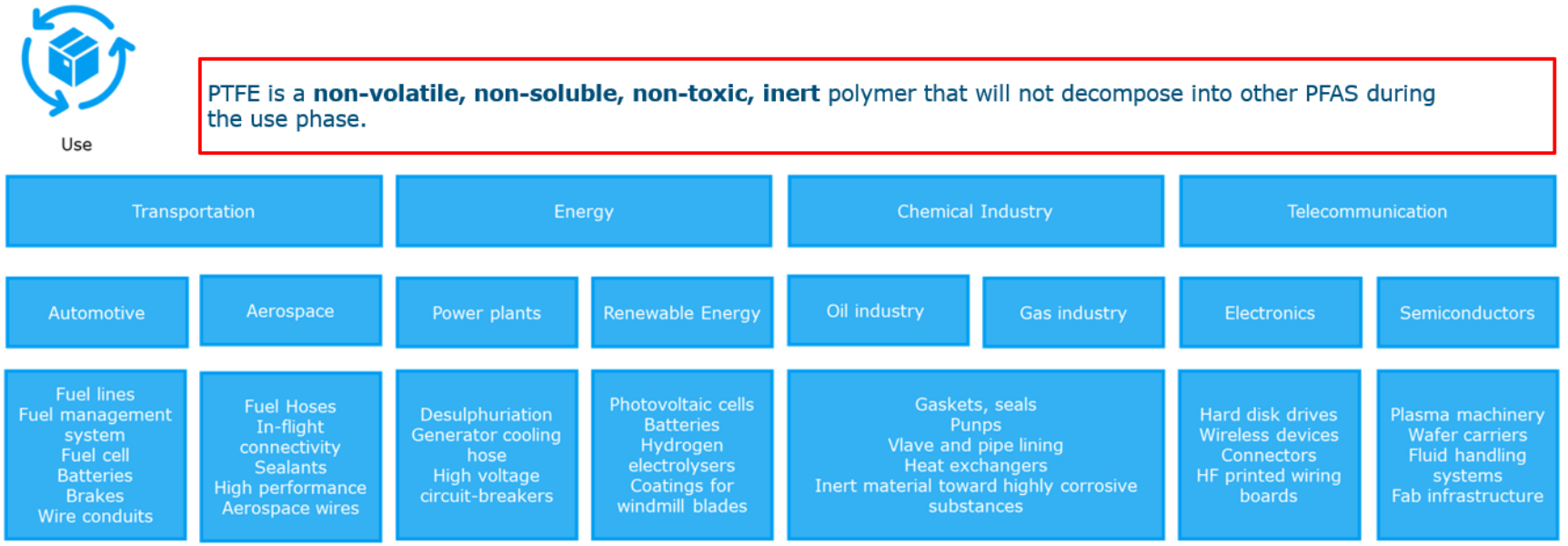


Figure 7: Representative main uses of PTFE in the society.

5.3 End-of-life stage of PTFE

Due to the fact that PTFE applications are typically smaller intricate components used in complex applications like seals in an airplane, they cannot be economically recovered by ordinary methods that are used for typical plastic recycling. A report from Conversio (Conversio Market & Strategy GmbH, 2022) and the PRO-K (Association of Fluoropolymer Downstream Usesrs in Europe) from 2020 indicated three main paths for the end-of-life of fluoropolymers which is also assumed applicable for PTFE. The most important disposal route in Europe is the incineration step that covers ~84 % of fluoropolymer waste collected, then the landfill with ~13 % and finally, the recycling with ~3%. Also to be taken into account, the typical lifespan of a PTFE application ranges between 5-30 years.

5.3.1 Incineration of PTFE

Incineration is the most convenient destruction technology of PFAS. A summary is available in the literature (Kewalramani, 2022). Incineration can be performed in municpal incinerators or in industrial incinerators. Due to the importance of PTFE in industrial installations, a significant amount of PTFE is incinerated in incinerators for industrial waste, while the rest is incinerated in municpal incinerators.

In 2020, it was reported that the amount of fluoropolymers incinerated was about 20,000 tons (Conversio Market & Strategy GmbH, 2022). Compared to the annual volumes of fluoropolymers manufactured in the European Union (i.e., 50,000 tons), this corresponds to a significant ratio of the produced volume (40%) and represents an efficient method to eliminate these polymers. Please note: The overall share of fluoropolymers in all waste streams in the EU is less than 0.01 % (w/w), while the total plastic waste accounts for approximately 4.8 % of the total collection volume (excl. mineral fractions) (Conversio Market & Strategy GmbH, 2022).

Please note that PTFE incineration was demonstrated to not emit PFAS (Wexler, 2019). Furthermore, an incineration study on PTFE pellets was conducted by Karlsruhe Institute of Technology (KIT) (Wexler, 2019). The results of KIT were based on methods involving a limit of quantification of 0.3 to 24 µg/Nm^3 and no PFAS could be quantified or identified from the combustion of PTFE except hydrofluoric acid, which is not a PFAS. Therefore, it appears that a controlled and selective combustion of PTFE will **not lead to emissions of PFAS**.

This is further confirmed by a new 2023 study conducted by Karlsruhe institue of Technology in cooperation with Société Générale de Surveillance (SGS) and final results of the pilot-scale FP incineration study (Dr. Gehrmann, et al., 2023) (Dr. Gehrmann, Herremans, & Dr. Taylor, 2023). The results show conversions of fluoropolymers to inorganic fluorides (i.e., mainly hydrogen fluoride and silicon tetrafluoride) and carbon dioxide under standard municipal and industrial waste incineration conditions (850°C – 1100°C for two seconds residence time respectively). Fluorine recoveries ranged from 69 to 84% using TDL (Tunable Diode Laser) which provides strong evidence for mineralization of the fluoropolymer feed mixture. TFA (Trifluoro acetic acid) was not detected for all samples at a reporting limit of 14 µg/m³. The targeted PFAS analysis demonstrates for a large majority of the samples (i.e., 99% of the samples associated with 860°C condition and >98% of the samples associated with 1100°C during incineration) that long-chain PFAS were at non-detectable at levels of <1 ng/m³. Short-chain fluorocarbons were analysed by means of GC-MS and were non-detectable at a reporting limit of 5-30 µg/m³. Furthermore, the analysis of wastewater and ash residue shows for a large majority of the samples that PFAS were non-detectable with reporting limits of 0.02 µg/l.

Total expected PFAS emission from fluoropolymers destructed in standard European waste incineration plants were calculated based on the following assumptions (Dr. Gehrmann, Herremans, & Dr. Taylor, 2023):

- Total waste incinerated in the EU: 62 million tons per year[8]
- Maximum sum of PFAS released (stack) at 860°C/1100°C with 0.3% FP feed: 18.4 ng/m³ N, dry assuming PFAS < LOQ = 0
- Specific flue gas amount released per ton of waste[9]: 4060 m³ N, dry
- Total load of PFAS emitted in the EU: 4.63 kilograms per year for 0.3% FP feed

BUT

- Actual FP waste incinerated (85% of 52,000 tons) = 44,200 tons per year (0.07% of total waste)

➔ Therefore, total emissions of PFAS from incineration of FPs in the EU are lower than 4.63 kg per year.

If this calculation is transferred to PTFE, the following results are obtained:

- Total waste incinerated in the EU: 62 million tons per year
- Maximum sum of PFAS released (stack) at 860°C/1100°C with 0.12% PTFE feed[10]: 7.36 ng/m³ N, dry assuming PFAS < LOQ = 0
- Specific flue gas amount released per ton of waste: 4060 m³ N, dry
- Total load of PFAS emitted in the EU: 1.85 kilograms per year for 0.12% PTFE feed

BUT

- Actual PTFE waste incinerated (85% of 20,000 tons) = 27,000 tons per year (0.03% of total waste)

➔ Therefore, total emissions of PFAS from incineration of PTFE in the EU are lower than 1.85 kg per year.

In conclusion, PFAS releases to the environment based on incineration of fluoropolymers – including PTFE – are minimal compared to annual production volumes.

5.3.2 Landfilling of PTFE

The inherent chemical and physical properties of PTFE are indicative that the polymer will not decompose when landfilled. This has been demonstrated through laboratory tests performed by Charles Rivers and mandated by the company W L Gore. The results support the stability of PTFE and lack of transformation to other PFAS, such as perfluoroalkyl acids. PTFE will not partition to air, water, or soil. Potential inhalation, oral or dermal exposure to PTFE for biota or the environment is unlikely based on this data (Dr. Barbara Henry, 2022). PTFE is an inert chemical and does not react with other chemical substances. It is also known to be the most suitable material to be used as liners for landfilling as PTFE has an exceptional resistance against corrosion (no reaction between pH 0 and 14). The corrosion represents a severe threat for material liners, as it is the main factor responsible for its degradation and ultimately for its tearing, which results in ground contamination. Because of the robustness of PTFE, the risk of geomembrane breaking is eliminated. PTFE extends the usual warranty of 10 to 20 years of geomembrane to a much longer time period, which is theoretically not limited in time (Tippett, 2023).

[8] Municipal waste statistics - Statistics Explained (europa.eu)

[9] VDI guideline 3925 "Methods for evaluation of waste treatment processes"

[10] Based on the annual production volume of PTFE and FP of 20,000 tons and 50,000 tons, the share of PTFE is 40% of the total FP feed

In addition, it has been demonstrated that PTFE is biologically inert and can not be degraded by microorganisms under aerobic or anerobic conditions (Henry, 2018). Therefore, PFAS emissions from PTFE resulting from its decomposition in landfill are not likely. **No PFAS emissions from PTFE applications due to landfilling are expected**.

5.3.3 Recycling of PTFE

The report from Conversio and the PRO-K association from 2020 indicates that recycling of fluoropolymers can be performed under two different ways: mechanical recycling and chemical recycling. Also the recycling method applied will depend on the type of PTFE (virgin or modified) to be recycled.

5.3.3.1 Mechanical recycling

Mechanical recycling is relevant for sufficently pure PTFE polymer waste without fillers (Achim Schmidt-Rodenkirchen, 2022). Figure 8 and Figure 9, respectively, represent examples of different mechanical recycling methods existing for PTFE.

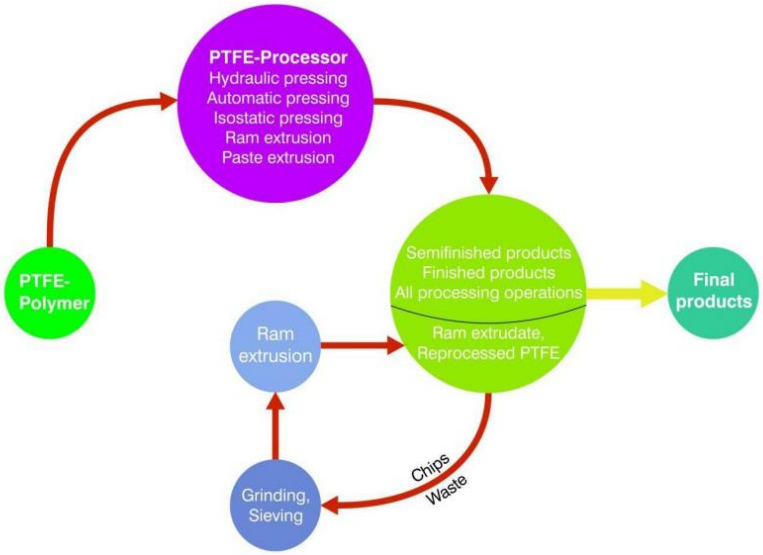


Figure 8: Primary (mechanical) recycling of PTFE (from Coversio)

In contrast to the primary mechanical recycling, the secondary one needs sorting of polymer waste streams, reduction of polymer waste size, followed by processing (extrusion, sintering or others; see Figure 9) (Bruno Améduri, 2022).

If the PTFE polymer runs through the recycling cycle several times this leads to a decrease in the overall polymer quality. To avoid final landfilling or incineration, chemical recycling is a valuable option.

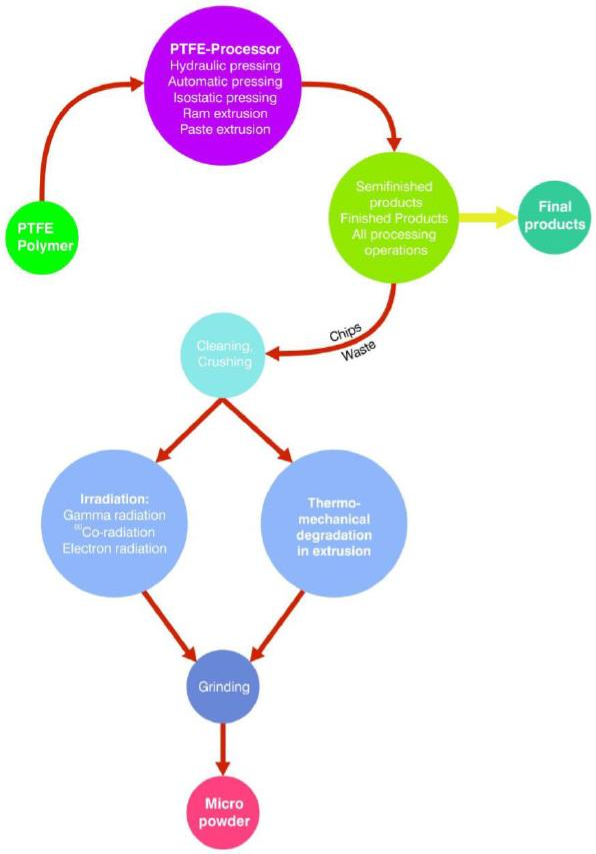


Figure 9: Secondary mechanical recycling of PTFE

5.3.3.2 Chemical recycling of PTFE

Chemical recycling is being operated at a pilot scale currently. PTFE is a valuable product for the recovery of monomers which can be achieved by pyrolysis of per fluoropolymers. As PTFE and other per fluorinated polymers consist solely of C and F, efficient recycling of the material can close the fluorine loop. In addition, it can reduce the consumption the mineral fluorspar, a critical raw material for the EU economy.

Figure 10 gives an overview of the chemical recycling of PTFE:

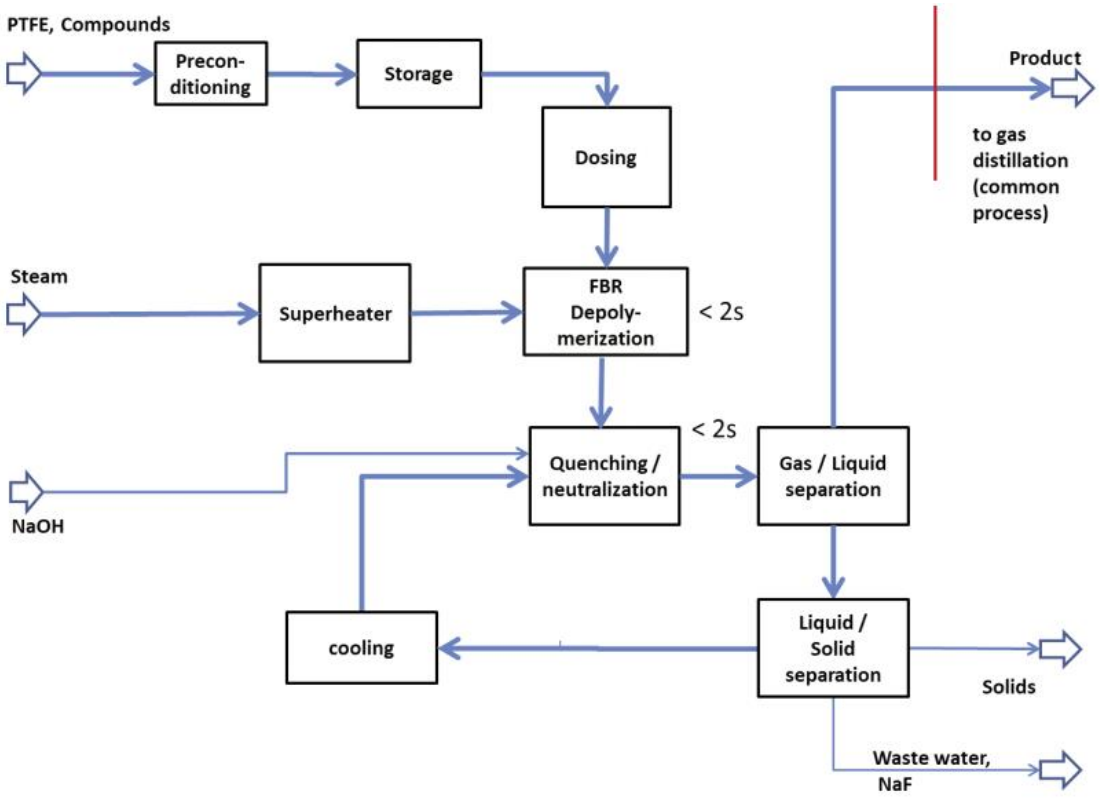


Figure 10: Depolymerization of PTFE (Achim Schmidt-Rodenkirchen, 2022)

5.3.3.3 Potential emissions from PTFE recycling

It can be assumed the same abatement techniques can be or are implemented at recycling sites as at FP/PTFE manufacturing sites. Therefore, it is adequate to assume the same percentage emissions from recycling as for manufacturing, which were deduced to be at 0.02% release to air and 0.01% release to water (REACH Competent Authorities, 2021). The recycling rate of FP is at 3% (Conversio Market & Strategy GmbH, 2022) and it is assumed the same applies to PTFE. With an actual production of 20,000 tons PTFE per year, the annually recycled amount is 600 tons PTFE per year. In the future, the amount of PFAS in 600 tons PTFE is **0.15 kg**, when applying the proposed limit value of 250 ppb for the sum of PFAS in products. Considering abatement at recycling sites with similar release rates as for manufacturing of 0.01% to water and 0.02% to air, the annual release of PFAS related to PTFE recycling in the EU could be further reduced to 15 mg to water and 30 mg to air.

6. Conclusion

PTFE may be manufactured by means of suspension polymerization or emulsion polymerization. The latter uses either fluorinated polymerization aids (FPA) – which are PFAS – or non-fluorinated polymerization aids (NFPA). Historically, the ammonium salts of perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) were the most commonly used FPAs. In recent years, many PTFE producers have transitioned to the use of shorter-chain FPAs, such as per- and polyfluoroalkylether carboxylic acids like HFPO-DA (Gen-X), ADONA and PFHxS. Regulators and environmentalists consider this transition of C8 PFOA by C6 PFAS as a regrettable substitution of one PFAS of concern by another and have started demanding to stop the use of any PFAS as polymerization aid in fluoropolymer manufacturing.

When considering PFAS emissions from the manufacturing of PTFE in the EU, emissions from the intentional use of PFAS in the production process must be distinguished from emissions of unintentional PFAS by-products generated during manufacturing. The main part of PFAS emissions can be attributed to the release of FPA and its degradation products in the emulsion polymerization process. The overall estimated range of current potential releases is between 4.2 and 140 tons FPA per year based on best-case and worst-case estimates, while the estimate based on release factors to water and air from PTFE manufacturing and processing industry (REACH Competent Authorities, 2021) is at 6 tons PFAS per year in total. Furthermore, these FPAs are highly water soluble and may break down to other low temperature volatile PFAS (Bao, et al., 2018) which are difficult to identify and to capture. In addition, it is important to also consider the environmental impact during the whole lifecycle of FPAs. For example, it is not possible to completely clean the packaging materials from the FPAs. Thus, to completely avoid additional releases of FPAs, packaging materials have to be incinerated.

With a full switch of technology to processes using non-fluorinated polymerization aids, environmental emissions can significantly be reduced as the release of FPA will stop completely. Only unintentional PFAS by-products formed during the production process can be potentially released. A significant reduction unintentional of PFAS by-product releases can be achieved by implementation of efficient abatement measures like ion exchange resins, filtration methods, scrubbing, foam fractionation, electrochemical oxidation and GAC followed by high-temperature incineration, and thermal oxidation. Based on release factors from actual production of PTFE with respective abatement technologies from one global production site – which are used as a blue-print in this case study by extrapolating the production conditions from this one producer to all European manufacturers for future FPA-free production of PTFE in the EU – future PFAS releases from manufacturing of PTFE can be projected at 2 kg PFAS per year in the EU based on an annual production a volume of 20,000 tons PTFE.

Related to the substitution of FPAs by NFPAs it should be noted that a NFPA should be chosen which is non-reactive with the monomers involved in the polymerization to reduce the potential of formation of unintentional PFAS by-products. Additionally, the NFPA influences the amount of initiator required in the polymerization reaction which in turn defines the amount of radicals present in the reaction. Higher amounts of radicals result in the formation of shorter polymer chains that are undesirable. Therefore, a NFPA needs to be chosen which is suitable to achieve higher polymer molecular weights, and less amount of low molecular weight fractions which reduce the formation of PFAS by-products.

Considering further steps in the life cycle of PTFE, a high-level estimate of releases from processing of PTFE can be based on the proposed future 250 ppb limit value for the sum of PFAS in products. Maximum 5 kg PFAS can be released during processing of 20,000 tons PTFE in the EU, while PFAS emissions during the use of PTFE are considered negligible based on its stability and inertness as intrinsic substance properties.

At the end-of life (EOL), it is assumed that 84% of PTFE is incinerated, while 13% is landfilled and 3% is recycled. As an example, potential total PFAS emissions from incineration of PTFE in the EU are below 1.85 kg/year. Landfilling – as demonstrated by testing – is not expected to lead to emissions to the environment as PTFE is highly inert and a preferred liner material for landfills. Actual emission values from the recycling of PTFE are not available. The potential PFAS emissions connected to recycling of PTFE with a recycling rate of 3% to 20,000 tons of PTFE per year, the amount of PFAS in PTFE is 0.15 kg. This PFAS amount could further be reduced by implementation of abatement technologies at recycling sites similar to manufacturing sites.

An overview and summary of emissions is given in Table 2.

Table 2: Overview of emissions in the EU from the life cycle of PTFE based on an annual production volume of 20,000 tons

Life-cycle stage		PFAS releases per year
Production:	- Emulsion polymerization with FPA	4,200-140,000 kgs (mostly as FPAs)
	- Emulsion polymerization without FPA **	2 kg (byproducts)
Processing	- Considering 250 ppb threshold in products	max. 5 kg
Use		Negligible
End-of-life:	- Incineration	< 1.85 kg
	- Landfilling	Negligible emissions
	- Future 250 ppb threshold in products, Recycling	≤ 0.15 kg

* Can completely by eliminated when full switch to non-FPA polymerization

** Does not yet take place in the EU, switch to alternative technology is planned by EU manufacturers.

Confidential

7. Bibliography

Achim Schmidt-Rodenkirchen, K. H. (2022). *Chemical Recycling of PTFE (as a Model for Other Polymers).*

Ameduri, B., Sales, J., & Schlipf, M. (2023). Developments in Fluoropolymer Manufacturing Technology to Remove Intentional Use of PFAS as Polymerization Aids. *International Chemcial Regulatory & Law Review (ICRL) (1)*, 18-28.

Ameduri, M. (2019). Polytetrafluoroethylene: Synthesis and Characterization of the Original Extreme Polymer. *Chemical Reviews*, 1763-1805.

Anonymous. (2023). *RAC-64 Plenary meeting presentation. UPFAS Restriction Proposal. (Unplublished report.).*

Atkinson. (1957). The Thermal Decomposition of Tetrafluoroethylene. *Journal of the Chemical Society*, 2086.

Bao, Y., Deng, S., Jiang, X., Qu, Y., He, Y., Liu, L., . . . Yu, G. (2018). Degradation of PFOA Substitute - GenX (HFPO-DA ammonium salt): Oxidation with UV/Persulfate or Reduction with UV/Sulfite? *Environ. Sci. Technol., 52 (20)*, 11728–11734.

Bruno Améduri, H. H. (2022). *Recycling and End of life assessment of Fluoropolymers: Recent Developments, Challenges and Future Trends.* ICGM, University of Montpellier, CNRS, ENSCM, 34095 Montpellier, France. Kanagawa University, Faculty of Science, 2946 Tsuchiya, Hiratsuka 259-1293, Japan.

C.H., L. (1997). Fatal acute pulmonary oedema after inhalation of fumes from polytetrafluoroethylene (PTFE). *Eur Respir J, 6*, 1408-1411.

Conversio Market & Strategy GmbH. (2022). *Fluoropolymer waste in Europe 2020–End of life (EOL) analysis of fluoropolymer applications, products and associated waste streams.*

Dr. Barbara Henry. (2022). *Summary of the PTFE Studies Performed with Independent Laboratories.* W. L. Gore & Associates.

Dr. Gehrmann, H. J., Dr. habil. Bologa, A. (., Dr. Aleksandrov, K. (., Bergdolt, P. (., Dr. Taylor, P. (., Dr. Schlipf, M. (., . . . Kapoor, D. (. (2023). *Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers.* 1: Institute for Technical Chemistry (ITC) at Karlsruhe Institute of Technology (KIT); 2: P Taylor & Associates, LLC, USA; 3: Pro-K, Germany; 4: ICGM, University of Montpellier, France; 5: Gujarat Fluorochemicals .

Dr. Gehrmann, H.-J. (., Herremans, S. (., & Dr. Taylor, P. (. (15. June 2023). Incineration of Fluoropolymers - Project presentation. 1: Karlsruhe Institute of Technology (KIT); 2: SGS Belgium NV; 3: P Taylor & Associates, LLC.

Ebnesajjad, S. (2000). *Fluoroplastics Volume 1: Non-Melt Processible Fluoroplastics The Definitive User's Guide and Databook.*

ECHA - European Chemicals Agency. (22. March 2023). Von https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e18663449b abgerufen

Environmental Protection Agency. (July 1993). Von https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-fifth-edition-volume-i-chapter-8-inorganic-1 abgerufen

Eurofluor. (2023). Von https://www.eurofluor.org/hf-production/ abgerufen

Glüge, J., Scheringer, M., Cousins, I. T., DeWitt, J. C., Goldenman, G., Herzke, D., . . . Wang, Z. (2020). An overview of the Uses of Per- and Polyfluoroalkyl substances (PFAS). *Environ. Sci.: Processes Impacts (22), 22*(12), 2345-2373. doi:https://doi.org/10.1039/D0EM00291G

Gujarat Fluorochemicals Limited. (2023). *Abatement technologies to control PFAS emissions during manufacturing of Fluoropolymers.*

Gujarat Fluorochemicals Limited. (2023). *Incineration study on Fluoropolymers at their End-of-Life.*

Henry, B. J. (2018). A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers. *Integrated Environmental Assessment and Management, 14*, 316-334.

Kewalramani, J. A. (2022). A Review of PFAS Destruction Technologies. *International Journal of Environmental Research and Public Health, 19*, 16397.

Lanxess. (29 October 2021). Reliable and efficient ion exchange resin for PFAS removal.

Lee, e. a. (2022). High-pressure membrane filtration processes for separation of Per- and polyfluoroalkyl substances (PFAS). *Chemical Engineering Journal, Volume 431, Part 2; https://doi.org/10.1016/j.cej.2021.134023*.

Lohman, R., I. T., DeWitt, J. C., Glüge, J., Goldenman, G., Herzke, D., . . . Wang, Z. (2020). Are fluoropolymers really of low concern for human and environmental health and separate from other PFAS? *Environ Sci Technol., 54 (20)*, 12820–12828.

Noort, M. v. (2022). Fluoropolymers: The Safe Science That Society Needs. *International Chemistry Regulatroy and Law Review*, S. 13-23.

Prevedouros, K., Cousins, I. T., Buck, R. C., & Korzeniowski, S. H. (2006). Sources, Fate and Transport of Perfluorocarboxylates. *Environmental Science & Technology, Vol. 40, No. 1*, 32-44.

RAC-64 Plenary Meeting Presentation. (15. March 2023). UPFAS Restriction Proposal.

REACH Competent Authorities. (2021). *2nd Stakeholder Consultation on a Restriction for PFAS. Report summary PFAS and PFAS polymer production.*

Ritter, A. B. (1988). Kinetics of the pyrolysis of chlorodifluoromethane. *Industrial & Engineering Chemistry Research*, 208-211.

S&P Global Commodity Insights. (2022). Von https://www.spglobal.com/commodityinsights/en/ci/products/fluoropolymers-chemical-economics-handbook.html abgerufen

Serio, M. D. (1989). Kinetics of Chloroform Fluorination by HF catalyzed by Antimony Pentachloride. *Journal of Fluorine Chemistry, 44*, 87-111.

Smith, e. a. (2023). Electrochemical Oxidation for Treatment of PFAS in Contaminated Water and Fractionated Foam—A Pilot-Scale Study. *ACS EST Water 2023, 3, 4, 1201–1211; https://doi.org/10.1021/acsestwater.2c00660*.

Sunavala, P. D. (1987). Thermodynamic and Kinetics for the Manufacture of Tetrafluoroethylene by the Pyrolysis of Chlorodifluoromethane. *Industrial & Enginering Chemistry Research , 26*, 1340-1344.

Tippett, J. (2023). Contamination from a leaking geomembrane - A necessary and imminent evil? . *Geosynthetics Magazine*.

Wang, Z. (2020). Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS? *Environmental Science & Technology, 54*, 12820-12828.

Wexler, M. (2019). Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-fluorinated alkyl substances (PFAS) in flue gas. *Chemosphere, 226*, 898-906.

Critical Use of Fluoropolymers in the Functioning of Modern Society

*Jaime Sales, Michael Schlipf and Deepak Kapoor**

In the context of the upcoming restriction of PFAS, there appears to be significant confusion concerning the most relevant sectors where fluoropolymers are used. This paper intends to clarify that fluoropolymers are used mainly in industrial sectors of high value to society. The outstanding combination of properties that fluoropolymers exhibit makes them extremely valuable materials in a wide variety of applications. While there have been some historic uses in consumer applications, these uses are currently anecdotic, particularly for those linked to very dispersive uses (which excludes use in cookware), and represent a minute proportion of the overall uses when compared to industrial applications, where fluoropolymers' outstanding properties are capitalized on. Fluoropolymers contribute decisively to the progress and well-being of society in five key areas: safety & well-being, environment and circularity, decarbonization, performance and comfort, being the latter the only one that can be attributed to dispersive consumer applications.

I. Introduction

For many years, Per- and polyfluoroalkyl substances (PFAS) have been at the centre of the regulatory debate in many jurisdictions. In Europe, this became even more intense in 2020, after 5 Member States of the European Economic Area expressed an intention to file a restriction proposal under the REACH Regulation on all PFAS.[1] Since then, different debates have taken place involving various stakeholders, trying to clarify which specific chemicals would be impacted by the restriction, and to which extent. The definition[2] used by regulators to define the scope of the proposal leads to approximately 10,000 chemicals potentially under the umbrella of this initiative. The fact that PFAS can be categorised in a significant variety of different sub-groups or sub-families requires certain technical knowledge to fully understand such differences and what is more, the different areas of applications of the components of those sub-groups, which can involve completely opposite fields of application.

Fluoropolymers are a differentiated sub-group in the PFAS universe, pertaining to the group of polymeric PFAS. Even in this group, they can be clearly separated from other polymers due to their composition and structures.[3] These differences apply also to the sectors in which the different materials covered by the PFAS definition can be used. For example, while fluoropolymers are used mainly in industrial applications, other fluorinated polymers (e.g., the so-called Side Chain Fluorinated Polymers) see extensive use in dispersive consumer applications, such as textiles, upholstery, leather, apparel and carpets (TULAC).

Due to their highly valuable properties (e.g., non-stick, temperature resistant, and durability) fluoropolymers have also seen some use in applications with potential consumer contact. The most classical

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1 ECHA, 'Five European states call for evidence on broad PFAS restriction' (2020) ECHA/NR/20/13 <https://echa.europa.eu/-/five-european-states-call-for-evidence-on-broad-pfas-restriction> accesed 1 May 2023.

2 OECD, Toward a new comprehensive global database of per- and polyfluoroalkyl substances (PFASs)' (2020) Series on Risk Management No. 39. Organisation for Economic Co-operation and Development.

3 Jaime Sales, Francisco Hernández, Deepak Kapoor, Marcel van den Noort, 'Fluoropolymers: The Safe Science That Society Needs' (2022) 5 International Chemical Regulatory and Law Review 1, 13-23.

one is the use for coating frying pans to grant anti-adherence properties, or in professional or technical clothing.[4] Direct consumer uses of fluoropolymers are possible, such as in cosmetics,[5] ski waxes [6] or as lubricant for chains in bicycles.[7] However, taking into consideration all the possible applications in which fluoropolymers are used, the contribution of dispersive consumer uses is minimal. Nonetheless, it appears that the relevance of those consumer uses in the regulatory discussion has been disproportionately magnified in comparison with the more critical industrial uses, which are frequently ignored or hidden by certain stakeholders.

Under REACH the correct reporting of the uses of a substance is essential to properly assess the risks associated with its use. Besides manufacture and formulation, the so-called 'end uses' need to be reported. According to ECHA Guidance,[8] 'end-use' means the use of a substance as such or in a mixture, as a last step before the end-of-life of the substance, namely before the substance is consumed in a process by reaction during use (including intermediate use), is emitted to waste streams or the environment or is included into an article. The corresponding definitions of the different end-uses following ECHA Guidance are as follows:

- **Use at industrial site**: All end-uses of the substance (as such or in a mixture) carried out at industrial sites should be reported under this life cycle stage.
- **Widespread use by professional workers**: Widespread uses by professional workers correspond to uses carried out in the context of commercial activities and assumed to take place in most towns of a certain size, by multiple actors each at low scale e.g., local garage, small cleaning businesses.
- **Consumer use:** All end-uses of the substance as such or in a mixture carried out by consumers can be reported under the consumer use life cycle stage.

However, if the substance becomes part of an article, the subsequent life cycle stage (the service life) is to be considered additionally, as follows:

- **Service life**: For a given substance incorporated into an article, the service life is considered to be the period of time an article remains in service (or in use). Articles containing the substance can be used or processed by consumers, by workers at industrial sites and/or by professional workers.

Based on these definitions, the use of frying pans coated with fluoropolymers is not a consumer use; instead, the use of those pans has to be evaluated as a service life. In contrary to the use of a frying pan coated with fluoropolymers uses like cosmetics, ski waxes or bicycle chain lubricants are direct consumer end-uses.

II. Reasons Why Fluoropolymers are Used and Benefits They Provide

The properties that fluoropolymers provide are well known and have been discussed previously by different authors[9] and can be summarised as follows:

- Inertness and non-reactivity; high resistance to corrosion and chemical attack.
- Low and high temperature resistance: with a range as large as -263°C to +260°C for Polytetrafluoroethylene (PTFE).
- Very low coefficient of friction to any solid.
- Low and ultra-low permeation rates.
- Ultraviolet radiation (UV) resistance.
- Excellent electrical insulation, low dielectric constant, low variations of conductivity.
- High level of fire safety; no flame propagation and low smoke generation.

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4 Performance Fluoropolymer Partnership, 'Consumer Products' (2023) <https://fluoropolymerpartnership.com/fluoropolymer-applications-and-uses/consumer-products/> accessed 1 May 2023.

5 US FDA, 'Per and Polyfluoroalkyl Substances (PFAS) in Cosmetics' (2022) <https://www.fda.gov/cosmetics/cosmetic-ingredients/and-polyfluoroalkyl-substances-pfas-cosmetics> accessed 1 May 2023.

6 Wood Group, 'Update of market data for the socio-economic analysis (SEA) of the European fluoropolymer industry' (2022) <https://fluoropolymers.plasticseurope.org/application/files/1216/5485/3500/Fluoropolymers_Market_Data_Update_-_Final_report_-_May_2022.pdf> accessed 1 May 2023.

7 Juliane Glüge, Rachel London, Ian T. Cousins, Jamie DeWitt, Gretta Goldenman, Dorte Herzke, Rainer Lohmann, Mark Miller, Carla A. Ng, Sharyle Patton, Xenia Trier, Zhanyun Wang, and Martin Scheringer, 'Information Requirements under the Essential-Use Concept: PFAS Case Studies' (2022) 56 Environ Sci Technol 10, 6232–6242.

8 ECHA, 'Guidance on Information Requirements and Chemical Safety Assessment' (2015) 12.

9 Barbara J Henry, Joseph P Carlin, Jon A Hammerschmidt, Robert C Buck, L William Buxton, Heidelore Fiedler, Jennifer Seed and Oscar Hernandez, 'A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers' (2022) 14 Integrated Environmental Assessment and Management 13, 316–334; Chemservice, 'Analysis of alternatives to fluoropolymers and potential impacts related to substitution in different sectors of use' (2022).

- High and ultra-high purity with extremely low leach out properties.
- Stress-crack and cut-through resistance.
- Flex fatigue properties enabling thermal expansion/contraction in temperature cycles.
- Biocompatibility.
- High Flex life.
- Durability.
- Hydrophobicity; neither water nor water-containing substances wet fluoropolymers, providing excellent repellent properties to many chemicals.
- Non-stick, and consequently non-fouling properties, along with sufficient bonding in certain multilayer applications.

The benefits that the use of fluoropolymers bring to the different applications in which they are used, based on the combination of the properties described above, can be categorised in mainly 5 groups.

1. Safety

Fluoropolymers are materials known for their outstanding chemical resistance. They can resist attack from virtually any chemical, particularly strong acids, bases and other corrosive substances. In parallel, they are also resistant to high and low temperatures, allowing high reliability in a broad temperature range. This grants fluoropolymers their extreme durability. Due to this combination of properties, fluoropolymers are essential materials in, for example:

- **Chemical processing industry**: whenever harsh chemicals or stringent conditions of use are required (e.g., high temperature operations), fluoropolymers are the material of choice. They ensure reliability of systems which, in case of failure, could result in high-risk situations for workers or the environment, due to potential leakage, spills or releases of highly corrosive substances at very high temperature.
- **Aerospace industry**: fluoropolymers are used for insulation of electrical and data transmission cables. These cables can be subject to extreme conditions where ensuring reliability is critical. As an example, it is estimated that around 300 km cables are needed in regular commercial airplanes, reaching close to 500 km in some of the most modern planes. These cables need to perform in variable conditions, such as high temperatures near the engine and low temperatures in areas close to the external part of the fuselage at high altitudes. On top of this, exposure to aggressive oils is to be expected for these cables. Any malfunction of the electrical system will lead to high-risk situations for passengers and crew. Fluoropolymers provide the best performance, particularly due to their excellent dielectric properties that prevent electric arc fires in cables. As an example, the case of the Swissair 111 flight that crashed near Peggy's Cove, Nova Scotia, on the night of 2 September 1998, resulting in the death of 215 passengers and 14 crew members can be highlighted. The conclusion from the accident investigation report[10] concluded that the accident was caused by a fire generated by electric arc effect, most likely via electrical cable associated with the in-flight entertainment network. It was determined that aircraft certification standards for material flammability were inadequate. It is also worth mentioning that fuel systems in aircrafts are based on fluoropolymer lined equipment, as they are stable in a kerosene environment.

The high chemical resistance of fluoropolymers, combined with smooth surfaces and extremely low amount of leachables, brings about enhanced durability and prevents degradation potential during use. This allows these materials to guarantee high purity of process streams that are handled with the aid of fluoropolymer-based products (e.g., pipes, tubes, pumps, valves, joints, gaskets, seals, o-rings). As previously discussed, this is relevant for the chemical processing industry. But high purity is also critical to ensure safety conditions in other areas, for example:

- **Pharmaceuticals**: the production of medicines and vaccines require highly pure streams avoiding contamination that may come from process equipment, due to degradation from wear or to the effect of aggressive chemicals. Failure to grant this property could result in undesired health effects for the general public via contamination. Furthermore, the fact that articles based on fluoropolymers can be cleaned at high temperatures provides an advantage in front of other materials

10 TSBC, 'Transportation Safety Board of Canada. Swissair 111 Investigation Report - Executive Summary' (2003) <https://www.tsb.gc.ca/eng/medias-media/fiches-facts/a98h0003/sum_a98h0003.html> accessed 1 May 2023.

that may be used in the pharma sector such as glass, which has a tendency to break.
- **Food processing**: a wide variety of food processes must be handled via complex equipment. From conveyor belts to tubes transferring liquids (e.g., coffee machines), fluoropolymer-based equipment guarantees high purity of food avoiding contamination with impurities that could otherwise reach humans. Here, fluoropolymers' outstanding non-stick properties due to their very low coefficient of friction play a key role.
- **Water filtration**: fluoropolymers are necessary elements in membranes used in water filtration systems. The use of lower performing products could reduce the ability of those membranes to ensure clean water that may later be consumed by the general population. Water systems are frequently cleaned with chlorine under pressure. While most materials tend to hold on to bacteria and algae, this is not the case of fluoropolymers.
- **Medical implants**: perhaps the most evident proof that fluoropolymers are intrinsically safe is that they are the material of choice for a variety of medical implants, including cardiovascular stents, patches and other products that are introduced in the human body and intended to remain there for a long time. It therefore becomes evident that fluoropolymers play a vital role in safety of humans.

2. Decarbonization

Fluoropolymers are critical materials that enable the EU Green Deal. Without these materials, key technologies that are expected to help Europe to achieve its ambitious energy transition will not be available, or their efficiency will be seriously compromised. Some examples are the following:
- **Lithium-ion batteries**: fluoropolymers are used as electrode binders and separator coatings in these batteries, providing interconnectivity within each electrode. This facilitates electronic and ionic conductivity, increasing the cell manufacturing productivity and the cell safety. Fluoropolymers offer unparalleled cohesive and adhesive properties under high voltage, allowing for closely packed cathode active materials for high density electrodes. With the use of fluoropolymers, different battery components can be packed more closely together, improving the energy efficiency of a single unit, and helping reduce overall size.
- **Proton exchange membranes in green hydrogen**: electrolysers and fuel cell membranes are used in the production of green hydrogen by an electro-chemical reaction. To enable the movement of protons from the anode to the cathode side of the fuel cell, a proton exchange membrane made of fluoropolymers is used due to the efficiency and unique durability, chemical and temperature resistance properties that fluoropolymers offer for this application.
- **Renewable energies**: fluoropolymers improve the efficiency and durability of photovoltaic panels used in solar energy, as well as for wind turbines.
- **Lambda sensors in automotive**: fluoropolymers are used in lambda sensor cables due to their resistance to high temperatures and chemicals, dielectric strength, flexibility, and electrical insulator properties. In vehicles, lambda sensors adjust the fuel amount that is sent to the engine cylinders by optimizing the air and fuel mixture, which in turn will make the engine work properly and reduce carbon monoxide emissions. Lambda sensors allow for this control system via measurement of oxygen in exhaust fumes. This is a critical element in cars and vehicles to control the rate of gas emissions by ensuring that the catalytic converter works in an efficient way. Lambda sensors ensure that the car complies with the European regulations on pollution and carbon emissions, allowing a better control of environmental emissions.
- **Heat pumps, air conditioning and refrigeration systems**: the contribution of the Heating, Ventilation, Air Conditioning and Refrigeration and hot water heating (HVACR) to the Green Deal and to the REPowerEU plan is acknowledged by the European Commission.[11] Fluoropolymers are fundamental parts in equipment and machinery used in this sector, since they ensure reliable performance. HVACR equipment is subject to continued

11 European Commission, 'Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions. A Green Deal Industrial Plan for the Net-Zero Age' (2023); European Commission, 'REPowerEU: A plan to rapidly reduce dependence on Russian fossil fuels and fast forward the green transition' (2022) <https://ec.europa.eu/commission/presscorner/detail/en/ip_22_3131> accessed 1 May 2023.

changes in temperature and pressure as well as potentially harsh chemicals (refrigerants). Efficient HVACR systems need to rely on materials that will not fail on demand and will last a long time without degradation, including sealings to avoid leakages. Efficient refrigeration also plays a role in safety since it is necessary for preservation of food and medicines.

3. Environment and Circularity

The extreme stability of fluoropolymers makes them long lasting in the applications where they are used. Most of those applications involve the use of equipment based on processed fluoropolymers, in the form of pipes, tubes, or other pieces. Fluoropolymers extend the life of the equipment and devices where they are used. This significantly contributes to the objectives of a circular economy by reducing the amount of waste that society needs to handle. Replacing fluoropolymers by other materials that would be less efficient in providing the required properties would result in reduced life span, increased need for maintenance and increased amount of waste. Since most of the inferior alternatives are also plastic or rubber materials, a ban on the use of fluoropolymers would force society to cope with significantly increased amounts of wastes of those materials. Here it is useful to underline that based on recent studies, fluoropolymer waste is estimated to represent only 0.14% of all plastic waste in Europe, and <0.01% total waste (Conversio, 2022)[12]; removing such an insignificant percentage of waste coming from fluoropolymers would dramatically increase the overall quantity of waste that would have to be managed. According to the World Business Council for Sustainable Development (WBCSD, 2023), the definition of a circular economy model must take into account 'long service life' of resources, products, parts and materials, and also keeping them in use. Under this perspective, it is unquestionable that fluoropolymers are key contributors to expanding the life span of products and to avoiding the increase of waste streams to society would eventually need to handle and manage.

12 Conversio, 'Fluoropolymer waste in Europe 2020 – End-of-life (EOL) analysis of fluoropolymer applications, products and associated waste streams' (2022).

The *construction* sector is of particular relevance when evaluating the contribution of fluoropolymers to circularity. Not only do they improve fire safety and energy efficiency of modern buildings, but they also reduce the need for maintenance, replacement and cleaning of structures built with fluoropolymer-based materials. There are a wide variety of modern buildings such as bridges, stadia and domes that have benefited from the use of modern fluoropolymer architectural and construction solutions.

4. Performance

Fluoropolymers are frequently the high-cost solution when top performance is required. Downstream users through their value chains see fluoropolymers as the only material of choice when highly demanding process conditions are required. This is intimately linked to the fact that such value chains usually lead to top of the range end-products in terms of technology or societal progress.

The *semiconductor industry* is a clear example of this. In the production of modern, high-tech microchips, particularly with extremely reduced size (indispensable in the production of modern gadgets such as small mobile phones, laptops or watches), it is absolutely necessary to ensure ultra-pure process stream – going as far as having to ensure absence of impurities to the levels of part per trillion (ppt). Lithographic processes (which are technically extremely complex) involve the use of extremely pure harsh chemicals (acids) which may easily attack process equipment made of other materials, hence liberating residuals of ancillary equipment, which may be passed to the process and ruining the whole production. Fluoropolymers are the only product class that ensure reliable and economic performance in the production of modern semiconductors.

A similar rationale can be established for *electric cables*. As in the case of aircrafts, fluoropolymers are used for insulation of high-volume data transmission cables. Modern technology (e.g., 5G) relies on top performance of the materials involved in the process. Furthermore, data centres involved in the storage and processing of information operate under extremely stringent specifications in terms of fire safety. With their excellent dielectric properties and fire resistance, fluoropolymers are practically the only reliable option to cover the high demands of this industry.

5. Comfort

Certain products that use fluoropolymers and are in direct contact with consumers are marketed for enhanced performance while this seems a disguise for better comfort. Waterproof apparel, cosmetics, ski waxes, bicycle chain lubricants would fall under that category

Frequently there is a thin line separating 'comfort' and 'safety'; for example, heating systems for seats in vehicles are based on fluoropolymer insulated electric cables. It could be argued if this feature is truly necessary for the functioning of society (a question that would likely need to be answered from the perspective that the feature is already available in most cars – hence population would need to face a downgraded in this option); but if the feature is to be maintained, efficient insulation for such cables is necessary in order to avoid fire and to prevent passengers from electrocuting. Similarly, again referring to the automotive industry, fluoropolymers are used for the manufacture of different parts of car equipment, such as door hinges and seat height adjustment bearings. These parts can be regarded as pivot points which are subject to sporadic demand while cars are running, requiring high reliability and very low friction conditions. Not providing an efficient material for this application would take car technology probably different years back and consumers would need to face squeaking and noisy driving experiences, in addition to increased maintenance, reparations and break-downs. While this property may not be necessarily linked to safety, it could be questioned whether European society is ready to accept reduced functionality in these applications which would lead to significantly reduced comfort when driving or traveling by car – or other means of transport.

Where comfort is truly the only reason for use of fluoropolymers (i.e., a 'nice to have' feature), there could be room for debate if society wishes to maintain those uses or not. The most renowned example is the use of fluoropolymers as anti-stick material in frying pans. Again, for this use it could be argued if 'comfort' alone is truly the only reason for use. Frying pans with highly anti-stick coatings allow for reduced use of oil during cooking (linked to a healthier and safer life-style), reduced use of cleaning agents (less chemicals in the environment) and improved durability of the article (helping circularity objectives). Furthermore, uses of frying pans coated with fluoropolymer are safe, because the temperatures required for decomposition of PTFE will not be reached during normal use, and food will burn before such temperatures are reached. In addition to this, in the event that small particles of PTFE may be released due to excessive use, there is no risk for health because such particles will be eliminated by the human body without any possibility of biological interaction, due to its inertness and the fact that they cannot cross biological membranes.[13] Also, those frying pans will eventually end-up in waste plants where they will be treated as metallic waste, therefore under conditions that should not result in environmental concerns. In summary, this use cannot be considered as very dispersive.

In contrast to designed functional or constructive fluoropolymer parts, dispersive uses of fluoropolymers by consumers (e.g., cosmetics, ski waxes, lubricants for bicycle chains), may eventually result in some releases of fluoropolymers to the environment. Again, the key factor is that those polymers are safe due to their nature and not pose a risk to humans or the environment. Still, if the aspiration of society is to not have these materials in the environment, it should be possible to remove such applications from the market without necessarily placing limits to the relevant industrial applications where fluoropolymers are extremely valuable for society, and where they play a significant role in enhancing safety, decarbonization, circularity, innovation and progress. For example, the already existing microplastics restriction under REACH could be a good instrument to force reduction and eventually elimination of such uses.

III. Key Sectors of Application of Fluoropolymers

The true value of fluoropolymers becomes apparent when they are used in industrial applications. Concerns expressed in the PFAS restriction proposal in relation to fluoropolymers are mainly related to low

13 Barbara J Henry, Joseph P Carlin, Jon A Hammerschmidt, Robert C Buck, L William Buxton, Heidelore Fiedler, Jennifer Seed and Oscar Hernandez, 'A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers' (2022) 14 Integrated Environmental Assessment and Management 13, 316–334

Wood, 2021 - Sector of use	Volume 2020 (MT)	Volume %
Transport	15,500	39.2%
Chemical and Power	11,000	27.8%
Electronics	3,500	8.9%
Food and pharmaceutical industry (F&P)	2,000	5.1%
Cookware	2,000	5.1%
Textiles and architecture	1,500	3.8%
Renewable energy	500	1.3%
Medical applications	500	1.3%
Other sectors, not included above	3,000	7.6%
TOTAL	39,500	

volume consumer applications of which the use is dispersive. Such applications are ultimately of very limited interest to the fluoropolymer industry, and claims are already being made that in most of those applications fluoropolymers could be a 'nice to have', but not truly necessary.[14]

Different initiatives on market research related to fluoropolymers have been performed, with the aim to provide volumes used in the different sectors in which these high value products are used.[15] However, it is difficult to get precise data on some of those consumer uses. In some occasions, such information is flagged as confidential.[16] Nevertheless, it is possible to extract valuable information from such market research activities. The following table shows the data that is available from both initiatives.

Differences in the definition of market segments used in various market research reports result in slightly different numbers. Nevertheless, for the purpose of our analysis, the information displayed on volumes clearly reflects that the major share of fluoropolymer uses is in high value, high technological sectors related exclusively to industrial applications. Putting these figures in context, it appears evident that minor consumer applications, such as uses in cosmetics, ski waxes or bicycle chain lubricants are extremely small and therefore of no interest to the fluoropolymer industry, and no significant impact is to be expected if those uses are discontinued.

IV. Conclusions

Fluoropolymers bring high value to society. This is achieved via the combination of extraordinary properties that they offer. Such value is maximised when fluoropolymers are used in industrial applications in high technology sectors. The use of fluoropolymers

14 C&EN, 'How fluoropolymer makers are trying to hold on to their business' (2023) <https://cen.acs.org/materials/polymers/fluoropolymer-makers-trying-hold-business/101/i8?linkId=100000191672537> accessed 1 May 2023.

15 Astute Analytics (2021). Global Fluoropolymers Market. Industry Dynamics, Market Size, and Opportunity Forecast for 2027. April 2021; Wood (2021). PFAS in the treatment of skis — Use, Emissions and Alternatives. Report for Miljødirektoratet/ Norwegian Environment Agency.

16 Wood Group, 'Update of market data for the socio-economic analysis (SEA) of the European fluoropolymer industry' (2022) <https://fluoropolymers.plasticseurope.org/application/files/1216/5485/3500/Fluoropolymers_Market_Data_Update_-_Final_report_-_May_2022.pdf> accessed 1 May 2023.

Astute Analytical, 2021 - Sector of use	Volume 2020 (MT)	Volume %
Industrial equipment: chemical industry	27,700	37.8%
Electronics W&C	9,450	12.9%
Industrial equipment: other	6,500	8.9%
Transport: automotive	5,280	7.2%
Industrial equipment: Semiconductors	4,515	6.2%
Household	3,840	5.2%
Batteries	3,000	4.1%
Construction	3,000	4.1%
Medical & Pharma	2,800	3.8%
Other	2,500	3.4%
Transport: aerospace	2,035	2.8%
Other electronics	1,425	1.9%
Transport: other	1,265	1.7%
TOTAL	73,310	

allows for very high standards related to protection of workers and the general population, efficient development of green energy systems, improved longevity of equipment and articles thus helping the circular economy, and outstanding performance in vital sectors that are critical to ensure Europe's autonomy and technological superiority in comparison to other global economies. In contrast, the value of fluoropolymer in some consumer applications that have been related to potential concerns is very limited and is only related to relative improvement of comfort features.

In addition to this, it should be noted that fluoropolymers have been traditionally the innovative solution of choice by many industries to improve process conditions, either related to safety, development of options to decarbonize the economy or to improve durability of materials. A ban on critical uses of fluoropolymers, or any regulatory initiative that may place barriers to the use of these low risk, high value materials will limit or slow down the speed of innovation in the EU.

Consumer uses, or uses of fluoropolymer-based products by consumers that may be regarded as dispersive (handling of which is understood to be more difficult to control in comparison with activities in an industrial set-up) are of no paramount interest to society, and while fluoropolymers are acknowledged to pose no risk themselves to human health or the environment, limitations to those uses would not result in major negative impact to the European society. Still, the fact that legislation to control such uses is already in place (e.g., via the EU REACH microplastics restriction) suggests that no further action is required, and that eventually those uses will progressively disappear from the European market. If there are societal preferences to limit such uses, a broad restriction of all uses of fluoropolymers via a REACH restriction does not appear to be neither efficient nor justified.

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Glossary

Abbreviation	Explanation
CEFIC	European Chemical Industry Council
DDT	Dichlorodiphenyltrichloroethane
DU	Downstream user
EBIT	Earnings before interest and taxes
EEA	European Economic Area
EU	European Union
FPA	Fluorinated polymerization aid
FPG	Fluoropolymers Product Group
FTE	Full-time equivalent
GDP	Gross domestic product
GFL	Gujarat Fluorochemicals Limited
GVA	Gross value added
ICT	Information and communication technology
JRC	Joint Research Centre
LCI	Labour cost index
NPV	Net present value
OEM	Original equipment manufacturer
OTT	Over-the-top
PBT	Persistent, bioaccumulative and toxic
pro-K	Industrieverband Halbzeuge und Konsumprodukte aus Kunststoff e.V.
vPvB	Very persistent, very bioaccumulative
PAH	Polycyclic aromatic hydrocarbon
PFAS	Per- and polyfluoroalkyl substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PTFE	Polytetrafluoroethylene
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RO	Restriction option

1. Executive summary

In the context of the ongoing EU REACH PFAS public consultation, the current report presents findings of an independent socio-economic impact assessment conducted to assess the costs for the EEA society due to the inclusion of fluoropolymers in the scope of the universal PFAS restriction proposal. To assess the socio-economic implications associated with such an inclusion, impacts occurring at different levels in the supply chain of fluoropolymer-dependent products were monetized wherever feasible. For the analysis, both secondary data available in the literature as well as primary data collected from downstream user surveys were used. The results indicate that an inclusion of fluoropolymers within the scope of the PFAS restriction would generate at least 33.86 – 148.92 million Euros per year (conservative estimation) as costs for the EEA society for a period of 45 years.

In a second stage, these results were used in a proportionality assessment with a focus on PTFE to compare the costs and the benefits with respect to additional emissions avoided for the EEA society following the inclusion of PTFE within the scope of the PFAS restriction. The assessment was conducted for two separate cases to account for the difference in terms of emissions additionally avoided depending on the technology used for the manufacturing of PTFE. For the case in which there would be a transition to a non-FPA polymerization process for the production of PTFE[1], a PFAS restriction covering PTFE would generate annually at least 1.5 – 6.5 million Euros of socio-economic costs per kilogram of additional PFAS emissions avoided.

By comparing this range against previously reported benchmarks and cost-effectiveness ratios of further REACH restrictions, it could be concluded that an inclusion of PTFE in the scope of the PFAS restriction under EU REACH would be disproportionate. While, due to limited data, the scope of the current proportionality assessment was restricted to the case of PTFE, it is expected that similar conclusions regarding proportionality could be reached for other fluoropolymers should their production be achieved through a non-FPA polymerization process.

Notably, the results presented in the current report with respect to socio-economic costs for the EEA society as well as consequently derived cost-effectiveness ratios must be treated as minimum estimates due to data limitations and conservative assumptions. The socio-economic impacts obtained would indeed be much larger if effects of a restriction at the level of OEMs and end customer segments could be monetized. Additionally, the producer surplus losses estimated here in case of a restriction are likely largely underestimated, as the annual foregone profits incurred at the different levels in the supply chain are expected to occur for much longer than the 2-year period considered in the current approach[2]. Furthermore, the cost-effectiveness ratios derived here do not account for the negative effects associated with a potential restriction with respect to an increased consumption of materials and energy as well as a reduced safety and well-being for the EEA society nor do such ratios consider the effect of a broad PFAS restriction on the EU Green Deal, autonomy in semiconductors or the decarbonization strategy in the EU through developments in the hydrogen sector and the electrification of vehicles.

[1] This transition is currently being planned by EU manufacturers.

[2] This expectation is in line with the anticipated limited potential for substituting fluoropolymers in the different applications (see footnote 17).

2. Introduction

Fluoropolymers are fluorocarbon-based polymers with multiple carbon–fluorine bonds that are characterized by high resistance to solvents, acids and bases, high resistance to temperature, non-stick properties, durability, low coefficient of friction, inertness and biocompatibility, to mention only a few. As a result of their unique combination of functional properties, they are used in a wide variety of many industrial and some consumer applications in the European Economic Area (EEA), contributing to an increased lifetime and high performance of products as well as ensured safety conditions for workers and the general population.

The decarbonisation and sustainability activities in the European region along with the safety and well-being of its population are some of the factors accelerating the growth of the European fluoropolymers market. Additionally, the increase in investments in electrical vehicles, chips manufacturing and hydrogen fuel cell technologies are expected to create profitable opportunities for the fluoropolymer market growth in the long run (Market Research Community, 2023).

Gujarat Fluorochemicals Limited (GFL) is an Indian chemicals company with over 30 years of experience in fluorine chemistry that holds domain expertise in manufacturing fluoropolymers, fluorospecialities, refrigerants and chemicals. As an independent consulting company, Ramboll was commissioned by GFL to prepare a socio-economic analysis concerning the consequences of a potential PFAS restriction covering fluoropolymers on the EEA society (1) and to evaluate the proportionality of including fluoropolymers in the scope of the PFAS restriction (2). Due to time limitations on the submission of data during ECHA's Public Consultation, data availability and in order to maintain a conservative approach, the proportionality assessment could only be conducted as a case study for one fluoropolymer, namely polytetrafluoroethylene (PTFE), in the form of a cost-effectiveness analysis.

3. Baseline scenario

This chapter introduces the baseline scenario in which fluoropolymers are used for the manufacturing of different products in the EEA and provides a basis for the current impact assessment by depicting the relevant supply chain as well as market and financial considerations.

3.1 The supply chain of fluoropolymer-dependent products

The supply chain of fluoropolymers and related products is complex, involving a variety of stakeholders and applications. At the first level in the supply chain there are companies which manufacture fluoropolymers in their basic resin forms such as powders, pellets and dispersions. At the next level there are fluoropolymer processors that receive fluoropolymer resins from manufacturers and further process these resins into basic forms and shapes (also called semi-finished articles). These companies further supply downstream to component manufacturers that require the semi-finished shapes for the production of different articles which are further supplied to Original Equipment Manufacturers (OEMs) as components used in a variety of applications (see Figure 1).

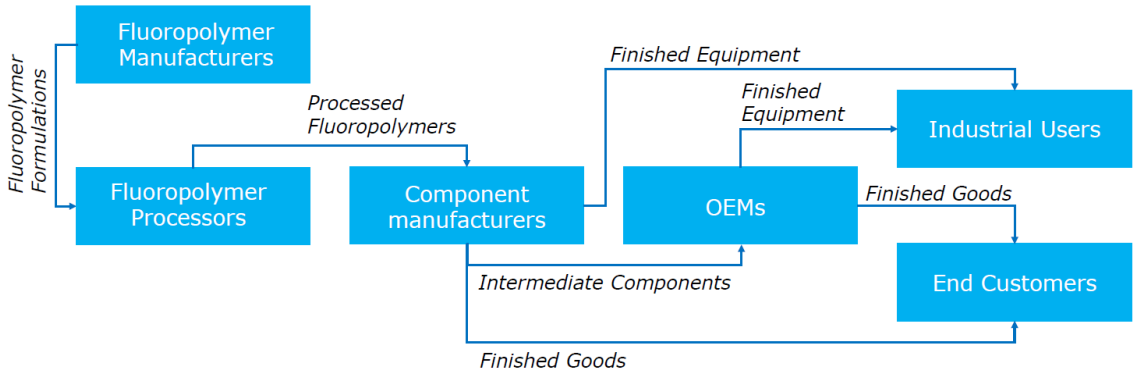


Figure 1: Simplified overview of the supply chain concerning fluoropolymers and related products.

Notably, the flows depicted in Figure 1 only correspond to a simplified general overview of the supply chain of fluoropolymers and related products. In reality, depending on the application for which fluoropolymers are required, additional downstream actors may be involved at different stages of product or equipment manufacturing. Additionally, depending on the level of integration within the supply chain of any given application, the functions of fluoropolymer processors and component manufacturers may be fulfilled by the same companies.

Table 1 presents a non-exhaustive list of fluoropolymer dependent products that in relation to Figure 1 can be categorized into intermediate components, finished equipment and finished goods. From the examples listed it becomes evident that fluoropolymers are used in a variety of industries and sectors, including among others transport (e.g. automotive, aerospace), chemical processing, energy, telecommunication, construction and medical sectors.

Table 1: Non-exhaustive list of examples of intermediate components, finished equipment and finished goods containing fluoropolymers (CHEMSERVICE, 2022).

Product category	**Non-exhaustive examples**
Intermediate Components	• Seals and gaskets for industrial machines • Sealing systems for compressors for air conditioning equipment • Lithium-ion batteries • Electrical cabling for aircrafts • Lambda sensors for automotives • Control cable liners for automotives and aircrafts • Auxiliary components for automotives • Pipe fittings and manifolds for plumbing systems
Finished Equipment	• Lined equipment for the chemical processing industry • Production systems used for food processing • Membranes for electrochemical processes • Membranes for water treatment • Filter systems for waste treatment • Proton exchange membranes for hydrogen production • Sealing systems for storage, transport, and production of green hydrogen • Pipes and tubes for the semiconductor industry • Equipment for vaccine preparation
Finished Goods	• Implants for medical applications • Cookware • Air conditioning equipment • Aircrafts • Automotives

3.2 Market and financial considerations

In the previous section key actors and applications within the supply chain of fluoropolymers and related products have been identified (Figure 1, Table 1). The focus of the current chapter is to present a market overview of the different stakeholders and industries dependent on the use of fluoropolymers in a business-as-usual scenario. In this sense, revenue data and employment figures

registered in the EEA are described where available for producers and downstream users of fluoropolymers as well as industry sectors relying on fluoropolymer-containing products.

3.2.1 Producers of fluoropolymers

At the first stage in the supply chain depicted in Figure 1 there are companies manufacturing fluoropolymers and selling the fluoropolymer resins to downstream processors. Overall, a value of about one billion Euros has been registered in 2020 for the sales of fluoropolymers produced in the EEA, accounting for exports to non-EEA countries (Table 2) (Wood Group UK Limited, 2022).

Assuming that the market of fluoropolymers experienced a contraction in 2020 due to the COVID-19 pandemic, this value may be an underestimation of the actual annual sales value of fluoropolymers produced in the EEA. In the medium to long term, this annual value is further expected to increase due to higher demand for fluoropolymers in sectors impacted by global trends such as the energy transition and digitalisation (Wood Group UK Limited, 2022).

Concerning employment figures, it has been reported that producers of fluoropolymers collectively employ over forty-three thousand people in the EEA (2020 estimate). About 10% of these jobs are directly associated with manufacturing processes producing fluoropolymers (Table 2) (Wood Group UK Limited, 2022).

Notably, the secondary data reported in this section and summarized in Table 2 is based on a survey conducted with members of the Fluoropolymers Product Group (FPG) within PlasticsEurope and is thus considered to cover a high share of the EEA fluoropolymer market (Wood Group UK Limited, 2022).

Table 2: Sales and employment figures in the EEA reported for fluoropolymer producers of the FPG group (Wood Group UK Limited, 2022).

Market indicator	Value
Sales value for fluoropolymers produced in the EEA, including exports to non-EEA [in million Euros per year]	1,030
Total number of employees in the EEA in FPG member companies	43,800
Number of employees directly associated with fluoropolymer production in the EEA in FPG member companies	4,500

3.2.2 Downstream users of fluoropolymers

Downstream from fluoropolymer producers in the supply chain there are the fluoropolymer processors and component manufacturers (see section 3.1, Figure 1). Based on survey data collected from fluoropolymer downstream users in the EEA (see Appendix section 12.1), the current section aims at providing a market overview of these downstream users with respect to financial, employment and customer information.

The data shown in this section is representative for 51 DUs[3] corresponding to 56 legal entities[4] located in different EEA countries, the majority of which are located in Germany (50.0%) and Italy

[3] This corresponds to roughly only a quarter of the downstream users originally targeted by the DU survey.

[4] In the DU survey the respondents were requested to provide all information per legal entity represented. Out of the 51 DUs, there was one DU only which indicated having provided aggregated data corresponding to 6 legal entities in the EEA.

(21.4%). With respect to size[5], the 51 DUs can be classified into small companies (3.9%), medium enterprises (72.5%) and large companies[6] (23.5%). No microenterprises answered the DU survey.

Overall, the responding fluoropolymer downstream users collectively gain total sales revenues between 1.58 and 1.97 billion Euros[7] on a yearly basis for their share of production activities in the EEA. Notably, a share between 59.0% and 63.6% of these total sales revenues directly depends on the use of fluoropolymers at downstream users' sites. In terms of earnings before interest and taxes (EBIT), the respondents collectively obtain between 197.15 and 382.15 million Euros[7] per year for their share of production activities carried out in the EEA, including the use of fluoropolymers. With respect to employment of the 51 survey respondents, a total between 10,450 and 12,620 full-time equivalents (FTEs)[7] are collectively employed at the downstream users' sites in the EEA (Table 3).

Notably, the participants in the downstream user survey reported to be acting to different extents as both fluoropolymer processors as well as component manufacturers in the EEA. Roughly 56.44% of the DUs' fluoropolymer-dependent annual sales revenues can in fact be attributed to activities constituting fluoropolymer processing, while 43.56% corresponds to activities consisting of component manufacturing.

Table 3: Sales and employment figures collectively representative for fluoropolymer downstream users (fluoropolymer processors and component manufacturers) in the EEA (based on survey data, see section 12.1).

Market indicator	Value
Aggregated sales revenues for fluoropolymer downstream users [in billion Euros per year] (based on survey data from 51 DUs)	1.58 - 1.97
Aggregated EBIT for fluoropolymer downstream users [in million Euros per year] (based on survey data from 51 DUs)	197.15 - 382.15
Aggregated number of full-time equivalents employed by fluoropolymer downstream users (based on survey data from 51 DUs)	10,450 - 12,620

A volume of about 16,654 tonnes of fluoropolymers is purchased by the 51 DUs on an annual basis from their suppliers for processing activities only[8]. Based on the overall annual volume of fluoropolymers reported to be processed in the EEA (51,000[9] tonnes per year), it can be derived that the results obtained in the DU survey only account for a share of 32.7% of the fluoropolymer processing activities in the EEA.

Figure 2 presents an overview of the main customer sectors in the EEA that are supplied by the downstream user respondents. Based on the data received in the downstream user survey, different sectors contribute to various extents towards the aggregated total yearly sales revenues registered by fluoropolymer downstream users in the EEA, the highest shares corresponding to the automotive industry (23.2%), consumer sector (13.2%), chemical processing sector (12.2%), construction sector (12.2%) and electrical and electronics industry (9.6%). Notably, as already mentioned in the introduction of the current report (see section 2), fluoropolymers are used in many industrial as well as in some consumer applications. With respect to the current survey results, the relatively

[5] The classification by size was conducted based on the total annual sales revenues and total number of full-time equivalents (FTEs) reported by the DUs in accordance with a guideline endorsed by ECHA (https://echa.europa.eu/support/small-and-medium-sized-enterprises-smes/how-to-determine-the-company-size-category/step-5).

[6] The one DU which provided aggregated data for 6 legal entities was classified as large.

[7] The lower and the upper bounds were obtained by aggregating the ranges applicable to the respondents (see section 12.1)

[8] To compute this amount, it was assumed that the entire tonnage of fluoropolymers received from suppliers by companies acting at least to some extent as fluoropolymer processors is used for processing activities.

[9] This value corresponds to a realistic annual tonnage estimate of fluoropolymers manufactured/processes in the EEA in 2015 based on a literature review. The value is slightly lower compared to the volume of 52,000 tonnes of fluoropolymers sold in Europe in 2015 (Plastics Europe, 2018).

high share attributable to the consumer sector could be explained by the high sensitivity in the food sector towards the PFAS restriction and therefore the resulting higher response rate.

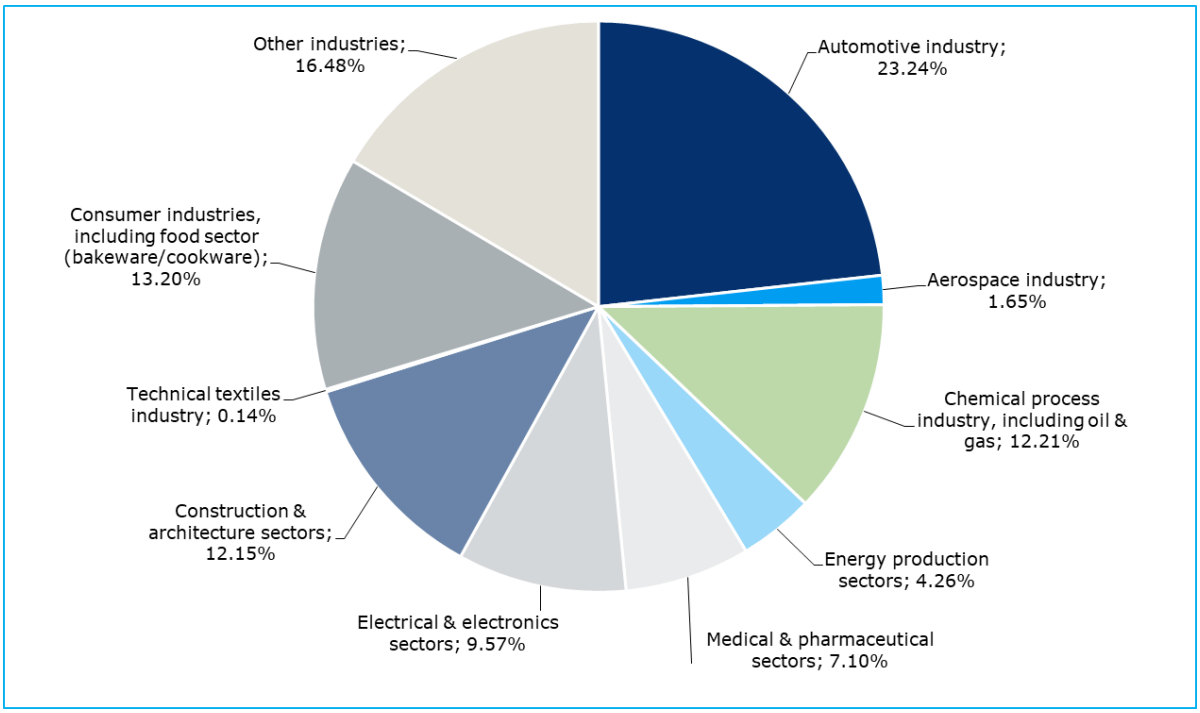


Figure 2: Overview of the main customer sectors in the EEA that rely on deliveries from the responding DUs (fluoropolymer processors and component manufacturers) and their associated contributions (%) towards the yearly total revenues of fluoropolymer downstream users (based on survey data, see section 12.1).[10]

Please note that, as previously mentioned, the aggregated data presented above is representative for the fluoropolymer processors and component manufacturers which answered the survey only. In this sense, the financial and employment figures shown do not capture OEM data.

3.2.3 Industry sectors relying on fluoropolymer-containing products

As highlighted in chapter 3.1, fluoropolymers are critical components imparting high performance in a variety of products used in many industry sectors. The most important sectors relying on products containing fluoropolymers are in this context highlighted in the current section.

3.2.3.1 Transport-related sectors/industries (automotive, aerospace, etc.)

The automotive industry sector provides direct and indirect jobs to 13.8 million Europeans, which means 7% of the total employment in the European Union (EU). Manufacturing accounts for 3.5 million jobs, of which 2.6 million people are employed directly in manufacturing of motor vehicles, 4.5 million are employed in sales and maintenance, and 5.1 million in transport. The turnover generated by the automotive industry represents over 7% of the gross domestic product (GDP) in the EU. Additionally, the automotive industry has a significant multiplier effect in the economy, both for upstream industries such as steel, chemicals, and textiles, and for downstream industries such as information and communications technology (ICT), repair, and mobility services. The automotive sector is the largest private investor in research and development, which is to a significant extent

[10] Under other customer industries, the following terms were mentioned among others by the DUs in the survey: general industry applications, food & beverages sector, analytical lab applications, sanitary sector, marine & hydraulic applications, mining and defence sectors.

funded by the European Commission (European Commission, 2023). In 2022, the market revenue of fluoropolymers in this sector amounted to about 100 million Euros (Market Research Community, 2023).

The aerospace industry sector supported 3.6 million jobs across Europe in 2021, with one direct job in the sector creating 2.8 additional (indirect and induced) jobs in the wider economy. Direct employees in this industry tend to be highly skilled and well compensated. Their average income in 2021 is with 56,000 Euros higher by 43% than the average European wage level. In 2021 this sector contributed with over 240 billion Euros to the European GDP. Total turnover supported by this sector was 578 billion Euros, with one Euro direct turnover generating further 1.40 Euros indirect and induced turnover. Thus, the aerospace and defence industry has a significant economic and strategic importance for Europe (ASD, 2022). The market revenue of fluoropolymers in the aerospace industry amounted to about 60 million Euros in 2022 (Market Research Community, 2023).

3.2.3.2 Chemical industry

The chemical industry sector provides 1.2 million direct highly skilled jobs with a labour productivity higher by 77% than the manufacturing average, creates about 3.6 million indirect jobs and supports around 19 million jobs across all supply chains. The sector represents around 7.5% of EU manufacturing by turnover, its sales amount to 565 billion Euros (2018), which is 17% of global chemicals sales, and generates a trade surplus of 45 billion Euros (2018). The chemical industry is a very innovative sector undergoing a rapid structural change, which is also due to challenges such as increased competition from other countries and a high level of regulations. The high energy intensity of the sector leads to a pressure due to rising energy and feedstock prices and the need for innovation and increase of resource efficiency. The European Commission fosters competitiveness and structural change in this sector and has launched the chemicals strategy for sustainability in 2020 (European Commission, 2023). With a market revenue of fluoropolymers in the chemical industry having amounted to about 270 million Euros in 2022, the chemical industry is the single industrial sector with the highest input of fluoropolymers in Europe (Market Research Community, 2023).

3.2.3.3 Energy and power industry

In the EU, the number of total jobs in renewable energy reached over 1.5 million in 2018. The largest of these sectors are solid biomass and wind, accounting for nearly half of the total EU renewable energy renewable energy sources (Czako, 2020). This study of the Joint Research Centre (JRC) further estimated that the transition to a low-carbon economy will be positive for the EU as a whole, both in terms of GDP and employment growth. Conventional energy industries (fossil fuel extraction, processing and generation), however, will be affected by job losses locally (Czako, 2020).

The energy industry sector is faced with an unprecedented increase in demand for strategic and critical materials. For the target to decarbonise the energy system, security and autonomy in this strategic sector has to be ensured, in view of the heavy dependency of the EU on many critical raw materials. Renewable energy technologies are far more material-intensive than conventional ones, and demand for these materials is projected to increase multiple times. Therefore, securing and increasing their supply becomes a strategic issue. This in particular pertains to hydrogen technologies where fluoropolymers are needed as precursors (Carrara, 2023). The market revenue of fluoropolymers in the energy and power industry amounted to about 47 million Euros in 2022 in Europe (Market Research Community, 2023).

3.2.3.4 Telecommunications industry

The telecommunications market segment in the EU can be sectioned into telecommunications equipment and services. The telecommunications industry is characterized by intense competition, e.g., by mobile operators with network infrastructure of their own, and internet companies with over-the-top (OTT) communication services. The rapid technological transformation in the telecommunications sector requires high investments to build next-generation network infrastructure. Telecommunications networks are continually being upgraded with optical fiber. Established telecommunications companies invest a substantial portion of their revenues in building network infrastructure and acquiring spectrum (Deutsche Telekom, 2020). In the telecommunications industry a market revenue of fluoropolymers of 27 million Euros was achieved in 2022 (Market Research Community, 2023).

4. Impact assessment scenarios

The current chapter introduces different hypothetical impact assessment scenarios, thus serving as a basis for the entire analysis conducted in this report. According to current expectations, a potential PFAS restriction is assumed to enter into force between 2025 and 2027, with an 18-month transition period being granted. In this sense, two restriction options (ROs) have been proposed (ECHA, 2023):

- RO1: A full ban with no derogations and a transition period of 18 months
- RO2: A full ban with use-specific time-limited derogations (18 month-transition period plus either a 5- or a 12-year derogation period)

Depending on whether and which derogations for fluoropolymer uses would be foreseen within the restriction text, there would be different socio-economic costs for the EEA society. To project such impacts associated with a potential PFAS restriction covering fluoropolymers in the EEA, the following hypothetical impact assessment scenarios are defined and evaluated:

- Scenario 1: Restriction and no derogations for fluoropolymer uses
- Scenario 2: Restriction and derogations for 25% of fluoropolymer uses
- Scenario 3: Restriction and derogations for 75% of fluoropolymer uses

Notably, the three hypothetical impact assessment scenarios formulated above are based on the restriction options discussed in the restriction proposal but should not be confused with the latter. Scenario 1 can be considered as an adaptation of RO1, while Scenarios 2 and 3 attempt to model the consequences within the EEA in case RO2 would be adopted.

Under a restriction with no use-specific derogations for fluoropolymers (Scenario 1), all activities within the EEA constituting production and downstream use of these substances would have to cease. This would directly imply losses associated with all such activities for all producers and downstream users of fluoropolymers in the EEA, while indirectly dependent industry sectors (see section 3.2.3) and ultimately the EEA society would be affected as well due to disruptions in existing critical technologies and significant impacts on innovation and new technology development.

Considering a different case in which time-bound derogations would apply for 25% of fluoropolymer uses (Scenario 2), socio-economic losses would be registered for those fluoropolymer manufacturing as well as downstream activities that directly depend on the remaining 75% of fluoropolymer uses, at least short-term. Medium- to long-term, after the use-specific derogations

have expired, additional losses may be incurred by the EEA society, depending on the degree of fluoropolymer substitution in such downstream uses.

In a scenario in which derogations would be granted for 75% of fluoropolymer uses (Scenario 3), losses would accrue for those fluoropolymer manufacturing as well as downstream activities that directly depend on the remaining 25% of fluoropolymer uses (short-term).

Notably, both defined impact assessment scenarios 2 and 3 implicitly assume that under RO2 the use-specific derogations would allow for the manufacturing of the fluoropolymers in the EEA that are required for the respective downstream uses. While making such an assumption results in an additional uncertainty for the current analysis, it nevertheless contributes to a conservative approach as it leads to an underestimation of the socio-economic impacts monetized for scenarios 2 and 3.

5. Socio-economic impacts associated with a restriction of fluoropolymers

Taking as basis the different hypothetical impact assessment scenarios presented in section 4, the current chapter aims at projecting in quantitative terms the socio-economic costs for the EEA society associated with a potential PFAS restriction covering fluoropolymers. Given that the restriction is expected to enter into force earliest in 2025[11] and considering an 18-month transition period, for simplification, the impacts are assumed to start occurring in 2027. For the entire analysis, 2025 is taken as a base year while a 45-year impact assessment period[12] (between 2025 and 2070) is considered. To monetize impacts, a social discount rate of 4% was consistently used throughout the assessment when deriving the net present value (NPV) or the annualized value for any given amount, in accordance with the latest guideline from ECHA on socio-economic analysis (ECHA, 2011).

The ECHA guidance on evaluating socio-economic impacts for restrictions defines compliance costs as the direct costs associated with the adoption of a particular measure (ECHA, 2008). The following sections will present the socio-economic impacts of a potential PFAS restriction covering fluoropolymers on the EEA society. Specifically, impacts occurring at the level of the following stakeholders in the supply chain will be discussed and monetized wherever feasible for each of the impact assessment scenarios described in section 4:

- Fluoropolymer producers
- Fluoropolymer downstream users (fluoropolymer processors and component manufacturers)
- OEMs and customer industry sectors

5.1 Impacts on producers of fluoropolymers

As previously introduced in section 5, a potential PFAS restriction covering fluoropolymers would directly impact producers manufacturing these substances in the EEA. In case of a restriction with no use-specific derogations for fluoropolymers (Scenario 1), such producers would have no option but shutting down all fluoropolymer manufacturing activities in the EEA. In case that use-specific

[11] Based on current estimations, a potential PFAS restriction is expected to enter into force between 2025 and 2027. For simplicity, the current assessment assumes an entry into force in 2025.

[12] An impact assessment period of 45 years (for the upper bound) was as well considered in the PFAS restriction proposal (ECHA, 2023)

derogations for fluoropolymers would be applicable (Scenarios 2 and 3), a partial shutdown of fluoropolymer production activities is expected. In Scenario 3, the cost of manufacturing fluoropolymers will overall become high, whereas in case of Scenario 2 the economic feasibility of producing fluoropolymers will become extremely low. In all cases, the cessation of fluoropolymer manufacturing activities would consequently result in losses of producer surplus and jobs for the EEA society.

5.1.1 Producer surplus losses

To evaluate the producer surplus losses resulting from the shutdown of fluoropolymer production activities in the EEA in case of a potential restriction, this section assesses the corresponding foregone profits that would be incurred by fluoropolymer manufacturers in the different impact assessment scenarios identified in chapter 4.

Methodology

According to a guideline published by ECHA on evaluating losses in producer surplus, these foregone profits are the result of premature retirement of productive capital assets and represent losses to the EU society (ECHA, 2021 a.). Based on this methodology, the foregone profits can be accounted for as producer surplus losses for the remaining service lifetime of capital assets at the point of decision making. The remaining service lifetime is based on the period of time needed by competitors to take over the respective market share dependent on the substance use (ECHA, 2021 a.).

Consequently, the following assumptions were made to monetize these producer surplus losses within the EEA due to foregone profits:

- To maintain a conservative approach and in line with the above-mentioned guideline (ECHA, 2021 a.), foregone profits were considered to accrue over a period of 2 years only[13].
- The valuation of producer surplus losses uses EBIT as a proxy. EBIT losses have been considered to start occurring in 2027.

In order to obtain an estimate for the EBIT losses accrued by manufacturers of fluoropolymers in case of a potential restriction, the 2020 sales value for fluoropolymers produced in the EEA reported in section 3.2.1 (Table 2) was used as a starting point for estimating an average gross profit. According to data published by the European Chemical Industry Council, in the chemical industry the gross operating surplus accounts for 11% of turnover (Cefic, 2020). It is assumed that a margin of at least 11% also applies to the production of fluoropolymers in the EEA, and that gross operating surplus can be taken as a proxy for EBIT. It should be noted however that fluoropolymers are high-margin, low-volume and high-performance products and that in reality the applicable turnover margin is likely higher than 11%, which leads to the foregone profits computed in this chapter to remain rather underestimated.

Notably, expected future trends assume positive growth rates for the yearly sales value registered by fluoropolymer manufacturers (Wood Group UK Limited, 2022). The growth is expected to be exceptionally high because fluoropolymers are expected to play a very critical role in sunrise sectors such as the green hydrogen and fuel cell technology, the electrification of vehicles and the chip manufacturing. In order to remain conservative however, such future growth rates are not considered for the current evaluation of producer surplus losses. Therefore, for the present analysis,

[13] Notably, this 2-year period is considered a minimum timeline as in reality, under a REACH PFAS restriction, competitors are expected to require a much longer period of time until they can take over the market shares of fluoropolymer manufacturers due to the limited feasibility to substitute fluoropolymers in the respective applications.

constant annual turnovers as well as a constant share of gross operating surplus have been assumed up to the years 2027 and 2028.

For modelling the consequences with respect to producer surplus losses in the different impact assessment scenarios formulated in section 4, the additional assumptions have been made:

- In case of a restriction with no use-specific derogations for fluoropolymers (Scenario 1), 100% of the registered annual sales value for fluoropolymers produced in the EEA would be lost.
- In case derogations for 25% of fluoropolymer uses would be applicable (Scenario 2), 75% of the losses registered in Scenario 1 would be incurred.
- In case derogations for 75% of fluoropolymer uses would be applicable (Scenario 3), 25% of the losses incurred in Scenario 1 would be registered only.

Results

Based on the methodology explained above, a potential PFAS restriction covering fluoropolymers would generate between 49.39 million Euros (Scenario 3) and 197.57 million Euros (Scenario 1) in terms of foregone profits in the EEA for fluoropolymer manufacturers (NPV 2025). This is equivalent to an annualized amount between 2.38 million Euros per year (Scenario 3) and 9.54 million Euros per year (Scenario 1) in terms of losses for the EEA society over an impact assessment period of 45 years (Table 4). Notably, these losses are likely largely underestimated due to the methodology used. In reality, the foregone profits experienced by all fluoropolymer producers in the EEA (estimated at 28.33 – 113.30 million Euros per year as shown in Table 4) are likely to be incurred for much longer than the 2-year period considered in the current approach. This is due to the expected low feasibility for substituting fluoropolymers with other substances in the individual applications and the consequent reduced likelihood for the market shares of fluoropolymer producers to be overtaken in the short- to medium-term by competitors (see footnote 13). Notably, it is widely accepted that fluoropolymers are generally irreplaceable. Any alternatives, if available, would result in severe trade-offs in terms of reduced safety, performance and lifetime associated with the respective applications. The irreplaceability of fluoropolymers over a wide range of applications in main industry segments has been explained in an analysis of alternatives conducted by Chemservice in 2022 (CHEMSERVICE, 2022).

Table 4: Estimated producer surplus losses in the EEA due to forgone profits at manufacturers of fluoropolymers in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Foregone profits per year at all manufacturers of fluoropolymers in the years 2027 and 2028	113.30	84.98	28.33
Net present value in the base year (NPV 2025)	197.57	148.18	49.39
Annualized amount over a period of 45 years	9.54	7.15	2.38

5.1.2 Job losses

This section evaluates the impact on employment resulting from the shutdown of fluoropolymer manufacturing activities in the EEA following a potential restriction. In this sense, job losses at directly impacted fluoropolymer producers will be quantified and monetized to capture the associated social cost of unemployment for the EEA society for each of the considered impact assessment scenarios defined in section 4.

Methodology

According to a valuation paper commissioned by ECHA (Dubourg, 2016), the social cost of unemployment associated with job losses can be evaluated based on the following components:

- The value of lost output/wages during the period of unemployment
- The cost of acquiring a new job
- Recruitment costs
- Scarring costs (i.e., the impact of being made unemployed on future earnings and employment possibilities)
- The value of leisure time during the period of unemployment

The latter component is defined as a negative cost (i.e., a benefit) of unemployment. As such, it is subtracted from the total cost resulting from the first four components.

For the current assessment, the figures from the aforementioned paper have been updated with recent data representative for 27 EU countries, by using 2021 estimates for wages (Rogers & Marques, 2021) and Eurostat 2021 data on the duration of unemployment (Eurostat, 2022 a.). The figures for average wages were projected to the year 2027 when they are assumed to accrue by using an average Labour Cost Index (LCI) of 2.425% based on the LCI values registered between 2016 and 2021 and provided by Eurostat (Eurostat, 2022 b.). Notably, although estimations for wages are already available for 2022, for consistency with the data on unemployment duration, 2021 data has been used.

This approach leads to a value of the costs associated with losing one job of 90,746 Euros (in 2027), which is comparable to the population-weighted average for EU-27 reported in the aforementioned valuation paper (Dubourg, 2016). To obtain the total social cost of unemployment resulting from the shutdown of fluoropolymer manufacturing activities in the EEA, this value was multiplied by the number of full-time equivalents associated with the respective production activities that would be dismissed in case of a restriction. Notably, all job losses were assumed to accrue in 2027 in case of a potential restriction. In line with the market data presented in section 3.2.1 (Table 2), it was assumed that a total of about 4,500 full-time equivalents (FTEs) are directly involved in fluoropolymer manufacturing activities in the EEA.

For modelling the social cost of unemployment in the different impact assessment scenarios formulated in section 4, the additional assumptions have been made:

- In case of a restriction with no use-specific derogations for fluoropolymers (Scenario 1), 100% of the full-time equivalents directly associated with fluoropolymer production activities in the EEA would have to be dismissed.
- In case derogations for 25% of fluoropolymer uses would be applicable (Scenario 2), 75% of the job losses registered in Scenario 1 would be incurred.
- In case derogations for 75% of fluoropolymer uses would be applicable (Scenario 3), 25% of the job losses incurred in Scenario 1 would be registered only.

Results

Given an estimated number of job losses between 1,125 (Scenario 3) and 4,500 (Scenario 1), based on the methodology above, a potential PFAS restriction covering fluoropolymers would lead to a total social cost of unemployment between 98.16 million Euros (Scenario 3) and 392.65 million Euros (Scenario 1) (NPV 2025). This is equivalent to an annualized amount between 4.74 million

Euros per year (Scenario 3) and 18.95 million Euros per year (Scenario 1) in terms of costs for the EEA society over an impact assessment period of 45 years (Table 5).

Table 5: The social cost of unemployment for the EEA society due to job losses at manufacturers of fluoropolymers in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
The social cost of unemployment for one job lost - net present value in the base year (in 2027)	0.10	0.10	0.10
The social cost of unemployment for all jobs lost - net present value in the base year (NPV 2025)	392.65	294.49	98.16
Annualized amount over a period of 45 years	18.95	14.21	4.74

5.2 Impacts on downstream users of fluoropolymers[14]

As previously emphasized in chapter 4, a potential PFAS restriction covering fluoropolymers would have different impacts on the downstream users of these substances in the EEA (fluoropolymer processors and component manufacturers), depending on whether and which derogations would be granted. By using survey data collected from such fluoropolymer downstream users (see Appendix section 12.1), the current section evaluates the impacts applicable in each of the hypothetical impact assessment scenarios identified in chapter 4 with respect to producer surplus, job losses as well as additional one-off costs and operating costs. Notably, before the analysis step, the data collected through the DU survey was cleaned in accordance with the procedure outlined in section 12.2.

5.2.1 Producer surplus losses

In case of a potential PFAS restriction covering fluoropolymers, the EEA downstream users requiring these substances for their processing/component manufacturing activities are expected to experience foregone profits due to reduced sales. These foregone profits would vary in volume based on whether and which of the DUs' fluoropolymer uses would be covered by derogations as well as based on the potential to substitute fluoropolymers in the uses not covered by any such derogations[15].

Methodology

In the DU survey presented in section 12.1 the participants were asked to estimate their expected annual foregone profits in terms of EBIT in case of two hypothetical scenarios:

- A scenario in which 25% of their product portfolio would be covered under use-specific derogations from the PFAS restriction – the impacts indicated in this scenario by the individual DUs were aggregated to compute the producer surplus losses in case of the impact assessment Scenario 2.

[14] This section captures only the impacts incurred in case of a potential PFAS restriction at the level of fluoropolymer downstream users in the EEA based on the answers of the 51 DUs (fluoropolymer processors and component manufacturers) who answered the DU survey (see section 12.1). The results shown here do not reflect the additional downstream impacts of a restriction on OEMs, customer industry sectors and consumers, due to data unavailability.

[15] A higher substitution potential could be associated with lower producer surplus losses.

- A scenario in which 75% of their product portfolio would be covered under use-specific derogations from the PFAS restriction – these impacts were aggregated to derive the producer surplus losses in case of the impact assessment Scenario 3.

To project the potential foregone profits incurred by fluoropolymer downstream users in case of a restriction without any fluoropolymer use-specific derogations (impact assessment Scenario 1), the following assumptions were made:

- In the absence of any use-specific derogations for fluoropolymers and assuming no potential for substitution until 2027 (worst case), all profits dependent on the use of fluoropolymers at the DUs' sites would be lost.
- To compute the fraction of the total annual EBIT that is dependent on the use of fluoropolymers for each DU, the share reported to indicate the dependency of total revenues on fluoropolymers was used (see section 12.1).

Notably, a differentiation could be made between the foregone profits associated with fluoropolymer processing activities and activities constituting component manufacturing, respectively. In this sense, it was assumed at DU level that the percentage of fluoropolymer-dependent revenues associated with processing/component manufacturing activities would be equal to the percentage of the impacts that would be associated with the respective activities (see section 12.1).

Additionally, the foregone profits expected to be incurred at the level of fluoropolymer processors based on the limited survey data corresponding to 51 DUs were extrapolated to provide a more realistic coverage for this segment in the supply chain. For this purpose the foregone profits associated with processing activities were multiplied by a factor equal to the ratio between the total annual volume of fluoropolymers reported to be processed in the EEA (conservatively estimated at 51,000[16] tonnes per year) and the aggregated annual volume of fluoropolymers processed by the 51 survey respondents (16,654 tonnes per year) (see section 3.2.2). This procedure yielded a multiplication factor of 3.06. Notably, this extrapolation exercise implicitly assumed a direct proportionality between the tonnage of fluoropolymers processed in the EEA and the magnitude of the impacts occurring at the level of processors in case of a PFAS restriction.

As in the case of computing producer surplus losses for fluoropolymer manufacturers, foregone profits are assumed to accumulate for 2 years only[17] as of 2027, in alignment with the general methodology for evaluating producer surplus losses explained in section 5.1.1.

Results

At the level of fluoropolymer processors, based on the methodology explained above, a potential PFAS restriction covering fluoropolymers would generate between 105.31 million Euros (Scenario 3, lower bound) and 563.71 million Euros (Scenario 1, upper bound) in terms of total foregone profits in the EEA (NPV 2025 - values after extrapolation). This is equivalent to an annualized amount between 5.08 million Euros per year (Scenario 3, lower bound) and 27.21 million Euros per year (Scenario 1, upper bound) in terms of losses for the EEA society over an impact assessment period of 45 years (Table 6). Notably, as previously explained in section 5.1.1, such losses are likely largely underestimated as the annual foregone profits registered at the level of all processors in the

[16] This value corresponds to a realistic annual tonnage estimate of fluoropolymers manufactured/processes in the EEA in 2015 based on a literature review. The value is slightly lower compared to the volume of 52,000 tonnes of fluoropolymers sold in Europe in 2015 (Plastics Europe, 2018).

[17] Notably, this 2-year period is considered a minimum timeline as in reality, under a REACH PFAS restriction, competitors are expected to require a much longer period of time until they can take over the market shares of fluoropolymer manufacturers due to the limited feasibility to substitute fluoropolymers in the respective applications.

EEA (estimated at 60.34 – 323.01 million Euros per year after extrapolation[18]) are expected to be incurred for much longer than the 2-year period considered in the current assessment (see footnote 17).

Table 6: Estimated producer surplus losses in the EEA due to foregone profits at processors of fluoropolymers in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Foregone profits per year at fluoropolymer processors in the years 2027 and 2028 (based on survey data collected from 51 DUs)	35.13 – 105.56	38.67 – 99.10	19.72 – 57.83
Foregone profits per year at all fluoropolymer processors in the years 2027 and 2028 (after extrapolation)	107.58 – 323.26	118.43 – 303.48	60.39 – 177.09
Net present value in the base year (NPV 2025) (after extrapolation)	187.60 – 563.71	206.52 – 529.20	105.31 – 308.82
Annualized amount over a period of 45 years (after extrapolation)	9.05 – 27.21	9.97 – 25.54	5.08 – 14.90

At the level of component manufacturers, based on the survey data alone, a potential PFAS restriction covering fluoropolymers would generate between 35.39 million Euros (Scenario 3, lower bound) and 172.76 million Euros (Scenario 1, upper bound) in terms of foregone profits in the EEA (NPV 2025). This is equivalent to an annualized amount between 1.71 million Euros per year (Scenario 3, lower bound) and 8.34 million Euros per year (Scenario 1, upper bound) in terms of losses for the EEA society over an impact assessment period of 45 years (Table 7). Importantly, this value is only representative for the 51 DUs that answered the survey and not for all component manufacturers in the EEA, as no extrapolation could be conservatively conducted in this regard. Additionally, as noted previously in the case of processors, such losses are likely underestimated as the annual foregone profits experienced by the responding component manufacturers (20.29 – 99.07 million Euros per year) are expected to be incurred for much longer than the 2-year period considered in the current approach (see footnote 17).

Table 7: Estimated producer surplus losses in the EEA due to foregone profits at component manufacturers in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Foregone profits per year at component manufacturers in the years 2027 and 2028 (based on survey data collected from 51 DUs)	43.35 – 99.07	30.08 – 76.40	20.29 – 52.87
Net present value in the base year (NPV 2025) (no extrapolation)	75.60 – 172.76	52.45 – 133.22	35.39 – 92.19
Annualized amount over a period of 45 years (no extrapolation)	3.65 – 8.34	2.53 – 6.43	1.71 – 4.45

[18] Range of values before extrapolation: 19.72 – 105.56 million Euros per year (see Table 6); Applicable extrapolation factor: 3.06 (see Methodology in section 5.2.1).

5.2.2 Job losses

Due to economic activities being disrupted in case of a potential restriction, job losses are expected to accrue at the sites of EEA fluoropolymer downstream users (fluoropolymer processors and component manufacturers). These job losses would in turn generate social costs for the EEA society, which are evaluated below.

Methodology

In the DU survey the respondents were asked to indicate the expected number of FTEs that would need to be dismissed at their sites due to reduced production activity. The companies had to answer the question separately for each of the 2 scenarios indicated above in the case of producer surplus losses (see section 12.1). By aggregating the individual estimates for FTEs dismissed, the number of job losses for impact assessment Scenario 2 and Scenario 3, respectively, could thus be computed.

For computing the expected number of job losses in Scenario 1, the following assumptions were made, similar as in the approach to compute the foregone profits:

- In the absence of any use-specific derogations for fluoropolymers and assuming no potential for substitution until 2027 (worst case), all FTEs dependent on the use of fluoropolymers at the DUs' sites would need to be dismissed.
- To compute the fraction of the total FTEs that is dependent on the use of fluoropolymers for each DU, the share reported to indicate the dependency of total revenues on fluoropolymers was used (see section 12.1).

As previously explained in the case of producer surplus losses, a differentiation could be made between the job losses experienced at the level of fluoropolymer processors and component manufacturers, respectively. Similarly, the impacts concerning unemployment computed based on the survey data were in case of the fluoropolymer processors extrapolated to provide a more realistic coverage of the consequences of the restriction on this segment in the supply chain (for more details please refer to section 5.2.1).

All jobs were assumed to be lost in 2027, and for computing the social costs for the EEA society associated with the job losses the general methodology previously described in section 5.1.2 was followed.

Results

At the level of fluoropolymer processors, based on the methodology explained above, a potential PFAS restriction covering fluoropolymers would lead to a total number between 1,923 (Scenario 3, lower bound) and 12,941 (Scenario 1, upper bound) jobs lost in the EEA (values after extrapolation). Overall, these job losses would consequently result in a social cost of unemployment between 167.81 million Euros (Scenario 3, lower bound) and 1,129.18 million Euros (Scenario 1, upper bound) (NPV 2025). This is equivalent to an annualized amount between 8.10 million Euros per year (Scenario 3, lower bound) and 54.50 million Euros per year (Scenario 1, upper bound) in terms of costs for the EEA society over an impact assessment period of 45 years (Table 8).

Table 8: The social cost of unemployment for the EEA society due to job losses at fluoropolymer processors in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Number of job losses at fluoropolymer processors in 2027 (based on survey data collected from 51 DUs)	3,158 – 4,226	1,609 – 2,796	628 – 1,365
Total number of job losses at fluoropolymer processors in 2027 (after extrapolation)	9,670 – 12,941	4,928 – 8,562	1,923 – 4,181
The social cost of unemployment for one job lost (in 2027)	0.1	0.1	0.1
The social cost of unemployment for all jobs lost (NPV 2025) (after extrapolation)	843.77 – 1,129.18	430.03 – 747.09	167.81 – 364.83
Annualized amount over a period of 45 years (after extrapolation)	40.72 – 54.50	20.75 – 36.06	8.10 – 17.61

At the level of component manufacturers, based on the survey data alone, a restriction would lead to a number between 1,047 (Scenario 3, lower bound) and 3,575 (Scenario 1, upper bound) jobs lost in the EEA. Overall, these job losses would consequently result in a social cost of unemployment between 91.39 million Euros (Scenario 3, lower bound) and 311.97 million Euros (Scenario 1, upper bound) (NPV 2025). This is equivalent to an annualized amount between 4.41 million Euros per year (Scenario 3, lower bound) and 15.06 million Euros per year (Scenario 1, upper bound) in terms of costs for the EEA society over an impact assessment period of 45 years (Table 9). Notably, these costs are only derived based on the number of job losses expected at the 51 DUs who answered the survey, as no extrapolation for this level in supply chain was conducted in order to remain conservative in the current approach.

Table 9: The social cost of unemployment for the EEA society due to job losses at component manufacturers in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Number of job losses at component manufacturers in 2027 (based on survey data collected from 51 DUs)	2,936 – 3,575	1,961 – 2,749	1,047 – 1,549
The social cost of unemployment for one job lost (in 2027)	0.1	0.1	0.1
The social cost of unemployment for all jobs lost (NPV 2025) (no extrapolation)	256.22 – 311.97	171.08 – 239.87	91.39 – 135.12
Annualized amount over a period of 45 years (no extrapolation)	12.37 – 15.06	8.26 – 11.58	4.41 – 6.52

5.2.3 Additional one-off costs

In case of a potential restriction, fluoropolymer downstream users could experience one-off costs due to various reasons:

- A reduction in economic activity following the restriction could lead to a partial or a complete business shutdown of any given DU, which would in turn result in additional one-

off costs for dismantling of facilities, decontamination and waste management for the respective DU.

- If potential alternatives for specific fluoropolymer uses would exist for some DUs, those DUs would incur one-off costs for further developing and implementing such potential alternatives.

Methodology

By considering the hypothetical scenarios previously outlined in the section for producer surplus losses, the respondents of the DU survey were asked to estimate the expected amount of one-off costs they would incur with respect to additional costs for dismantling, decontamination and waste management as well as additional costs for further investments. Thus, for both impact assessment Scenario 2 and Scenario 3 the expected additional one-off costs could be computed by aggregation of survey data. In lack of better estimates, for Scenario 1 it was conservatively assumed that costs for dismantling, decontamination and waste management would incur at least at the level of Scenario 2. All additional one-off costs were assumed to incur for one year only in 2027.

As in the approach for computing foregone profits and the social cost of unemployment, a differentiation was made between the one-off costs expected to incur at the level of fluoropolymer processors and component manufacturers, respectively. Additionally, only in the case of the results corresponding to the fluoropolymer processors, an extrapolation was conducted to obtain a representative coverage of the entire segment in the supply chain (for more details please refer to section 5.2.1).

Results

At the level of fluoropolymer processors, a potential PFAS restriction covering fluoropolymers would generate between 99.51 million Euros (Scenario 3, lower bound) and 406.99 million Euros (Scenario 2, upper bound) in terms of total additional one-off costs in the EEA (NPV 2025 – values after extrapolation). Overall, this is equivalent to an annualized amount between 4.80 million Euros per year (Scenario 3, lower bound) and 19.64 million Euros per year (Scenario 2, upper bound) in terms of total one-off costs for the EEA society over an impact assessment period of 45 years (Table 10).

Table 10: Estimated additional one-off costs in the EEA at fluoropolymer processors in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Additional one-off costs for dismantling, decontamination and waste management at fluoropolymer processors in 2027 (based on survey data collected from 51 DUs)	37.76 – 96.65	37.76 – 96.65	18.12 – 51.54
Additional one-off costs for dismantling, decontamination and waste management at fluoropolymer processors in 2027 (after extrapolation)	115.64 – 295.96	115.64 – 295.96	55.48 – 157.82
Additional further one-off investments[19] at fluoropolymer processors in 2027 (based on survey data collected from 51 DUs)	N/A	29.62 – 52.85	18.43 – 42.69

[19] In the survey the respondents mentioned the following cost categories for additional further investments: costs for development, validation and commercialization of new products; costs for new equipment and machinery; costs for rebuilding facilities; costs for new training for employees.

Additional further one-off investments[19] at fluoropolymer processors in 2027 (after extrapolation)	N/A	90.71 – 161.84	56.45 – 130.72
Total net present value in the base year (NPV 2025) (after extrapolation)	102.81 – 263.11	183.44 – 406.99	99.51 – 256.51
Total annualized amount over a period of 45 years (after extrapolation)	4.96 – 12.70	8.85 – 19.64	4.80 – 12.38

At the level of component manufacturers, based on survey data only, a potential PFAS restriction covering fluoropolymers would generate between 19.90 million Euros (Scenario 1, lower bound) and 124.73 million Euros (Scenario 2, upper bound) in terms of additional one-off costs in the EEA (NPV 2025). Overall, this is equivalent to an annualized amount between 0.96 million Euros per year (Scenario 1, lower bound) and 6.02 million Euros per year (Scenario 2, upper bound) in terms of one-off costs for the EEA society over an impact assessment period of 45 years (Table 11). As before, this value is only representative for the 51 DUs who answered the survey and cannot be considered a realistic coverage for the entire segment in the supply chain.

Table 11: Estimated additional one-off costs in the EEA at component manufacturers in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Additional one-off costs for dismantling, decontamination and waste management at component manufacturers in 2027 (based on survey data collected from 51 DUs)	22.39 – 61.15	22.39 – 61.15	14.13 – 41.16
Additional further one-off investments[19] at component manufacturers in 2027 (based on survey data collected from 51 DUs)	N/A	50.08 – 79.15	46.12 – 78.42
Total net present value in the base year (NPV 2025) (no extrapolation)	19.90 – 54.37	64.42 – 124.73	53.56 – 106.31
Total annualized amount over a period of 45 years (no extrapolation)	0.96 – 2.62	3.11 – 6.02	2.59 – 5.13

5.2.4 Additional operating costs

In case of a restriction, fluoropolymer downstream users could experience additional annual operating costs as a result of the use of potential alternatives if the latter would be available at all.

Methodology

By considering the hypothetical scenarios previously outlined in the other sub-sections of chapter 5, the respondents of the DU survey were asked to estimate the expected amount of additional annual operating costs they would incur in case of a potential restriction. Thus, for both impact assessment Scenario 2 and Scenario 3 the expected additional operating costs could be computed by aggregation of survey data. To remain conservative and in lack of any appropriate estimates, no additional operating costs were considered to accrue in Scenario 1. All additional annual operating costs were conservatively assumed to incur for 2 years only as of 2027 (as in the case of foregone profits). As previously, a differentiation could be made between operating costs incurred by fluoropolymer processors and component manufacturers. The survey data aggregated for the

fluoropolymer processors only could be extrapolated based on the conservative approach previously outlined (for more details please refer to section 5.2.1).

Results

At the level of fluoropolymer processors, a potential PFAS restriction covering fluoropolymers would generate between 0.57 million Euros (Scenario 2, lower bound) and 4.06 million Euros (Scenario 3, upper bound) in terms of additional operating costs in the EEA (NPV 2025 – values after extrapolation). This is equivalent to an annualized amount between 0.03 million Euros per year (Scenario 2, lower bound) and 0.20 million Euros per year (Scenario 3, upper bound) in terms of losses for the EEA society over an impact assessment period of 45 years (Table 12).

Table 12: Estimated additional operating costs in the EEA at fluoropolymer processors in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Additional operating costs per year at fluoropolymer processors in the years 2027 and 2028 (based on survey data collected from 51 DUs)	N/A	0.11 – 0.32	0.16 – 0.76
Additional operating costs per year at fluoropolymer processors in the years 2027 and 2028 (after extrapolation)	N/A	0.33 – 0.98	0.50 – 2.33
Net present value in the base year (NPV 2025) (after extrapolation)	N/A	0.57 – 1.71	0.87 – 4.06
Annualized amount over a period of 45 years (after extrapolation)	N/A	0.03 – 0.08	0.04 – 0.20

At the level of component manufacturers, based on the survey data only, a potential PFAS restriction covering fluoropolymers would generate between 0.15 million Euros (Scenario 3, lower bound) and 0.66 million Euros (Scenario 2, upper bound) in terms of additional operating costs in the EEA (NPV 2025). This is equivalent to an annualized amount between 0.01 million Euros per year (Scenario 2 / Scenario 3, lower bound) and 0.03 million Euros per year (Scenario 2 / Scenario 3, upper bound) in terms of losses for the EEA society over an impact assessment period of 45 years (Table 13). Notably, this value is only representative for the 51 DUs that answered the survey and not for all component manufacturers in the EEA, as no extrapolation in this sense could be conservatively conducted.

Table 13: Estimated additional operating costs in the EEA at component manufacturers in case of a potential restriction.

Socio-economic impact factor	**Value [in million Euros]**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Additional operating costs per year at component manufacturers in the years 2027 and 2028 (based on survey data collected from 51 DUs)	N/A	0.09 – 0.38	0.09 – 0.34
Net present value in the base year (NPV 2025) (no extrapolation)	N/A	0.16 – 0.66	0.15 – 0.59

Socio-economic impact factor	Value [in million Euros]		
Annualized amount over a period of 45 years (no extrapolation)	N/A	0.01 – 0.03	0.01 – 0.03

5.3 Impacts on OEMs and customer industry sectors

Beyond the impacts expected to be registered at fluoropolymer downstream users such as fluoropolymer processors and component manufacturers in the EEA in case of a potential PFAS restriction covering fluoropolymers, noticeable consequences would be further incurred by downstream OEMs and industrial customers (see Figure 1). Although the fluoropolymer-containing components may be relatively small in relation to the size of the equipment pieces/technologies within which such components are integrated, they are often essential for the safety, performance and overall feasibility of the respective technologies.

For instance, the use of fluoropolymer-containing fuel hoses in the transport sector contributes to fuel savings and thus reductions of environmental emissions, estimated at about 140 million Euros per year in the EU. Similarly, in the context of the chemical and power sector, the use of fluoropolymers in installations increases machinery lifetime by more than a factor of 2, while saving hundreds of million Euros yearly through corrosion prevention. Meanwhile, their use in combined heat and power results in energy savings of up to 8 billion Euros (Plastics Europe, 2018).

Critical for the generation of green hydrogen, fluoropolymers are essential constituents of electrolysers and fuel cell membranes. It is estimated that in the absence of an exemption from the PFAS restriction for the use of fluoropolymers in the hydrogen sector up to 200,000 direct and over 260,000 indirect jobs would become jeopardized within 10 years. Within the same period of time, foregone investments of about 30 billion Euros are anticipated (Hydrogen Europe, 2023).

In order to maintain a conservative approach, such impacts occurring at the level of OEMs and customer industries are only presented at this stage as examples and not included towards the monetization of impacts conducted in the current assessment. Therefore, the socio-economic consequences for the EEA society associated with a PFAS restriction covering fluoropolymers as derived in the present report remain largely underestimated.

Based on these selected examples alone it becomes evident that a PFAS restriction covering fluoropolymers would not only lead to the targeted yet limited[20] reduction of PFAS emissions from the lifecycle of fluoropolymers in comparison to the total PFAS emissions in the EEA but would also result in increased environmental emissions due to reduced fuel savings, reduced machinery lifetime and thus higher consumption of resources as well as higher energy consumption. Due to the dependency of green hydrogen generation and electrification of vehicles (via the use of Lithium-ion batteries) on the use of fluoropolymers, a broad PFAS restriction would hinder the planned decarbonization of the EU and the consequent reduced dependency on imported fossil fuels. Additionally, fluoropolymers ensure the safety and longer lifespans of applications, resulting in

[20] As per the Annex XV restriction proposal on PFAS, the total volume of PFAS used in the year 2020 is estimated to be approximately 840,000 tonnes, out of which the overall emissions of PFAS from all types of PFAS applications is estimated at 200,282 tonnes per year. Out of this amount, the PFAS emissions related to fluoropolymers based on an annual volume of 75,610 tonnes of fluoropolymers produced per year in the EU are estimated to be 19.6 tonnes per year (note: this emissions estimate accounts for the use of polymerization aids for the manufacturing of fluoropolymers) (REACH Competent Authorities, 2021). Therefore, it is evident that the PFAS emissions related to the fluoropolymers lifecycle is significantly lower compared to the overall PFAS emissions.

It should be further noted that PFAS emissions are associated to dispersive consumer applications such as Textiles, Upholstery, Leather, Apparel and Carpet (TULAC) applications and fluorinated gases, which account for about 31% and 63% of the total PFAS emissions respectively. Notably, fluoropolymers are not related to any of these applications.

reductions in terms of waste generation. Although critical for the EEA society, these environmental effects can nonetheless not be accounted for in a monetized form in the present impact assessment.

5.4 Summary of socio-economic impacts

To summarize the results presented in sections 5.1 and 5.2, in case of a potential PFAS restriction covering fluoropolymers, total losses of at least 33.86 million Euros per year (Scenario 3, lower bound) to 148.92 million Euros per year (Scenario 1, upper bound) can be expected for the EEA society over a 45-year impact assessment period. These values account for effects at the level of mostly fluoropolymer producers and processors as well as, to a smaller extent, some component manufacturers in the EEA. Notably, as previously emphasized in section 5.2, the projection of impacts in case of component manufacturers only relies on the limited survey data collected from the 51 DUs and thus cannot be considered a complete representation of this entire stakeholder segment in the supply chain.

Additionally, due to data limitations and in order to maintain a conservative approach, these results explicitly do not include further socio-economic impacts downstream in the supply chain, at the level of OEMs and customer industry sectors. Such effects are nonetheless expected to be large, given the critical importance of fluoropolymers for the safety, performance and feasibility of different types of equipment and technologies used in a multitude of sectors in the EEA (see section 5.3 and Table 1). Also not taken into account is the impact on EU's efforts to achieve strategic autonomy in developing critical technologies in case of the non-availability of fluoropolymers. Moreover, as previously explained in sections 5.1.1 and 5.2.1, the producer surplus losses computed in the current assessment are likely largely underestimated. In reality, under a PFAS restriction, the annual foregone profits experienced by the different stakeholders in the supply chain are expected to be incurred for much longer than the 2-year period considered in the current approach due to the limited feasibility of fluoropolymer substitution in the different applications (see footnote 17). Furthermore, the socio-economic results summarized here do not account for the negative environmental effects associated with a potential restriction (e.g., increased emissions due to reduced fuel savings, increased consumption of energy and materials, reduced safety of chemical operations and heavy equipment), nor do they account for the negative effects of such a restriction on the EU decarbonization strategy in relation to the planned developments in the hydrogen, electric vehicles and semiconductor sectors (see section 5.3).

Thus, the monetized impacts presented in Table 14 only represent a fraction of the real consequences incurred in the EEA in case of a PFAS restriction covering fluoropolymers.

Table 14: Summary of the monetized socio-economic impacts incurred in the EEA in case of a potential PFAS restriction covering fluoropolymers given the different impact assessment scenarios considered in section 4.

Socio-economic impact factor	**Annualized value [in million Euros per year] over a period of 45 years**		
Impact assessment scenario	Scenario 1	Scenario 2	Scenario 3
Impacts on producers of fluoropolymers			
Producer surplus losses	9.54	7.15	2.38
Social cost of unemployment due to job losses	18.95	14.21	4.74
Impacts on fluoropolymer processors			
Producer surplus losses	9.05 – 27.21	9.97 – 25.54	5.08 – 14.90

Socio-economic impact factor	Annualized value [in million Euros per year] over a period of 45 years		
Social cost of unemployment due to job losses	40.72 – 54.50	20.75 – 36.06	8.10 – 17.61
Additional one-off costs	4.96 – 12.70	8.85 – 19.64	4.80 – 12.38
Additional operating costs	N/A	0.03 – 0.08	0.04 – 0.20
Impacts on some component manufacturers[21]			
Producer surplus losses	3.65 – 8.34	2.53 – 6.43	1.71 – 4.45
Social cost of unemployment due to job losses	12.37 – 15.06	8.26 – 11.58	4.41 – 6.52
Additional one-off costs	0.96 – 2.62	3.11 – 6.02	2.59 – 5.13
Additional operating costs	N/A	0.01 – 0.03	0.01 – 0.03
Total socio-economic impacts	**100.20 – 148.92**	**74.87 – 126.74**	**33.86 – 68.34**

6. Environmental impacts – a case study for PTFE

Whereas chapter 5 describes the socio-economic impacts in the EEA that would be associated with a PFAS restriction covering fluoropolymers, this section presents the environmental impacts in terms of additional PFAS emissions that could be avoided in case of a potential PFAS restriction covering PTFE. This quantity of additional emissions prevented is consequently used in the proportionality assessment conducted as a case study for PTFE in chapter 7.

Based on the conclusions derived in another report prepared by Ramboll in 2023 to assess the PFAS emissions during the lifecycle of PTFE as a case study, the annual quantity of PFAS emissions associated with the lifecycle of PTFE in the EEA can vary significantly depending on the technology implemented for the production of PTFE. If during the production stage an emulsion polymerization process with Fluorinated polymerization aids (FPA) is applied, annual PFAS emissions of roughly 4 – 140 tonnes can be attributed to the annual PTFE volume produced in the EEA (20,000 tonnes). However, if during the production of PTFE a non-FPA polymerization process would be applied at all manufacturing facilities in the EEA, the same annual PTFE volume would be associated with only 9 kilograms of emissions annually (Table 15).

Notably, such a non-FPA polymerization process is suggested to be proposed by the 5 PFAS restriction Dossier Submitters in the restriction proposal[22] and is currently planned by the majority of fluoropolymer manufacturers.

[21] In case of the component manufacturers, the results presented are only based on survey data collected from 51 DUs and are thus considered to not be representative for the entire stakeholder group in the supply chain.

[22] According to the Annex XV restriction report on PFAS, the use of polymerization aids in the production of PTFE, PVDF and FKM was proposed to be restricted, while a time-limited derogation was proposed for the use of polymerization aids for the production of other polymeric PFASs.

Table 15: Estimated PFAS emissions released in the environment in the EEA during the lifecycle of PTFE based on an annual production volume of 20,000 tonnes of PTFE.

Environmental impact factor	Quantity [in kilograms / year]
Annual PFAS emissions associated with PTFE in the EEA – accounting for a PTFE production process relying on FPA polymerization	4,207 – 140,007
Annual PFAS emissions associated with PTFE in the EEA – assuming a transition to a PTFE production process relying on a non-FPA polymerization[23]	9

7. Proportionality assessment – a case study for PTFE

Based on the socio-economic impacts monetized in chapter 5 and considering the estimated environmental PFAS emissions associated with the tonnage of PTFE produced annually in the EEA (20,000 tonnes) (see chapter 6), the current section presents the results of a proportionality assessment for the case of a PFAS restriction covering PTFE as a case study representative of the fluoropolymers substance group.

Methodology

Previous section 5.4 has already summarized the monetized annual socio-economic impacts that would be associated with a PFAS restriction covering fluoropolymers. By dividing the corresponding impacts to the annual tonnage of fluoropolymers produced in the EEA (51,000 tonnes / year)[24], the socio-economic costs for the EEA society per tonne of fluoropolymer restricted can be derived. Assuming that such cost estimates can be considered as averages for fluoropolymers and accounting for the total tonnage of PTFE produced in the EEA annually (20,000 tonnes), the socio-economic costs associated with a PFAS restriction covering PTFE can be computed. By comparing these socio-economic costs against the quantity of additional PFAS emissions potentially avoided through such a restriction, cost-effectiveness ratios could be obtained.

Results

Overall, a potential PFAS restriction covering PTFE would generate socio-economic costs for the EEA society of at least 13.28 – 58.40 million Euros per year. Depending on the technological process used to produce PTFE, different cost-effectiveness ratios can be derived for such a restriction. Accounting for a PTFE production process relying on FPA polymerization, socio-economic costs of roughly at least 94.8 – 13,881.6 Euros would be generated for each additional kilogram of PFAS emissions prevented. Considering the expected transition of EU manufacturers to a PTFE production process not dependant on FPA polymerization, the socio-economic costs associated with such a restriction covering PTFE become at least 1.5 – 6.5 million Euros per kilogram of additional PFAS emissions avoided (Table 16). At least in the context of the current case study on PTFE, the considerable difference between the cost-effectiveness ratios associated with the two different technologies used for PTFE production as in the use/non-use of FPA is attributed to the fact that the intentional use of FPA is the main source of PFAS emissions to the environment during the lifecycle of PTFE (see section 6).

[23] A transition to a technology relying on a non-FPA polymerization is currently planned by EU manufacturers.

[24] This value corresponds to a realistic annual tonnage estimate of fluoropolymers manufactured/processes in the EEA in 2015 based on a literature review. The value is slightly lower compared to the volume of 52,000 tonnes of fluoropolymers sold in Europe in 2015 (Plastics Europe, 2018).

It must be noted that these cost-effectiveness ratios represent minimum estimations derived based on the limited socio-economic data available. As explained in section 5.4, the actual impacts for the EEA society associated with a potential PFAS restriction remain largely underestimated due to incomplete data on component manufacturers and a lack of appropriate data on impacts at the level of OEMs and end customers. Moreover, as previously emphasized in section 5.4, the annual producer surplus losses computed in the present report are in fact expected to be incurred for much longer than the 2-year period considered in the current approach, which leads to the underestimation of the actual cost-effectiveness ratios derived here. Finally, the ratios presented here do not account for the expected negative effects of a potential restriction with respect to an increased consumption of energy and materials or in relation to the EU Green Deal and the functioning of the modern society (see section 5.3).

Table 16: Cost-effectiveness ratios associated with a potential PFAS restriction covering PTFE.

Measure	***Estimated result***
Socio-economic costs associated with a PFAS restriction covering fluoropolymers [Euros / year] considering a total tonnage of 51,000 tonnes of fluoropolymers (see section 5.4)	*33,860,000 – 148,920,000*
Socio-economic costs associated with a PFAS restriction covering fluoropolymers [Euros / year] per tonne of fluoropolymers	663.92 – 2,920.00
Socio-economic costs associated with a PFAS restriction covering PTFE [Euros / year] considering a total tonnage of 20,000 tonnes of PTFE	13,278,431 – 58,400,000
Annual PFAS emissions associated with PTFE in the EEA – accounting for a PTFE production process relying on FPA polymerization [kilograms / year] (see section 6)	4,207 – 140,007
Cost-effectiveness ratio for a PFAS restriction covering PTFE [Euros / kilogram] – accounting for a PTFE production process relying on FPA polymerization	**94.84 – 13,881.63**
Annual PFAS emissions associated with PTFE in the EEA – assuming a transition to a PTFE production process relying on a non-FPA polymerization[25] [kilograms / year] (see section 6)	9
Cost-effectiveness ratio for a PFAS restriction covering PTFE [Euros / kilogram] – assuming a transition to a PTFE production process relying on a non-FPA polymerization	**1,475,381.26 – 6,488,888.89**

8. Proportionality considerations

The principle of proportionality is laid down in Article 5(4) of the Treaty on European Union and it seeks to set actions taken by European Union (EU) institutions within specified bounds. Under this principle, EU measures must be suitable and necessary to achieve the desired end, while not imposing a burden that is excessive in relation to the objective sought to be achieved.

[25] A transition to a technology relying on a non-FPA polymerization is currently planned by EU manufacturers.

As described on page 159 of the PFAS restriction proposal, a proportionality evaluation of a restriction requires to assess whether (ECHA, 2023):

- The restriction in question is targeted to the identified risk and does not inadvertently affect users or actors in the supply chain that are not associated with the identified risk
- The efforts required from supply chain actors and from authorities to implement and enforce the given restriction, respectively, correspond in amount or degree to the adverse effects that are being avoided
- The restriction in question ensures a good balance between costs and benefits while being cost-effective

According to ECHA, the standard approach used to assess proportionality in the case of PBT/vPvB chemicals is a cost effectiveness analysis (CEA), provided that a cost-benefit analysis (CBA) cannot be conducted due to a lack of safe concentration levels of PBT/vPvB chemicals. In this sense, for assessing the cost effectiveness of a restriction the expected reduction in quantity of emissions is used as a proxy (ECHA, 2016).

Notably, due to lack of sufficient data for projecting the expected costs and emissions avoided as a result of a potential restriction, the PFAS restriction proposal has only assessed cost-effectiveness and proportionality in a qualitative manner (ECHA, 2016). Accounting for the expected transition of EU manufacturers to a PTFE production process not dependant on FPA polymerization, this report arrived at a cost effectiveness ratio between 1.5 – 6.5 million Euros / kilogram[26] for a PFAS restriction covering PTFE (see section 7). In the following this ratio is compared against benchmarks identified in the literature to conclude on the proportionality of including PTFE in the scope of a potential PFAS restriction.

8.1 Cost-effectiveness ratios and other benchmarks available in literature

Since there are several uncertainties with regards to the actual impact on human health and the environment of reduced exposure when discussing PBT substances, benefits of restriction proposals (in the case of PFOA-related substances for example) have in the past taken reduced emissions as a proxy of the benefits of the proposed restriction - in line with the approach to evaluate restriction dossiers for PBT/vPvB substances (ECHA, 2016). Although in case of fluoropolymers only persistence is discussed, cost-effectiveness ratios for PBT substances are still considered as a basis in view of the lack of generic benchmarks for persistent substances.

Table 17 summarizes different cost estimates available in the literature identified in two benchmark studies conducted by Vrije Universiteit Amsterdam and Wageningen University, respectively, to support regulatory decision making under REACH for PBT and vPvB substances.

[26] It must be noted that, as explained in section 5.4, this cost-effectiveness ratio is in fact largely underestimated due to limited data on socio-economic impacts.

Table 17: Cost estimates derived in benchmark studies for regulatory decision making under REACH concerning PBT and vPvB substances.

Substance class	Central estimate [Euros per kilogram]	Lower bound [Euros per kilogram]	Upper bound [Euros per kilogram]	Cost category	Source
DDT	N/A	95	1,303	Remediation costs	(Gabbert, Hahn, Klein, Nendza, & Oosterhuis, 2017)
PAHs	N/A	8	1,300	Remediation costs	(Gabbert, Hahn, Klein, Nendza, & Oosterhuis, 2017)
PFOA-related substances	636	83	2,333	Costs for emissions avoided	(Gabbert, Hahn, Klein, Nendza, & Oosterhuis, 2017)
PFOS	N/A	274	35,000	Remediation costs	(Gabbert, Hahn, Klein, Nendza, & Oosterhuis, 2017)
PFOS	N/A	1,500	28,000	Costs for emissions avoided	(Oosterhuis & Brouwer, 2015)

Based on the benchmark study conducted by Vrije Universiteit Amsterdam, with regards to society's maximum willingness to pay for reducing PBT emissions, a range between 1,000 Euros and 50,000 Euros per kilogram of PBT was found. In other words, cost values within this range are identified as being either still acceptable (proportionate) or too high for reducing PBT emissions by one kilogram (Oosterhuis & Brouwer, 2015). Notably, the minimum of this range was also referred to in Appendix E of the PFAS restriction proposal when evaluating the level of cost increase for cookware that could be justified against the change in emissions of fluoropolymer to the environment (ECHA, 2023).

To complement on the values shown above, Table 18 presents an overview of cost-effectiveness ratios previously derived in REACH restriction proposals / restrictions. Notably, while discussing proportionality in the context of the restriction proposals for bisphenols, the dossier submitters considered a cost-effectiveness ratio of 19,150 Euros per kilogram of emissions prevented to be likely proportionate (ECHA, 2022 a.).

Table 18: Cost-effectiveness ratios derived in previous REACH restriction proposals / restrictions.

Substance class	Central estimate [Euros per kilogram]	Lower bound [Euros per kilogram]	Upper bound [Euros per kilogram]	Source
Bisphenols	19,150	N/A	N/A	(ECHA, 2022 a.)
Chloroalkanes	N/A	53	66	(ECHA, 2022 b.)
D4, D5 in wash-off cosmetics	415	N/A	N/A	(ECHA, 2021 b.)
DecaBDE	464	N/A	N/A	(ECHA, 2021 b.)
Lead in PVC	308	N/A	N/A	(ECHA, 2021 b.)

Substance class	Central estimate [Euros per kilogram]	Lower bound [Euros per kilogram]	Upper bound [Euros per kilogram]	Source
Lead in shot in wetlands	9	N/A	N/A	(ECHA, 2021 b.)
PFASs in firefighting foams	N/A	498	520	(ECHA, 2022 c.)
PFOA	<1,649	0	6,551	(ECHA, 2015)
PFOA-related substances	734	4	3,533	(ECHA, 2015)
Phenylmercury compounds	649	N/A	N/A	(ECHA, 2021 b.)

8.2 Conclusion on ratios comparison: costs of the restriction vs. benchmarks

Taking into account the above presented overview of literature-derived benchmarks and cost-effectiveness ratios previously discussed in the context of REACH restriction, it can be observed that the lower bound of the cost-effectiveness ratio derived in the current report (1.5 million Euros / kilogram) lies well above the values presented in section 8.1 (by a factor of at least 29.5 considering the highest benchmark identified, namely 50,000 Euros / kilogram). By additionally accounting for the fact that the ratio derived here is based only on an underestimated fraction of the actual socio-economic impacts that would be incurred by the EEA society in case of a potential restriction (see section 7), it can be concluded that a PFAS restriction covering PTFE produced without the use of FPA would generate unproportionally high costs for the generated benefits[27].

9. Limitations and uncertainties

9.1 Data limitations and assumptions

As emphasized in previous chapters, there are certain limitations and uncertainties within the impact assessment conducted here that need to be addressed in the present section. Notably, in order to overcome such uncertainties, conservative assumptions were made wherever possible, which in many cases led to an underestimation of the cost-effectiveness ratio results presented in section 7.

One limitation in the current assessment was the uncertainty with respect to which derogations (if any) would be granted for fluoropolymer uses in case of a PFAS restriction. To circumvent this uncertainty while maintaining a conservative approach, the three different impact assessment scenarios were defined in section 4. Thus, the socio-economic consequences associated with a potential restriction were examined on a broad spectrum between a so-called worst-case (Scenario 1 with no derogations for fluoropolymers) and a so-called best-case (Scenario 3 with derogations for up to 75% of fluoropolymer uses).

Another relevant limitation was the uncertainty with regards to the extent to which socio-economic impacts would accrue in each of the different impact assessment scenarios defined in section 4.

[27] This conclusion holds as long as there will be a technological transition away from PTFE production based on FPA at the level of EU manufacturers (transition currently planned).

Particularly for Scenario 2 and Scenario 3 linear effects had to be assumed in lack of a better approach. Specifically, when deriving the impacts at the level of fluoropolymer producers, a 25% (or 75%) reduction in fluoropolymer-dependent profits and jobs, respectively, was assumed in a case of derogations for 75% (or 25%) of fluoropolymer uses. While this linearity effect had a particular influence on the results obtained in case fluoropolymer producers, this aspect was counterbalanced by the results obtained in case of fluoropolymer downstream users based on the data collected in the DU survey (see section 12.1).

Furthermore, it must be noted that, while computing the impacts incurred at the level of fluoropolymer producers, it was assumed that in case of a potential restriction such producers could not switch to alternative production processes in the EEA to compensate for foregone profits and jobs lost otherwise associated with fluoropolymers production. This assumption was deemed appropriately conservative and realistic while in line with current market expectations. Moreover, while substitution to fluoropolymer-free substances was not explicitly addressed in the current impact assessment, it is expected that such substitution efforts at the level of fluoropolymer downstream users have been implicitly accounted for while using the data collected through the DU survey (see section 12.1).

Additionally noteworthy at this stage is the assumption that was made to enable data collection through the downstream user survey (see footnote 31). In this sense, it was assumed that a case of derogations for 75% (or 25%) of fluoropolymer uses would result in 75% (or 25%) of each of the respondent's product portfolios to be covered under such derogations. Notably, as previously mentioned throughout this report, the DU survey was answered by 51 companies only, representing different industry sectors (see section 3.2.2). This corresponds to roughly one-third of the downstream users originally targeted by the DU survey.

Additionally, to differentiate between the impacts incurred at the level of fluoropolymer processors and component manufacturers, it was assumed at DU level that the percentage of fluoropolymer-dependent revenues associated with processing/component manufacturing activities would be equal to the percentage of the impacts that would be associated with the respective activities (see section 12.1). Despite these simplifications, the results obtained for fluoropolymer downstream users (see section 5.2) are deemed to be robust.

Finally, in order to obtain a more representative coverage of the impacts associated with a potential restriction at the level of fluoropolymer processors in the EEA, an extrapolation of the survey data was conducted based on the estimated annual tonnage of fluoropolymers processed in the EEA. The latter implicitly assumed a direct proportionality between the tonnage of fluoropolymers processed in the EEA and the magnitude of the impacts occurring at the level of processors in case of an inclusion of fluoropolymers in the PFAS restriction (see section 5.2). By comparing the results obtained at the level of fluoropolymer manufacturers and fluoropolymer processors in terms of producer surplus losses however, it can be noted that this implicit assumption led to robust socio-economic outcomes (see section 12.3).

Overall, as previously emphasized in section 7, the cost-effectiveness ratios derived in the current impact assessment are largely underestimated for different reasons. First and foremost, the socio-economic impacts derived here represent only a fraction of the real consequences for the EEA society in case of a potential PFAS restriction. The socio-economic impacts would be indeed much larger if effects at a large proportion of EEA component manufacturers relying on fluoropolymers as well as at EEA OEMs and end customers could be accounted for. Furthermore, as previously outlined in sections 5.1.1 and 5.2.1, for the computation of producer surplus losses throughout this assessment a period of 2 years only was considered before the annualization of the derived impacts

over a 45-year impact assessment period. Nevertheless, under a REACH PFAS restriction the annual foregone profits experienced at the different levels in the supply chain are expected to be incurred for much longer than the 2-year period considered here, due to the expected low potential for substituting fluoropolymers in different applications (see footnote 13). This in turn leads to a likely large underestimation of the actual socio-economic impacts and the cost-effectiveness ratios in case of a restriction. Finally, the cost-effectiveness ratios derived in the current assessment do not account for the negative effects associated with a potential restriction with respect to an increased consumption of energy and materials, nor do they account for the consequences of such a restriction for the EU Green Deal, decarbonization strategy in relation to the hydrogen economy and electrification of vehicles, safety and well-being considerations and the strategic autonomy in sectors like semiconductors (see section 5.3).

9.2 Sensitivity analysis

As already emphasized in section 9.1, despite the inherent data limitations and the outlined assumptions, a conservative approach was taken throughout the current impact assessment which overall led to an underestimation of the computed cost-effectiveness ratios. Nonetheless, to ensure that the conclusion of the current report remains robust in spite of uncertainties, the following sensitivity analysis was conducted:

- For the computation of socio-economic impacts associated with the inclusion of fluoropolymers in the scope of the PFAS restriction, no extrapolation of the results obtained at the level of fluoropolymer processors based on the survey data was conducted (as opposed to the approach explained in 5.2). In this sense, only consequences that would be incurred by fluoropolymer producers as well as only a fraction of the fluoropolymer processors and component manufacturers in the EEA were counted towards the cost-effectiveness ratio associated with a restriction covering PTFE.

Such an approach without any extrapolation yields a total annualized value between 21.72 million Euros (Scenario 3, lower bound) and 85.34 million Euros (Scenario 1, upper bound) per year in terms of socio-economic costs for the EEA society over the impact assessment period, which still amounts to 57.3% to 64.1% of the previously obtained socio-economic impacts in the main analysis (see section 5.4). By accounting for the previously presented quantity of additional environmental emissions avoided in case of a PFAS restriction covering PTFE (see section 6) and by assuming a transition to PTFE production technologies not dependant on FPA, a cost effectiveness ratio of at least 946,405.23 Euros per kilogram is obtained. As this ratio is still larger compared to the benchmark and cost-effectiveness ratios presented in chapter 8.1, the conclusion of this report regarding proportionality remains valid, even after conducting such a highly conservative sensitivity analysis.

10. Conclusions

To conclude on the current impact assessment, a potential PFAS restriction covering fluoropolymers is expected to generate at least 33.86 to 148.92 million Euros per year in terms of socio-economic costs for the EEA society over an impact assessment period of 45 years. Conversely, by limiting the scope of the restriction to PTFE, socio-economic costs of at least 13.28 – 58.40 million Euros per year are expected to arise for the EEA society. Considering the quantity of additional PFAS emissions avoided per year through such a restriction and assuming a transition away from FPA-dependent PTFE production, a PFAS restriction covering PTFE would be associated with a cost-effectiveness

ratio of at least 1.5 million Euros per kilogram[28]. Given that this value is much larger than the benchmarks and cost-effectiveness ratios presented in chapter 8.1, the proportionality of including PTFE produced without the use of FPA in the scope of a potential PFAS restriction can be questioned and evidence suggests it to be disproportionate. A similar statement is expected to be valid for the case of different fluoropolymers other than PTFE should their production also become independent of FPA-based polymerization processes. Importantly, the values derived in the current assessment in terms of socio-economic costs as well as cost-effectiveness ratios must be treated as minimum estimates as they only reflect a fraction of the actual estimates that could be derived if complete socio-economic data were available. The results presented here could not account for the impacts in case of a restriction at the level of many component manufacturers, nor could they account for any impacts at OEMs and end-customer sectors. Moreover, while computing the producer surplus losses in case of a restriction, the annual foregone profits incurred at the different levels in the supply chain were considered to be incurred for 2 years only before an annualization of the impacts over the 45-year impact assessment period could be conducted. This led to a large underestimation of the overall derived socio-economic costs for the EEA society, as such foregone profits are expected to occur for much longer than 2 years only[29]. Finally, the cost-effectiveness ratios derived in the current report could not account for the negative impacts associated with a potential restriction in relation to the EU Green Deal, decarbonization efforts through the hydrogen economy and electrification of vehicles, safety and well-being considerations and the strategic autonomy in sectors like semiconductors, nor could these ratios account for other environmental effects such as an increased consumption of energy and materials (see section 5.3).

[28] Please note that this lower bound is in fact largely underestimated considering the limitations presented in chapter 9.

[29] This expectation is in line with the anticipated limited potential for substituting fluoropolymers in the different applications (see footnote 17).

11. Bibliography

ASD. (2022). *New Report Demonstrates European Aerospace and Defence Industries' Significant Contribution to European Economy. Press Release.* Brussels: Aerospace, Security and Defence Industries Association of Europe (ASD). Retrieved 04 14, 2023, from https://www.asd-europe.org/new-report-demonstrates-european-aerospace-and-defence-industries-significant-contribution-to

Carrara, S. B. (2023). *Supply chain analysis and material demand forecast in strategic technologies and sectors in the EU – A foresight study. JRC Science for Policy Report.* Joint Research Centre (JRC). Luxembourg: Publications Office of the European Union. Retrieved from https://publications.jrc.ec.europa.eu/repository/handle/JRC132889

Cefic. (2020). *2020 Facts & Figures of the European chemical industry.* Brussels, Belgiom: European Chemical Industry Council (Cefic). Retrieved 04 06, 2023, from https://www.francechimie.fr/media/52b/the-european-chemical-industry-facts-and-figures-2020.pdf

CHEMSERVICE. (2022). *TECHNICAL REPORT: Analysis of alternatives to fluoropolymers and potential impacts related to substitution in different sectors of use.*

Czako, V. (2020). *Employment in the Energy Sector. Status Report 2020. JRC Science for Policy Report.* Luxembourg: Publications Office of the European Union. Retrieved from https://publications.jrc.ec.europa.eu/repository/handle/JRC120302

Deutsche Telekom. (2020). *Annual Report 2020 - Telecommunications market.* Retrieved 04 14, 2023, from https://report.telekom.com/annual-report-2020/management-report/the-economic-environment/telecommunications-market.html?tabc=1e3

Dubourg, R. (2016). *Valuing the social costs of job losses in applications for authorisation.* Retrieved 02 14, 2022, from https://echa.europa.eu/documents/10162/13555/unemployment_report_en.pdf/e0e5b4c2-66e9-4bb8-b125-29a460720554

ECHA. (2011). Guidance on the preparation of socio-economic analysis as part of an application for authorisation. Retrieved from https://echa.europa.eu/sv/reach_en.asp

ECHA. (2015). Opinion on an Annex XV dossier proposing restrictions on Perfluorooctanoic acid (PFOA), its salts and PFOA-related substances. Retrieved 04 14, 2023, from https://echa.europa.eu/documents/10162/0e9f3f50-df19-47a6-d711-2702cd479354

ECHA. (2016). Evaluation of restriction reports and applications for authorisation for PBT and vPvB substances in SEAC. Retrieved 04 14, 2023, from https://echa.europa.eu/documents/10162/13580/evaluation_pbt_vpvb_substances_seac_e%20n.pdf/af4a7207-f7ad-4ef3-ac68-685f70ab2db3

ECHA. (2021 a.). SEAC's approach to assessing changes in producer surplus. Retrieved from https://echa.europa.eu/documents/10162/0/afa_seac_surplus-loss_seac-52_en.pdf/5e24c796-d6fa-d8cc-882c-df887c6cf6be?t=1633422139138

ECHA. (2021 b.). ANNEX XV RESTRICTION REPORT – PAHS IN CLAY TARGETS FOR SHOOTING. Retrieved 11. 05 2023 from https://echa.europa.eu/documents/10162/ca0e70c1-db56-5d5f-55e1-76668c2d9623

ECHA. (2022 a.). ANNEX XV RESTRICTION REPORT – BPA and bisphenols of similar concern for the environment. Retrieved 11. 05 2023 from https://echa.europa.eu/documents/10162/450ca46b-493f-fd0c-afec-c3aea39de487

ECHA. (2022 b.). ANNEX XV RESTRICTION REPORT Chloroalkanes: C14-17. Retrieved 11. 05 2023 from https://echa.europa.eu/documents/10162/94119671-ad55-a7ea-0908-e53d1346eb12

ECHA. (2022 c.). ANNEX XV RESTRICTION REPORT – PFASs IN FIREFIGHTING FOAMS. Retrieved 11. 05 2023 from https://echa.europa.eu/documents/10162/d5b4e564-c5f5-e41a-306d-423ebb194551

ECHA. (2023). ANNEX XV RESTRICTION REPORT – Per- and polyfluoroalkyl substances (PFASs). Retrieved from https://echa.europa.eu/documents/10162/1c480180-ece9-1bdd-1eb8-0f3f8e7c0c49

European Commission. (2023). *Internal Market, Industry, Entrepreneurship and SMEs - Sectors*. Retrieved 04 14, 2023, from https://single-market-economy.ec.europa.eu/sectors_en (and related links)

Eurostat. (2022 a.). *Unemployment by sex, age and duration of unemployment (1 000)*. Retrieved 07 22, 2022, from http://appsso.eurostat.ec.europa.eu/nui/submitViewTableAction.do

Eurostat. (2022 b.). *Labour cost index by NACE Rev. 2 activity - nominal value, quarterly data*. Retrieved 07 22, 2022, from https://ec.europa.eu/eurostat/web/products-datasets/-/LC_LCI_R2_Q

Gabbert, S., Hahn, S., Klein, M., Nendza, M., & Oosterhuis, F. (2017). Approach for Evaluation of PBTs Subject to Authorisation and Restriction Procedures in context of Socio-economic analysis. Retrieved 11. 05 2023 from https://op.europa.eu/en/publication-detail/-/publication/ff4fea17-704d-11e8-9483-01aa75ed71a1/language-en/format-PDF/source-71659651

Hydrogen Europe. (2023). Hydrogen Europe Position Paper on PFAS.

Market Research Community. (2023). *Europe Fluoropolymers Market. Forecast to 2030.* Pune (India): MRC Market Research Community.

Oosterhuis, F., & Brouwer, R. (2015). *Benchmark development for the proportionality assessment of PBT and vPvB substances. Report R-15/11.* Amsterdam: IVM Institute for Environmental Studies. Retrieved from https://echa.europa.eu/documents/10162/17241/R15_11_pbt_benchmark_report_en.pdf/a695a7fd-e2bd-4dc5-b69a-bc02f9f98fef?t=1449837319194

Plastics Europe. (2018). The fluoropolymer industry in Europe.

Rogers, J., & Marques, N. (2021). *The Tax Burden on Global Workers. A Comparative Index. First Edition.* Paris, Brussels: Institut Économique Molinari in partnership with THOLOS Foundation. Retrieved 07 21, 2022, from https://www.institutmolinari.org/wp-content/uploads/2021/07/tax_burden_on_global_workers2021.pdf

Wood Group UK Limited. (2022). *Update of market data for the socio-economic analysis (SEA) of the European fluoropolymer industry.*

12. Appendix

12.1 Framework for the DU survey

To analyse the impacts on the downstream users of fluoropolymers in case of the different impact assessment scenarios presented in section 4, an online survey was designed and distributed to fluoropolymer downstream users in the EEA as well as companies in the pro-K Group[30]. The survey recipients were requested to identify themselves and the legal entities in the EEA represented and provide legal entity specific information on the following variables:

- Total number of full-time equivalents (FTEs) employed
- Annual total revenues and EBIT registered
- Percentage share of annual total revenues depending on fluoropolymers
- Main customer sectors in the EEA that rely on fluoropolymer-containing products and the corresponding percentage contributions towards annual total revenues
- Expected annual losses in terms of EBIT due to reduced sales in case of Scenario 2 and Scenario 3, respectively[31].
- Expected number of FTEs dismissed due to reduced production activity in case of Scenario 2 and Scenario 3, respectively[31].
- Expected additional one-off costs for dismantling, decontamination of facilities and waste management due to a partial or complete business shutdown in case of Scenario 2 and Scenario 3, respectively[31].
- (If applicable) Expected further additional one-off costs/investments in case of Scenario 2 and Scenario 3, respectively[31].
- (If applicable) Expected additional annual operating costs in case of Scenario 2 and Scenario 3, respectively[31].

In a second survey round conducted at a short interval from the first one and targeting the same group of participants, information on the following additional variables was collected:

- Annual tonnage of fluoropolymers purchased from suppliers
- Percentage of fluoropolymer-dependent revenues associated with processing activities/component manufacturing activities

To encourage participants to provide data in spite of potential confidentiality concerns, in case of information pertaining to actual financial and employment figures as well as expected socio-economic impacts in case of a potential restriction, the DUs had to indicate their answers by selecting from predefined ranges instead of providing exact estimates. By aggregating the respective ranges across the DUs, lower and upper bounds for the different variables could thus be obtained. Notably, when indicating socio-economic impacts in case of a potential restriction, the DUs had the option to mark individual impact categories as not applicable for their legal entity for each of the hypothetical scenarios presented.

[30] Über den pro-K Kunststoffverband (pro-kunststoff.de)

[31] For simplification, to explain impact assessment Scenario 2, the companies were asked to consider a hypothetical scenario in which 25% of their product portfolio would be covered under use-specific derogations from a PFAS restriction. Scenario 3 was in turn described as a scenario in which 75% of their respective product portfolio would be exempted through derogations.

12.2 Data cleaning procedure for the results obtained in the DU survey

In order to ensure data quality and consistency for the information collected through the DU survey as well as to maintain a conservative approach for the impact assessment, data checks were conducted in agreement with the data cleaning procedure presented in Table 19. Notably, although there were 66 DUs who answered the first round of the survey, the pool of respondents was eventually restricted to 51 DUs who additionally provided information on the variables requested in the second survey round (see section 12.1).

Table 19: Data cleaning procedure implemented before analyzing the results obtained through the DU survey.

Condition to be fulfilled per DU	**Consequence(s) in case the condition is not fulfilled**	**Number of observations affected by consequence(s)**
Criteria concerning the first survey round		
The actual annual total EBIT must be smaller than the annual total revenues reported.	In case the condition was not fulfilled, the ranges indicated by the respective DU for total revenues, total EBIT, EBIT losses, one-off costs as well as operating costs were discarded from the analysis.	The condition was not fulfilled by 1 of the 66 DUs only.
The expected amount of annual EBIT losses in case of Scenario 3 cannot be larger than in case of Scenario 2.	In case the condition was not fulfilled, the ranges indicated by the respective DU for EBIT losses in case of Scenario 2 and Scenario 3 were discarded from the analysis and replaced with the minimum between the EBIT losses indicated and conservative estimates derived based on baseline data reported by the DU[32].	The condition was not fulfilled by 24 DUs (36.4%).
The expected amount of annual EBIT losses in case of Scenario 2 and Scenario 3, respectively, cannot be larger than the actual annual total EBIT.	In case the condition was not fulfilled, the ranges indicated by the respective DU for EBIT losses in case of Scenario 2 or Scenario 3 were discarded from the analysis and replaced with conservative estimates derived based on baseline data reported by the DU[32].	The condition was not fulfilled by 9 DUs for Scenario 2 and 3, respectively (13.6%).
The expected number of FTEs dismissed in case of Scenario 3 cannot be larger than in case of Scenario 2.	In case the condition was not fulfilled, the ranges indicated by the respective DU for FTEs dismissed in case of Scenario 2 and Scenario 3 were discarded from the analysis and replaced with the minimum between the FTEs dismissed indicated and conservative estimates derived based on baseline data reported by the DU[32].	The condition was not fulfilled by 17 DUs (25.8%).
The expected number of FTEs dismissed in case of Scenario 2 and Scenario 3, respectively, cannot be larger than the actual total number of FTEs employed.	No consequence was needed as this condition was fulfilled by all DUs.	The condition was fulfilled by all DUs.

[32] In lack of better estimates, it was assumed that in case of Scenario 2 any given DU would lose 75% of the EBIT and need to dismiss 75% of the FTEs depending on fluoropolymers. In case of Scenario 3, 25% of the respective EBIT and FTEs were assumed to become lost and dismissed, respectively. To compute the fluoropolymer dependent EBIT and FTEs for any given DU, the % share of total revenues depending on fluoropolymers reported by the respective DU was assumed to remain applicable for the dependencies with respect to EBIT and FTEs.

The expected amount of additional one-off costs due to dismantling/decontamination/waste management (in case of a partial/complete shutdown) in case of Scenario 3 cannot be larger than in case of Scenario 2.	In case the condition was not fulfilled, the ranges indicated by the respective DU for additional one-off costs in case of Scenario 2 and Scenario 3 were discarded from the analysis.	The condition was not fulfilled by 12 DUs (18.2%).
The expected total amount of additional one-off costs for dismantling/decontamination/waste management as well as further investments in case of Scenario 2 and Scenario 3, respectively, cannot be larger than 55% of actual annual total revenues.	No consequence was needed as this condition was fulfilled by all DUs.	The condition was fulfilled by all DUs.
The expected amount of additional annual operating costs in case of Scenario 2 and Scenario 3, respectively, cannot be larger than 35% of actual annual total revenues.	No consequence was needed as this condition was fulfilled by all DUs.	The condition was fulfilled by all DUs.
For any further additional one-off costs indicated as expected in case of Scenario 2 and Scenario 3, respectively, a valid description had to be provided.	In case either no description for the indicated costs was specified or the description specified accounted for cost categories which could not be considered in the impact assessment[33], the one-off costs indicated for Scenario 2 or Scenario 3 were discarded from the analysis.	The condition was not fulfilled by 12 DUs for Scenario 2 and Scenario 3, respectively (18.2%).
For any additional annual operating costs indicated as expected in case of Scenario 2 and Scenario 3, respectively, a valid description had to be provided.	In case no description for the indicated costs was specified, the operating costs indicated for Scenario 2 or Scenario 3 were discarded from the analysis. In case the description specified referred to one-off costs, the operating costs indicated for Scenario 2 or Scenario 3 were considered as one-off costs.	The condition was not fulfilled by 12 DUs for Scenario 2 and Scenario 3, respectively (18.2%). Out of the 12 DUs, only 2 DUs indicated one-off costs as operating costs only.
Criteria concerning the second survey round		
The total annual tonnage of fluoropolymers purchased from suppliers had to be provided.	In case no information was provided, the entire data provided by the respective DU was discarded from the analysis.	The condition was not fulfilled by 15 DUs.
The percentage of fluoropolymer-dependent revenues associated with processing activities/component manufacturing activities had to be provided.	In case no information was provided, the entire data provided by the respective DU was discarded from the analysis.	The condition was not fulfilled by 15 DUs.

[33] Cost categories such as severance payments and loans were not considered net impacts in the EEA and thus excluded from the current impact assessment.

12.3 Analysis to verify robustness of results after extrapolation

In order to re-confirm that the extrapolation conducted in case of the socio-economic results obtained at the level of fluoropolymer processors (see section 5.2) yielded robust values, the present section introduces a comparative analysis based on further survey data collected independently by the pro-K Group.

Methodology

Independent from the data collection efforts conducted by Ramboll for the present assessment (see sections 12.1 and 12.2), information with respect to annual tonnage of fluoropolymers used and annual fluoropolymer-dependent sales revenues registered by fluoropolymer processors in the EEA was separately collected by the pro-K Group. Such data corresponding to 18 respondents covering overall a tonnage of fluoropolymers used of 8,964.60 tonnes was obtained by Ramboll from the pro-K Group. For comparison purposes, by multiplying the aggregated annual sales revenues of these 18 respondents by a factor equal to the ratio between the total annual tonnage of fluoropolymers processed in the EEA (51,000[9] tonnes per year) and the aggregated tonnage corresponding to the respondents (yielding a multiplication factor of 5.69), an extrapolation of the reported annual sales revenues could be conducted to obtain a representative value for all EEA fluoropolymer processors.

Results

By following the approach described above, annual sales revenues associated with fluoropolymer processing activities of roughly 3.45 billion Euros per year are estimated for all EEA fluoropolymer processors (Table 20). Notably, these revenues are roughly 3 times larger compared to the revenues registered by the fluoropolymer producers in the EEA (1.03 billion Euros per year) (see section 3.2.1). Assuming that the economic losses incurred in the EEA in case of a restriction are proportional to the revenues associated with the use of fluoropolymers, it can be expected that the economic costs computed for fluoropolymer processors in the EEA are about 3 times larger than those derived in the case of fluoropolymer manufacturers. This expectation is indeed re-confirmed by the results obtained for producer surplus losses in the current impact assessment (see Table 14). In this case, the forgone profits in case of a restriction computed for fluoropolymer processors are estimated at least between 5.08 – 27.21 million Euros per year, whereas the foregone profits associated with fluoropolymer manufacturers lie at least between 2.38 – 9.54 million Euros per year (see Table 14). Overall, this re-confirms the robustness of the extrapolated results obtained in case of fluoropolymer processors (see section 5.2). Importantly, as previously emphasized in the current report, the producer surplus losses summarized in Table 14 are likely largely underestimated due to the methodology used[34].

[34] The producer surplus losses derived in this report are computed by assuming that foregone profits would be incurred for a period of 2 years only. However, it is likely that such foregone profits are accumulated for much longer than this 2-year period, considering the limited feasibility for substituting fluoropolymers in the different applications (see footnote 13).

Table 20: Annual sales revenues associated with fluoropolymer processing activities estimated for fluoropolymer processors in the EEA based on data collected independently by the pro-K Group.

Measure	***Estimated result***
Annual sales revenues associated with fluoropolymer processing activities registered by 18 responding fluoropolymer processors in the EEA [in million Euros / year]	607.15
Estimated annual sales revenues associated with fluoropolymer processing activities registered by all fluoropolymer processors in the EEA [in million Euros / year] (after extrapolation)	3,454.10

CHEMSERVICE

TECHNICAL REPORT:

Analysis of alternatives to fluoropolymers and potential impacts related to substitution in different sectors of use

Version 1

19 July 2022

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Executive Summary

This report describes in detail a selection of specific applications in which different fluoropolymers are used. The objective of the report is twofold; on one side, it intends to highlight the key combination of properties that fluoropolymers provide in a selection of high technology industries. On the other side, a detailed description of possible alternatives to fluoropolymers is given, and expected trade-offs related to a hypothetical substitution of fluoropolymers by such alternatives are described and justified. This aims at explaining what could be the consequences that should be expected (not only for direct industrial users, but for the European society as a whole) if the use of fluoropolymers was to be discontinued due to a potential regulatory ban that could be derived from the inclusion of fluoropolymers in the scope of the upcoming PFAS restriction under REACH.

It is worth highlighting that the scope of this report is limited to fluoropolymers as a clearly separate family of substances within the broad group of PFAS, including other polymeric PFAS such as perfluoropolyethers and side chain fluorinated polymers, which should not be confused with fluoropolymers and are definitely not in the scope of the present report.

The case studies that are described in this report are based on specific applications as reported by a selection of downstream users of fluoropolymers. Those downstream users were requested to provide information via a detailed questionnaire developed specifically for this project. Where relevant, one-to-one conferences with the respondents were set-up in order to expand on the replies provided, in order refine and expand on the information provided. This information has been complemented with publicly available literature or references with the objective to further clarify the application described.

Where available, information on expected socio-economic impacts related to a potential substitution (or lack of availability) of fluoropolymers has been provided. Information in this case has been usually sought from industry associations involved in some of the specific industrial sectors covered.

It should be noted that the applications described in this report should be considered as a reduced sample of the broad industrial sectors that rely on fluoropolymers today. Further work is expected to be developed in order to add further cases, and to expand on the socio-economic impacts of fluoropolymers for critical industrial sectors in Europe.

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List of abbreviations and acronyms

ACEA	European Automobile Manufacturer's Association
ACM	Acrylic Rubber
AEM	Ethylene acrylate copolymer
ASTM	American Society for Testing and Materials
BAT	Best Available Techniques
BPA	Bisphenol A
BPS	Bisphenol S
C/A	Chlor/Alkali
CMR	Carcinogenic, mutagenic, or toxic for reproduction
COM	European Commission
DHBP	4,4'-dihydroxybiphenyl
EEA	European Economic Area
EFPIA	European Federation of Pharmaceutical Industries and Associations
EL	Electrolyser
EPDM	Ethylene propylene diene rubber
EPR	Ethylene propylene rubber
ETFE	Ethylene tetrafluoroethylene
ESIA	European Semiconductor Industry Association
EU	European Union
EV	Electric vehicles
FEP	Fluorinated ethylene propylene
FKM	Vinylidene fluoride-hexafluoropropylene copolymer
FPG	Fluoropolymers Product Group - PlasticsEurope
GDP	Gross domestic product
GHG	Greenhouse Gases
JRC	Joint Research Centre
HFC	Hydrofluorocarbons
HFFR	Halogen free flame retardants

HFO	Hydrofluoro-olefins
HNBR	Hydrogenated nitrile butadiene rubber
HVACR	Heating, Ventilation, Air Conditioning and Refrigeration
ISO	International Organization for Standardization
MBR	Membrane bioreactor
MDI	Methylene diphenyl isocyanate
MLD	Minimal Liquid Discharge
MNB	Mononitrobenzene
MVQ	Methyl Vinyl Silicone Rubber
NBR	Nitrile butadiene rubber
NSF	National Sanitation Foundation (USA)
OECD	Organisation for Economic Co-operation and Development
PAG	Polyalkylene glycol
PAI	Polyamideimide
PBI	Polybenzimidazole
PE	Polyethylene
PEEK	Polyether ether ketone
PEI	Polyetherimide
PEM	Proton Exchange Membrane
PES	Polyether sulfone
PET	Polyethylene Terephthalate
PFA	Perfluoroalkoxy polymer
PFAS	Per- and polyfluoroalkyl substances
PLC	Polymer of Low Concern
POE	Polyester oil
POM	Polyoxymethylene
PP	Polypropylene
PPSU	Polyphenyl sulfone
pro-K	German Association for Semi-Finished Plastics and Consumer Products

PTFE	Polytetrafluoroethylene
PU/TPE-U	Thermoplastic Polyurethane
PVC	Polyvinyl chloride
PVDF	Polyvinilidene fluoride
PVE	Polyvinyl ether oil
RACHP	Refrigeration, Air Conditioning, and Heat Pump
REACH	EU Regulation 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals
RES	Renewable energy sources
R&D	Research and Development
SME	Small and medium enterprise
UHMWPE	Ultra-high molecular weight polyethylene
UV	Ultraviolet radiation
VoP	Velocity of Propagation

1. Introduction

Fluoropolymers are a separate family of fluorinated polymers, which can be clearly differentiated from other substances typically included in the Per-and polyfluoroalkyl substances (PFAS) group of chemicals. In fact, they can also be further differentiated from other polymeric fluorinated substances, such as side-chain fluorinated substances or perfluoropolyethers (FPG, 2022a). Fluoropolymers are structurally characterised by having fluorine atoms directly attached to their carbon-only backbone.

Existing scientific data demonstrates that, because of their unique characteristics such as the negligible solubility in water or the high molecular weight, fluoropolymers cannot enter or accumulate in the human bloodstream, and cannot degrade into other PFAS under intended use conditions, nor under environmental conditions at the end-of-life phase of their applications. Therefore, it is considered that fluoropolymers do not impact water quality, and do not pose a significant risk human health, or the environment (Henry et al., 2018). This allows the conclusion that by far most fluoropolymers meet the Organisation for Economic Co-operation and Development (OECD, 2009) criteria to be identified as Polymers of Low Concern (PLC). While originally the focus was placed on a set of 4 fluoropolymers, more recent research has expanded these conclusions to cover a larger number of substances, reaching an estimate of >96% volume of fluoropolymers in the global market (Korzeniowski et al., 2022).

However, since fluoropolymers match the OECD definition of PFAS, they could be included in the scope of the restriction proposal that five Competent Authorities from Member States of the European Economic Area[1] (EEA) have announced on the broad PFAS group of chemicals under the REACH Regulation[2]. Therefore, fluoropolymers could face market restrictions in the EEA if their differentiated properties are not clearly highlighted in such restriction proposal. This could even lead to a ban on the uses of these high value materials in the different applications in which they are used.

While the uses of fluoropolymers are primarily related to industrial applications, these substances are involved in value chains that have a strong impact in many sectors and articles that will eventually reach end-users. Fluoropolymers also play a key role in enhancing key avenues of progress that have been highlighted as extremely relevant to ensure environmental objectives and industrial autonomy in the EEA, such as transport, semiconductors, telecommunications, renewable energy, or chemical processing industries.

Fluoropolymers have unique physicochemical properties which render them specialty plastics that are virtually chemically inert, non-wetting, non-stick, and highly resistant to temperature variability, fire, and weather and exhibit low flammability. They also display features such as low coefficient of friction, dielectric strength, and flexibility. These properties, and particularly the joint combination of all of them in single products, make them irreplaceable in many

[1] European Union (EU) 27 + Iceland, Norway, and Liechtenstein

[2] Regulation (EC) No 1907/2006

applications, and it is commonly accepted that their unique set of properties cannot be matched by alternative materials, particularly in the wide range of operability they offer. In fact, fluoropolymers are frequently the high-cost option in many industries, being the material of choice only when other products are known to fail to provide the required properties for the desired application.

The objective of this report is to highlight specific examples of uses of fluoropolymers, with details on how the benefits that these materials provide to the use are related to the combination of properties they offer. In addition, an evaluation of potential alternative substances that could be used to replace fluoropolymers in each use has been performed. Potential trade-offs that could be expected due to substitution have been highlighted, not referring to impacts on the direct uses, but on potential consequences that could be expected down the value chain and which could affect the general population, as well as broader environmental and innovation expectations within the EEA.

Information on the case studies that are described in this report has been collected via questionnaires that were delivered to a set of downstream users involved in primary handling of fluoropolymers. The questionnaire was also shared with a number of associations representing different industrial sectors involved in the use of fluoropolymers. Since some of these associations delivered the questionnaire to their members, it is not possible to establish the number of users that received it. A total of 27 responses were collected, which were then filtered in terms of quality of the information provided. Where deemed useful for a better understanding of the case, one-to-one videoconferences were organized with the respondents. It should be noted that due to time constraints and complexity issues, most of the cases described have been built with feedback from only one responding company. Efforts have been made to reassure the reliability of replies received (with cross-checking information from public literature), and final versions of the cases have been double-checked with experts from the German Association for Semi-Finished Plastics and Consumer Products (pro-K) for final validation. A copy of the questionnaire that was delivered to the downstream users can be found in **Annex I**.

Where available, information on the relevance of each sector of use in terms of socio-economic importance for the European society has been highlighted. This information has been provided by the sectorial associations that could be impacted due to a ban on the use of fluoropolymers. However, most of the respondents were primary users of the fluoropolymer substances in very complex value chains. For this reason, the potential impact of a restriction on the use of fluoropolymers in each application may be difficult to quantify. In any case, it is clear that the socio-economic importance of fluoropolymers increases significantly through the different steps in the multiple value chains in which they are involved.

The list of fluoropolymers covered in this report can be found in **Annex II**.

2. Properties of fluoropolymers and socio-economic importance

The key properties that fluoropolymers provide to a wide variety of industrial applications can be summarised as follows (FPG, 2021):

- Inertness and non-reactivity; high resistance to corrosion and chemical attack.
- Low and high temperature resistance: with a range as large as -263°C to +260°C for PTFE.
- Very low coefficient of friction to any solid.
- Low and ultra-low permeation rates.
- Ultraviolet radiation (UV) resistance.
- Excellent electrical insulation, low dielectric constant, low variations of conductivity.
- High level of fire safety; no flame propagation and low smoke generation.
- High and ultra-high purity with extremely low leach out properties.
- Stress-crack and cut-through resistance.
- Flex fatigue properties enabling thermal expansion/contraction in temperature cycles.
- Biocompatibility.
- High Flex life
- Durability.
- Hydrophobicity; neither water nor water-containing substances wet fluoropolymers, providing excellent repellent properties to many chemicals.
- Non-stick, and consequently non-fouling properties, along with sufficient bonding in certain multilayer applications.

In terms of socio-economic value of fluoropolymers, the Fluoropolymer Group of PlasticsEurope (FPG) has currently updated information (FPG, 2022b) from a previous socio-economic analysis that was performed on these substances (FPG, 2017). However, it is worth noting that this information is limited to the production, employment and revenue values of the fluoropolymer manufacturers and importers in the European Union (EU). While relevant, the importance of these figures is clearly minimised in comparison of the value that fluoropolymers enable downstream for end use applications. For example, while total revenue obtained from the whole fluoropolymer industry in the EEA in 2020 was of 740 million EUR (with 70 million EUR directly sold to the electronics industry), the revenue reported by the European Semiconductor Industry Association for the same year was 32.85 billion EUR (ESIA, 2020). As reported by downstream users, modern semiconductors cannot be produced without the use of fluoropolymers in the process, as will be explained in one of the case studies covered in this report. This means that fluoropolymers can multiply their direct value by nearly 500 times in the applications in which they are used, which gives a clear indication of their critical relevance for many important industries in Europe.

3. Case studies evaluated

3.1. Sector of use 1: Industrial uses

3.1.1. Application 1.1: Use of PTFE, PFA and ETFE in the production of lined equipment in the chemical processing industry

Description of the application

Polytetrafluoroethylene (PTFE), Perfluoroalkoxy polymer (PFA), and Ethylene tetrafluoroethylene (ETFE) are used in pipes, expansion joints, vessels, and fittings for the chemical processing industry, with the objective to protect equipment from direct contact at high temperatures (up to 230°C) and very aggressive media, such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4) or hydrofluoric acid (HF). Other highly aggressive substances may be sodium hydroxide (NaOH), potassium hydroxide (KOH), or sour gases.

As an example, desorption columns lined with PTFE are used in the recycling process of hydrochloric acid in the chemical industry. Streams with low acid concentrations are treated in these desorption columns, resulting in more concentrated streams that are then reused in the initial or further processes within chemical plants.

When there is no need to protect equipment or chemical products from the effect of corrosion, black steel piping and fitting systems are currently used by the chemical processing industry. An example of this could be the mineral oil industry. Such unprotected steel constructions are however limited to situations in which:

- Chemicals are not corrosive (or less corrosive) to steel.
- Processes in which short system lifetime (e.g., cycles of 2 years) is acceptable.
- Metallic ion impurities in the streams handled in the relevant processes do not raise situations of concern, neither from a quality nor from a safety perspective.
- Additional cleaning steps are available, that can remove the above-mentioned impurities. However, such systems add costs to the process.

It should be noted that such cases are not frequent in the chemical process industries, and that some sort of corrosion protection on the equipment to be used is typically required.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Flexibility
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation, between (-250°C to + 230°C)
- Barrier properties (low permeation of process media through fluoropolymer liner)

- Non-stick properties
- Flex fatigue properties to enable thermal expansion/contraction during temperature cycles

General description of alternatives and comparison with fluoropolymers

Some alternatives that could be considered for these applications are**:**

- Polypropylene (PP) lining systems
- Rubber lining systems
- Tantalum-based piping
- Stainless steel (V2, V4, 316 L, Hasteloy, Inconel) and some precious metals
- Enamel / glass lining systems

PP and rubber lining systems

These alternatives could work only under a narrower range of operating conditions. PP or rubber-based systems would only withstand temperatures up to 100-120°C without degradation, in comparison to higher temperatures (230°C) that are required for some processes, in which fluoropolymers are effective. Furthermore, the lifetime and duration of these lining systems is lower than 5 years.

These alternatives are sufficiently available and at a competitive price in comparison with fluoropolymers. In fact, where the process conditions do not require the use of fluoropolymers, they are already implemented by industry as the material of choice. However, it needs to be considered that due to much shorter lifetimes, PP or rubber lined equipment for the chemical industry would need to be frequently replaced if these systems were to be used under aggressive conditions, and therefore costs would be significantly increased.

Tantalum based piping

In principle, tantalum may offer similar performance as compared to fluoropolymers in the chemical process industry.

However, tantalum is more expensive and not competitive when compared to fluoropolymers. In addition to this, it is highly unlikely that tantalum supply could cover the demand that would be required to completely replace fluoropolymers in this application for the whole European chemical industry. Furthermore, tantalum is ranked as a conflict mineral which is frequently mined under unclear conditions. Therefore, supply (as well as prices) of this metal could be subject to significant constraints and result in business uncertainty in the future.

Stainless steel (V2, V4, 316 L, Hasteloy, Inconel) and some precious metals

Stainless steel offers similar chemical resistance like PTFE or PFA. Harsh, corrosive chemicals may extract metal ions in low concentration from the steel. While this could be acceptable in

some applications, it renders this alternative not feasible for use in cases in which high purity would be required.

This alternative is much more expensive compared to the combination black steel + PTFE/PFA used in current piping systems. The costs of using this alternative may go up to 5 times higher than the use of fluoropolymer lined systems. In special cases, metals like silver or even gold may be considered; in such cases, the cost of the alternative options could be 10 times higher, or more.

Enamel / glass lining systems

Enamel or glass based lined pipes could work under certain conditions, but not reaching the wide range of temperatures and aggressive media that fluoropolymers can withstand. These materials are brittle and could break easily when subject to temperature changes or acid attack. Service life of piping systems would be much shorter than with the use of fluoropolymers (perhaps reaching 5 years, but certainly below 10 years, in comparison to fluoropolymers that can last decades in operation).

Enamel glass linings are also more expensive than fluoropolymers (estimated at twice the price). Again, the need for further maintenance and higher replacement rates of these systems renders them as a non-viable option as an alternative to fluoropolymers in this application.

Potential impacts related to substitution

Use of PP, rubber or enamel/glass lined piping and fitting systems could create high risks situations for workers and the environment. The probability of cracking and integrity failure would be significantly increased in the process industry. This would be particularly critical when strong acids such as hydrochloric acid, sulfuric acid or hydrofluoric acid are used, which are highly corrosive and could generate great damage on workers and the environment.

Related to the hydrochloric acid example, PTFE linings are used to protect steel shell, pipes, and other equipment from direct contact to hot, concentrated hydrochloric acid. PTFE linings are critical for safe operation since they eliminate or minimize corrosion. Corrosion on equipment results in risk of leakage and severe accidents. Depending on process conditions, corrosion can appear within hours of operation and can have sudden, unpredictable effects, potentially leading to serious injuries to workforce, contamination of the environment and operational downtime. Hence, PTFE liners allow for the safe production of high-quality hydrochloric acid.

Many chemical establishments in the EU are multi-purpose plants, which means that they can run different processes at different times. For example, one process may be run for which P systems could be effective, but after a few weeks, a new process could be undertaken in which the combined properties that fluoropolymers provide are required. A scenario in which fluoropolymers would not be available for use in the process industry would create a significant challenge in terms of restructuring and reorganizing chemical establishments and in the end, it is likely that companies would decide to run their processes involving harsh

conditions (e.g., involving strong acids at high temperatures) in other locations outside the EEA where the use of fluoropolymers would still be allowed. This could result in the loss of a significant part of basic chemicals production within the EEA and severely damage the objectives of developing a stronger industry.

The possibility to replace fluoropolymer-based lining systems with stainless steel or other metals, which could work from a technical perspective in certain cases, would likely generate significant market distortions. This is because only the larger chemical companies may afford replacing the piping, vessels and fitting systems lined with fluoropolymers, and still this could also reduce the flexibility of those companies to run certain processes. Small and Medium Enterprises (SMEs) in the EU would be significantly impacted if they were forced to substitute fluoropolymers with metal-based alternatives.

It should also be noted that the use of PP or rubber lined piping systems would lead to the need of more frequent maintenance and replacement. This would significantly increase the amount of these products that would need to be disposed. For PP, recycling options are not identified, therefore the amount of waste of this material would increase dramatically, and therefore objectives related to a circular economy in the EEA would be jeopardized. Moreover, if fluoropolymers were to no longer be used in chemical plants, this could imply the need to take down such installations and subsequently starting them up again, which are two high risk instances that should be avoided

Regarding the hydrochloric acid example, it should be noted that this is a main chemical base material (~20 million tonnes produced per year worldwide) which is used in the production of further essential chemical base materials. For example, hydrochloric acid is used for the production of polysilicon materials (wafer, computer chips and connected markets), in the steel industry (refining ore, pickling and cleaning of metal, etc.), for food production, in the oil industry, for production of pulp and paper, and other industries, all of which would be directly impacted if fluoropolymer lined piping and fitting systems would not be available.

In addition to these end users, a significant number of companies supplying using fluoropolymers for the production of this kind of systems to the general chemical industry would face significant challenges, since they have developed high technical expertise on fluoropolymer-based piping equipment. Continuity of all these business in the EEA would be at risk.

Conclusions on the application

Single alternatives could eventually cope with some of the requirements required in the chemical industries, in terms of equipment protection. However, it is the combination of properties that fluoropolymers provide, particularly high resistance to chemical attack and wide range of temperature of operation, combined with low permeation and non-stick properties for a smooth development of chemical processes, which render them as the material of choice for many chemical industries in the EEA. Substitution by the limited set of

alternative materials would create a wide variety of problems both for the industries directly involved (e.g., suppliers and users of piping and fitting systems), as well as for the European society as a whole. On one hand, high risk situations for workers and the environment may be created, involving processes dealing with strong acids at high temperature. On the other hand, the use of alternatives could lead to situations in which conflict minerals would be required (tantalum), with significant ethical constraints as well as economic ones (related to volatile pricing and supply uncertainty), or to significant increase of waste streams of other plastics or rubber that could pose a challenge to the circular economy objectives. Ultimately, it is reasonable to assume that, should fluoropolymers not be available for this application, significant relocation outside the EEA of a large number of companies (mostly, but not only, SMEs) may occur, not only of direct downstream users of fluoropolymers, but of end-use industries that work with fluoropolymer based piping and fitting systems in the chemical industry.

In conclusion it can be stated that, evaluating jointly the benefits of continued use of fluoropolymers, as well as the negative effects that could be generated for the European society if fluoropolymers were not available for these applications, the continued use of fluoropolymers in in lined piping and fitting systems for the chemical industry should be granted to ensure a safe, sustainable, and competitive chemical industry.

3.1.2. Application 1.2: Use of PFA, PTFE, FKM in the production of lined pumps in the chemical processing industry

Description of the application

PFA and PTFE are used for lining pumps in the chemical processing industry, with the objective to avoid corrosion under specific conditions of chemical attack. In addition, vinylidene fluoride-hexafluoropropylene copolymer (FKM) based seals such as o-rings are used in those processes to avoid releases of hazardous materials.

An example that can be highlighted of this use is related to chemicals involved in the manufacture of polyurethane foams, which are used for example in building insulation. mononitrobenzene (MNB) is used for the production of methylene diphenyl isocyanate (MDI), which is a raw material for the production of polyurethane. In the process, sulfuric acid is diluted with nitric acid (HNO3) to produce MNB. The use of nitrosulfuric acid leads to a highly corrosive environment.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical properties, e.g., flexibility (ASTM D2176 - Test Method for Folding Endurance of Paper and Plastics Film by the MIT tester, with MIT > 1 million)
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation (between (-60°C to + 200°C)
- Barrier properties (minimum wall thickness 3.5 mm)

General description of alternatives and comparison with fluoropolymers

Chrome/Nickel alloys are usually considered as possible alternatives for this use. While these materials can be used for lining in pumps to operate certain chemical processes, and are still in use today, they are not able to cope with every specific anti-corrosion situation. In fact, those alloys were used for the lining of pumps and seals used for the MNB plants in the 1970s, however this led to frequent failure of the equipment, resulting in significant challenges in terms of maintenance and safety, related to corrosion and leakage from mechanical seals.

The introduction of PFA/PTFE lined pumps in the 1980s solved safety (related to unexpected releases of highly corrosive material that could reach operators) as well as environmental issues (due to release of ecotoxic mixtures). These systems offer a much higher protection against corrosion in this chemical process and minimise the need for replacement of the equipment, resulting in higher efficiency but also in increased worker and environmental protection. Particularly, PTFE-based systems (magnetic coupling pumps with stationary sealing) replaced mechanical sealed (rotating sealing) pumps which are more effective to avoid leakage to the environment.

It should be noted that in the past, other materials such as those described in **Application 1.1** (enamel/glass or rubber-based lined pumps) were used for this application, however corrosion always led to significant difficulties for developing the process in a safe and reliable way.

Potential impacts related to substitution

Returning to the use of chrome/nickel alloys would significantly damage the efficiency of the MNB/MDI process in the production of polyurethane foams. More importantly, it would increase risk of corrosion in processing plants and increase risk of damage to humans and the environment, not to mention the reduction in efficiency of the process and higher costs related to the need for more frequent maintenance and replacement of equipment. It is to be expected that such increases in costs would be transferred through the supply chain, reaching the end users of polyurethane foams. Replacement by other materials such as rubber or enamel is not considered as they are of even inferior performance compared to chrome/nickel alloys for this application.

Conclusions on the application

Industrial equipment based on chrome/nickel alloys is still in place and used nowadays to provide for corrosion protection in certain chemical plants. Corrosion guides are available for critical fluids and conditions which describe the corrosion resistance. The selection of the adequate material for key industrial equipment such as pumps must be done on a case-by-case basis, however frequently mixed fluids (e.g., sulfuric acid and nitric acid) are not always described in those guides, and therefore the company developing specific processes needs to test the specific material of choice on a case-by-case basis.

Removing fluoropolymer lined pumps and seals from the market would push technology back to levels of the 1970s and reduce the choice of materials for extremely corrosive chemical processes, which would result in a decrease of safety and environmental standards, as well as a reduction of the competitiveness of the European industry. Processes that today are run using fluoropolymer- based solutions (which occurs only when other materials that continue to be available on the market, such as chrome/nickel alloys, do not perform properly) would likely be moved to other countries where fluoropolymers are still allowed, and products manufactured in such processes would likely need to be imported rather than manufactured in the EEA.

3.1.3. Application 1.3: Use of PTFE matrix composites in the production of seals and gaskets for industrial machines

Description of the application

PTFE-based materials are essential components of highly reliable sealing mechanisms. These mechanisms are applied in a wide variety of industrial sectors, such as the chemical processing industry, automotive, aviation, food processing, and power generation.

Gaskets are a typical system to keep two pieces of an equipment together. They are defined as a mechanical seal which fills the space between two or more mating surfaces, generally to prevent leakage from or into the joined objects while under compression. It is a deformable material that is used to create a static seal and maintain that seal under various operating conditions in a mechanical assembly.

PTFE based seals and gaskets are used across a broad range of industries that require processing harsh chemicals. They are used in the vast majority of manufacturing plants involving chemical processes. One example is the Chlor/Alkali (C/A) process in which chlorine, sodium hydroxide and hydrogen are produced via electrolysis. These chemicals are then used in a broad range of applications. This process requires highly reliable sealing systems which are based on PTFE to guarantee adequate performance.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (15-40 MPa)
- Flexibility
- Low coefficient of friction (maximum 0.2)
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation (-100°C to + 250°C)
- Weather resistance
- Non-stick properties
- Fire retardancy / smoke suppression
- Low bacterial / algae growth

General description of alternatives and comparison with fluoropolymers

Asbestos fibre gaskets have been highlighted as potential replacements for PTFE-based sealing systems. These systems were used in the past and they could have satisfactory performance but certainly not at the levels that fluoropolymers provide, particularly in extreme conditions of mechanical strength required, variability of temperatures and chemical conditions. Other elastomers such as hydrogenated nitrile butadiene rubber (HNBR) and plastic materials, such

as polyethylene (PE) or PP, could eventually be used but providing limited mechanical strength and chemical resistance.

Potential impacts related to substitution

Ensuring proper sealing systems is a critical feature in the chemical processing industry. Failure in these systems could result in the release of hazardous materials and pose a risk to workers and the environment. Furthermore, the lower performance of alternatives would result in the need for increased maintenance procedures, resulting in additional costs for companies as well as an increase of waste material. Materials such as polyurethane, PP or HNBR, are expected to have a lifetime of 50% compared to PTFE based seals and gaskets. PTFE-based solutions are frequently more expensive and are used only when it is known that other materials will not provide the desired performance, to a point in which the application may result not viable.

Looking at the C/A example, according to the Best Available Techniques (BAT) for this process (JRC, 2014), the development of non-asbestos sealing systems started in the 1970s, taking about 10-15 years until viable alternatives to asbestos were introduced. These alternatives are all based on PTFE-based sealing systems. According to the Joint Research Centre (JRC), "With its superior characteristics regarding stability against chlorine, caustic soda, and other chemicals, as well as its dimensional stability, it was considered an ideal alternative to asbestos. Asbestos swells during operation in a diaphragm cell and this increases the energy demand. PTFE does not show this swelling effect, and therefore the energy demand would be lower. In addition, the high stability against chlorine and caustic soda should result in the diaphragm having a very long lifetime."

In terms of economic relevance, it is estimated that the C/A process covers approximately 25% of the EU specialty chemical industry which has a revenue of roughly 225 million EUR[3]. C/A is a good proxy for harsh chemicals because it tracks with the key processing attributes that rely on PTFE sealing solutions. These processes outstand for their reduced risks of leaks which protect safety of people and the environment. Harsh chemical processing has an essential function for the EU chemical manufacturing industry, and it is interlinked with a large number of downstream industries. Just to name a few, the following very different sectors can be considered:

- Agriculture: 178.4 billion EUR turnover and 9.7 million jobs in 2020[3].
- Chemical manufacture: 588.88 billion EUR turnover and 1.2 million jobs in 2019[3].
- Semiconductors: 40.43 billion EUR turnover and 200,000 jobs in 2021 (ECIA, 2022)

The economic impact of disruption in EU chlorine production would flow from initial production through all end use applications of the material, amplifying the effect. The propagation of the impact would be similar for other harsh chemicals such as sulfuric acid.

[3] Data provided by responses to the questionnaire based on information from Statista and Eurostat.

The use of asbestos fibre gaskets as an alternative to fluoropolymers would result in an increased risk of cancer due to the well-known carcinogenic properties of this material. Because of this, disposal of materials containing asbestos is complex and regarded as a hazardous activity, which needs to be considered as sealing systems using asbestos in the chemical industry would need to be more frequently replaced.

Conclusions on the application

Ensuring adequate sealing of machinery and equipment used by a wide variety of industries is of outmost importance. Materials used for this function need to be reliable and frequently withstand extreme conditions in terms of temperature, mechanical strength, and chemical attack. If those industries are not able to provide the required performance, significant impacts would be expected in terms of malfunctioning of such equipment, which could result in damage to people and releases of chemicals to the environment. Furthermore, inefficient sealing systems would result in sub-optimal operating conditions which could result in increased energy consumption leading to higher emissions of greenhouse gases (GHG), which could have a negative impact on the overall environmental objective established in the Green Deal.

Downgraded performance would imply reduce competitiveness of the European industry in many sectors. Industrial companies based in the EEA would face significant issues to maintain their high levels of performance and efficiency, so it is quite possible that those companies would eventually relocate their production to non-EU countries where the use of fluoropolymer-based seals and gaskets may still be allowed (even more so if the restrictions are expanded to other components that would also require fluoropolymers, see case 1.1). This situation will imply also that the technology will be transferred to the non-EU area so a loss of knowledge will occur.

Removal of PTFE-based seals and gaskets would kick technology backwards by 50 years, since technical solutions to asbestos in sealing systems in, for example, the C/A process were initiated in the 1970s. The use of PTFE for this process is currently considered Best Available Technique and removing it from the market would go against significant achievements made in the field of chemical process innovation, in addition to having replaced a well-known human carcinogen substance, a feature that is not shared by PTFE which is regarded as a Polymer of Low Concern (PLC) due to the lack of hazardous properties for human health and the environment.

3.1.4. Application 1.4: Use of PSEPVE and PTFE matrix composites in the production of membranes for electrochemical processes

Description of the application

Sulfonated tetrafluoroethylene (PSEPVE) is used in the production of membranes used in the C/A process. PTFE matrix is used to reinforce those membranes. In the C/A process, chlorine and its co-products are created by electrolysing a salt solution with a direct electric current that ultimately converts chloride ions into chlorine.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (15-40 MPa)
- Flexibility
- Resistance to harsh chemicals
- Resistance to high temperature
- Wide temperature range of operation (-100°C to + 250°C)

General description of alternatives and comparison with fluoropolymers

The manufacture of chlorine is an industrial process that has been on-going for more than 100 years. Traditionally, the only two alternatives to the use of membrane cells are mercury cells and diaphragm cells. In the mercury cell process, sodium forms an amalgam (a 'mixture' of two metals) with the mercury at the cathode. This amalgam reacts with the water in a separate reactor called a decomposer where hydrogen gas and caustic soda solution at 50% are produced.

The diaphragm cell process works with a combination of water and sodium chloride to create a brine solution, which is processed and filtered to remove impurities. Heat is applied to the solution and more salt is added until the purified brine solution is prepared for the electric current. In this case, an asbestos diaphragm is usually used to separate the cathode and anode, which will create the current (Mesothieloma, 2017).

Potential impacts related to substitution

Both mercury and asbestos are toxic materials and could generate significant issues to human health. In fact, according to Eurochlor (2022), the mercury cell system for the C/A process has been discontinued in Europe since 2017. As per asbestos, indications provided in the application described previously (**Application 1.3** describing gaskets and sealing systems) remain valid. Socio-economic relevance of the C/A process described previously can also be considered relevant for the production of membranes for C/A cells.

Conclusions on the application

In addition to safety considerations, the membrane cell system to produce chlorine via the C/A process is much more effective, and it requires less energy to produce the same quantity of product (at a higher purity), than the two alternatives (mercury and diaphragm cells). There is currently no other alternative known that would work in this process, which would withstand the combination of chemical aggressive environment of operation and very high temperatures that can be achieved in the process. This is a perfect example to demonstrate how the use of fluoropolymers has allowed for innovation and improved safety conditions of operation, removing the use of well-known hazardous materials from a very important industrial use and replacing them by materials that meet the conditions of PLC. For this application, different types of fluoropolymers are relevant, such as sulfonated TFE (for the production of the membrane itself) and PTFE matrix composites (to protect and reinforce durability of the membrane).

3.1.5. Application 1.5: Use of PTFE, PVDF, PFA in the production of filter systems for waste treatment in the chemical processing industry, power plants and other sectors

Description of the application

PTFE, PFA and Polyvinilidene fluoride (PVDF) are used in filter bags and filter systems which are needed to convert predominantly toxic or hazardous components, such as gaseous dioxins and furans or nitrous oxides from highly aggressive and corrosive gas streams, bringing concentrations of those chemicals below established regulatory limits. Furthermore, PTFE is used in large heat exchangers that enable the desulphurisation process at power plants by maintaining required temperature conditions of treated streams.

Typical sectors involved are chemical processing industries, but also waste incineration, metallurgical processes, cement manufacturing and power plant flue gas cleaning, which have stringent environmental requirements in terms of limiting emissions to air.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength
- Wear resistance
- Flexibility
- Low coefficient of friction
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation
- Barrier properties
- Non-stick properties

General description of alternatives and comparison with fluoropolymers

There are potential alternatives materials such as fibre threads available from different suppliers. In the past, some of these contained asbestos, which needs to be taken into account from an overall safety perspective. Currently, these fibres provide lower performance, which results in higher power consumption and shorter lifespan of these materials (resulting in higher replacement rates, adding costs to the process and the value chain).

Such fibres are less resistant to higher temperatures, they have limited ability to incorporate catalysts and other active components which destroy or capture harmful emissions. Lower chemical resistance results in higher filter failures, increased emissions, and more frequent replacement.

Other materials such as PP and polyether sulfones (PES) can also be used for filter systems, but again they are not expected to perform at the same demanding conditions under which fluoropolymer-based filter pieces can provide reliable operation.

Potential impacts related to substitution

Emission control in harsh and aggressive environments is an essential function across many industries (e.g., construction, manufacturing of petroleum products, metallurgy, etc.) and is interlinked with many downstream industries. Filters containing fluoropolymers are used in the most demanding applications such as hazardous waste incinerators, to prevent toxic pollutants from being released to the environment. Products containing fluoropolymers have a common benefit of reducing risk of emissions, which protect health and safety for people and the environment. They are necessary for many industries to meet existing environmental emissions regulations.

Filters made with fluoropolymers also provide necessary cooling and cleaning for advanced electrical products to avoid overheating. It is assumed that nearly all the advanced semiconductor chip sets and memory devices imported into the EU use filters containing fluoropolymers. Semiconductors and memory devices are essential devices for the function of many end-uses across many industries. Likewise, the pharmaceutical industry may also require high levels of performance for filtering systems, which can only be achieved with the use of fluoropolymers.

Furthermore, when alternatives are evaluated, their potential toxicological and ecotoxicological impacts should be taken into consideration. In the case of PES, publications suggest that they may have potential endocrine disrupting properties and may actually be considered of equivalent concern to bisphenol A – BPA (Kang et al., 2014), and based on recent research, they are related to generation of other bisphenols during degradation (Li et al., 2022), therefore this and similar materials may not be considered a suitable alternative from a safety perspective, as this could lead to regrettable substitution.

Conclusions on the application

Fluoropolymers such as PTFE, PFA and PVDF are key components of filtering systems that are required in several industries in which hazardous chemicals are handled. The efficiency of such filtering systems is crucial to ensure adequate environmental protection, and operation within predefined regulatory limits. If fluoropolymers were not available for use in such applications, the possibility to comply with such limits could be impaired and operation in a number of sectors and industries may have to be discontinued due to failure to comply with existing regulatory standards. This would effectively force shutdowns and relocation of industries. In some processes with less demanding conditions, alternative materials may be used but this could imply more frequent demands, higher replacement rates and ultimately increased costs, which could be transferred through the value chains reaching the end users. More important, if substitution is forced with some alternative materials such as PES, there may be a risk of introducing potentially hazardous materials that could be related to endocrine disrupting effects.

3.2. Sector of use 2: Energy production

3.2.1. Application 2.1: Use of PTFE, PVDF and FKM in the production of lithium-ion batteries

Description of the application

PTFE and PVDF are used as electrode binders and separator coatings in lithium-ion (Li-ion) batteries, providing interconnectivity within each electrode. This facilitates electronic and ionic conductivity, increasing the cell manufacturing productivity and the cell safety. PVDF offers unparalleled cohesive and adhesive properties under high voltage, allowing for closely packed cathode active materials for high density electrodes. Thanks to PVDF, different battery components can be packed more closely together, improving the energy efficiency of a single unit, and helping reduce overall size.

In parallel to PVDF, FKM is used for the production of cell gaskets used in Li-ion batteries, improving the electrolyte containment efficiency and safety of each cell.

Fluoropolymers also offer high durability, flexibility and other exceptional mechanical properties when used in separators and gaskets, helping resist the harsh conditions faced within a Li-ion battery. This dramatically improves performance, as well as the lifespan of batteries, which are increasingly used in applications that require a guaranteed and dependable level of output.

In this application, the fire retardancy property offered by fluoropolymers also plays a critical role, as the use of these materials allows for the creation of a non-flammable matrix that prevents batteries to catch fire due to overheating, which is a well-known concern related to these batteries.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength
- Wear resistance
- Flexibility
- Low coefficient of friction
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation
- Barrier properties
- Non-stick properties
- Fire retardancy / smoke suppression

General description of alternatives and comparison with fluoropolymers

Other polymeric materials could be used for the application such as PE or Polyethylene Terephthalate (PET). Alternatives to Li-ion batteries are lead acid batteries, which do not contain fluoropolymers.

Potential impacts related to substitution

The use of PE or PET in Li-ion batteries would not be a sustainable solution, as these materials would not offer the combined set of properties that fluoropolymers provide, particularly in terms of both fire retardancy and battery efficiency.

In the case of replacement of Li-ion batteries with lead-acid batteries, it needs to be noted that these batteries offer reduced performance notably in terms of energy efficiency because a lower proportion of the energy stored in lead acid batteries. In addition, lead-acid batteries are heavier resulting in reduced functionality and increased energy consumption compared to Li-ion batteries. In addition, it needs to be considered that lead acid batteries involve the use of a known carcinogenic, mutagenic, or toxic for reproduction (CMR) substance (lead) which is a known human reprotoxicant, with additional hazards related to neurotoxicity and environmental damage.

Conclusions on the application

In the automotive sector, batteries are being increasingly used to power up electric vehicles (EV). And this number is only set to grow, with predictions that by 2030 EV sales will reach nearly 60% of the total car sales (Bloomberg NEF, 2021). In order to achieve the objectives of the EU Green Deal, the development of Li-ion batteries particularly in the transport sector is expected to play a key role. Those batteries could not perform at optimal level if fluoropolymer-based solutions (including PTFE and PVDF as electrode binder and FKM in sealing gaskets) were not available.

3.2.2. Application 2.2: Use of PSEPVE and PTFE in the production of proton exchange membranes for hydrogen production

Description of the application

Electrolysers (EL) and fuel cell membranes are used in the production of green hydrogen (H_2) by an electro-chemical reaction. To enable the movement of protons from the anode to the cathode side of the fuel cell, a Proton Exchange Membrane (PEM) made of sulfonated TFE and reinforced with PTFE is used due to the efficiency and unique durability, chemical and temperature resistance properties that fluoropolymers offer for this application. The technical principles behind this case are similar to those described in **Application 1.4**.

The membrane is the core component in ELs as well as in fuel cells. In the former, the electric current and the catalyst coated membrane split water into hydrogen and oxygen, hence hydrogen is produced, with oxygen obtained as a by-product. In the latter, the membrane separates protons and electrons by using a catalyst, and it provides proton conductivity (thereby producing electric current) while separating hydrogen and oxygen.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (<12 MPa)
- Mechanical properties (E-Modulus <500 MPa)
- Low coefficient of friction (0.05-0.1)
- Wear resistance (<5E-7 $mm^3/N \cdot m$)
- Resistance to high pressure (250°C)
- Resistance to harsh chemicals
- Resistance to high temperatures
- Resistance to low temperatures (-263°C)
- Wide temperature range of operation (-263°C to +250°C)
- High limiting oxygen index
- Ionic conductivity
- Barrier properties

General description of alternatives and comparison with fluoropolymers

Hydrocarbon-based ionomers / sulfonated polymers

Some existing hydrocarbon-based ionomers and hydrocarbonated sulfonated polymers could be considered as alternatives to sulfonated TFE for the PEM production, however they offer significantly lower ionic conductivity, especially at low humidity and they are not sufficiently stable against chemical and mechanical degradation to be used in reliable and efficient fuel cell applications. The life span of alternatives is significantly shorter than fluoropolymers implying a higher maintenance cost and probability of failure, therefore resulting in an

increase in the risk of accidents. Furthermore, the likelihood of replacement is substantially higher as well, leading to higher waste generation.

Polyether ether ketone (PEEK)

Research work has been ongoing for PEEK membrane development. Usually, the properties and performance of these materials can be reasonably good whereas the durability is often poor, as oxidation by oxygen radicals, which are inevitably generated at the cathode electrode, occurs. Activities to replace the conventional fluorinated ionomers with fluorine-free materials have existed for the last 25 years but so far, no commercial product has been released due to poor stability against oxidation.

Switch to other hydrogen-based energy solutions

Production of grey or blue hydrogen comes with carbon emissions as well, as those forms of hydrogen are based on the reformation of natural gas and release carbon (COx), that either get emitted into the environment or are questionably captured underground.

Potential impacts related to substitution

Alternatives do not meet the performance required for hydrogen-based energy production as they fail to achieve the demanding conditions in terms of flexibility, stability, resistance to chemicals and performance (superior ion conductivity) under the ranges of temperature variability that are required in the process, therefore the durability and reliability is significantly reduced along with an increased rate of potential failure. If such failure occurs during e.g., use of a hydrogen vehicle, this could result in accidents and risk for population.

Fuel cell manufacturers are in close contact with the suppliers of components, establishing collaborations to test new materials at a relatively early stage. They are thus able to identify and qualify promising options, promote their industrialisation, and introduce the use of innovative materials, as early as possible. However, building from past experience, at present time it is not possible to establish when a validated alternative material may be available in sufficient volume and with equivalent performance compared to fluoropolymers.

Conclusions on the application

In the case of a ban on fluoropolymers for this use, ELs and PEM for green hydrogen production may no longer be available, at least not in the parameters that modern technology involving the use of sulfonated TEF and PTFE allows. It is possible to produce hydrogen by using combustion engines, but this option will result in an increase in GHG emissions and carbon footprint, therefore the decarbonization objectives planned in the European Green Deal and sustainability policies would be jeopardized, and the transition to cleaner energies would be significantly delayed, if at all possible.

Hydrogen has seen unprecedented development over the last years. Starting as an innovative niche technology, it is fast becoming a systemic element in the European efforts to transition to a climate-neutral society in 2050. It will become a crucial energy vector and the other leg

of the energy transition, alongside renewable electricity, by replacing coal, oil, and gas across different segments of the economy. The rapid development of hydrogen is not only important for meeting the EU's climate objectives but also for preserving and enhancing the EU's industrial and economic competitiveness.

A very large proportion of planned projects involving ELs and fuel cells (and in some applications 100%) are based on this PEM technology. Amongst tracked water electrolysis projects to be completed by 2030 in EU/EEA/UK for which information is available, PEM electrolysis accounts for 53% of the projects and 13% of the capacity. PEM are a non-replaceable and high-priority component enabling this fuel cell technology. Without these membranes, the roll-out of such high-performance fuel cell and water electrolysis applications would be delayed by 10-15 years, thereby impacting a wide range of industries.

According to the Hydrogen Council (2021), there are 200 hydrogen fuel cell projects currently announced in Europe, with investments focussed across multiple industries, from transport to heavy industry. In fact, according to this source, the majority of global hydrogen-related investments expected for this decade will be made in Europe. If the use of fluoropolymers in this sector was to be banned, companies will relocate such investments to non-EEA countries where these restrictions do not apply. This situation will imply also that the technology will be transferred outside of the EEA so a loss of knowledge and competitiveness will occur.

Hydrogen is essential to the production of green energy and will be critical in the achievement of the EU Green Deal objectives as well as the objectives set out at COP21. It is estimated that by 2030, 110,000 fuel cell trucks and busses could be on the road (Ruf et al., 2020), and fuel cell EVs could account for 1 in 22 passenger vehicles; in the construction sector, hydrogen could replace an estimated 7% of natural gas by volume (Hydrogen Roadmap Europe, 2019).

Moreover, based on input provided by Hydrogen Europe (2022), the following impact assessment on a potential ban that could cover fluoropolymers in the EEA can be anticipated:

a) In 3 years

Banning materials under a restriction would slow down deployment of clean hydrogen technology in several markets, as it will effectively eliminate PEM ELs and PEM fuel cells from the market.

An analysis of the current pipeline of renewable hydrogen production projects shows ca. 25% all ELs capacity in projects under current development in the EU rely on PEM technology. Taking the EU hydrogen strategy targets as a predictor of future investments (EU-wide target of 6 GW of ELs capacity by 2024), a ban on key products would jeopardise investments worth ca. 1.125 billion EUR by 2024 in ELs only.

It is worth stressing that PEM ELs (due to capacity for flexible load operation) are best suited for coupling with variable renewable energy sources (RES) and are therefore an indispensable technology for large scale RES integration with power grid. Hence a ban would not only jeopardize green hydrogen markets, but it could also significantly affect

the EU's ability to deploy needed RES generation and make reaching decarbonisation targets practically impossible for 2030 and 2050.

b) In 10 years

Based on same strategy's 2030 target of 40 GW of EL, a ban would: jeopardise investments worth 7.5 billion EUR in ELs only (and total estimate of EL capacity in the EU project pipeline is even greater than strategy targets: 141 GW with 35 GW in PEM ELs, worth an estimate of 18 billion EUR). In summary, bans on fluoropolymers may put at risk a total investment estimate value in clean hydrogen sector of 26-36 billion EUR. In terms of employment and put between 84,000 and 140,000 direct jobs at risk, with an estimation of potentially 242,000-261,000 indirect jobs impacted, resulting in a total potential negative impact of 326,000-401,000 full time employees.

3.2.3. Application 2.3: Use of PTFE and FEP in the production sealing systems for storage, transport and production of green hydrogen

Description of the application

PTFE and fluorinated ethylene propylene (FEP) are materials of choice for sealing components used in production, transport and storage of green hydrogen. This application is challenging particularly from the temperature perspective. On one hand, cryogenic conditions (e.g., close to -268°C) are involved during storage of hydrogen. On the other hand, hydrogen is one of the few gases (with helium and neon) that actually heat up when expanded. Fluoropolymers are well suited to cope with increased temperatures that may occur during hydrogen production.

Fluoropolymer based sealing systems can be involved in may steps in the hydrogen process involving cryogenic conditions, for example for rotatory swivels for loading arms at transport of liquid hydrogen, during storage for hydrogen liquefaction or at pumps and valves used at fuelling stations.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical properties (<12 MPa)
- Wear resistance (<5E-7 $mm^3/N \cdot m$)
- Flexibility (E-Modulus <500 MPa)
- Low coefficient of friction (0.05 – 0.1)
- Resistance to harsh chemicals: for example, carbon dioxide (CO_2) acts as a solvent for many polymers in cryogenic stage, also for hydrogen or methane (CH_4).
- Resistance to high temperature
- Resistance to low temperatures
- Wide temperature range of operation (between (-263°C to + 250°C)
- Barrier properties (No swelling when exposed to carbon dioxide, hydrogen, methane)
- Vibration dampening: >0.9
- Impact resistance (IZOD Shrinkage: >8 kJ/m^2)

General description of alternatives and comparison with fluoropolymers

Steel seals and other rubber materials such as nitrile butadiene rubber (NBR) may be seen as potential alternatives

Potential impacts related to substitution

Steel seals would eventually fail because they could not provide the reliability required during the hydrogen cycle. Flanges and bolts to be used in the process require significantly stronger materials during harsh temperature conditions and steel solutions would eventually break leading to releases and significant risks for the operators and the environment.

Similarly, NBR is a material that cannot resist temperatures below -70°C, which is significantly far from the lowest possible temperature during the hydrogen storage and transport processes, which can go as low as -263°C.

Conclusions on the application

A significantly innovative and modern process to generate clean energy such as hydrogen production could be put at risk if fluoropolymers were to be banned for use in the EEA. Because fluoropolymers existed before this technology was developed, these materials have been essential in facilitating this promising energy source, and therefore it cannot be expected that this may continue without the use of PTFE or FEP sealing systems, even if lower performance with the use of other materials was possible. Put simply, the technology could not exist without the use of fluoropolymers.

There are high hopes placed on hydrogen currently as a key vector to support the achievement of a carbon-free energy mix in Europe, as an essential component of the EU Green Deal objectives. Removing fluoropolymers from the EU market could lead to significant damage to those objectives. References to the impact of such a ban on the EEA society are the same as those described for **Application 2.2**.

Conclusions on this application could be extrapolated to other energy considerations such as offshore windmill shafts (involving complex maintenance operations, therefore requiring maximum reliability of components).

3.3. Sector of use 3: Semiconductors and electronics

3.3.1. Application 3.1: Use of PTFE and PFA in the production of pipes and tubes for ultra-high purity requirements in the semiconductor industry

Description of the application

Similar to **Application 1.1**, PTFE and PFA are used in vessels, pipes, fitting systems (e.g., diaphragms in valves) and related infrastructure for the semiconductor industry, with the objective to protect equipment under very aggressive media while granting an extremely high purity of the materials involved in the process. A relevant example of this application would be the use of PTFE or high purity PFA lined columns and tanks to produce high purity sulfuric acid for etching silicon wafers to manufacture electronic chips. This technology allows for larger wafers and ultimately, a more efficient microchip production process. However, it needs to be stressed that most piping and tubing systems used in the semiconductor industry are not lined systems, but the 100% based on fluoropolymer material, as this is the most effective solution to adequately design piping systems in environments that require very high chemical and temperature resistance with flexibility and other properties.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (<10 MPa)
- Flexibility (E-module <500 MPa)
- Resistance to harsh chemicals
- Resistance to high temperature (250°C)
- Wide temperature range of operation
- Barrier properties (low permeation of process media through fluoropolymer liner)
- Non-stick properties
- Flex fatigue properties to enable thermal expansion/contraction during temperature cycles
- Extremely high product purity

General description of alternatives and comparison with fluoropolymers

Some alternatives that could be considered for these applications are**:**

- PP lining systems
- Rubber lining systems
- Tantalum-based piping
- Stainless steel: V2, V4, 316 L, Hasteloy, Inconel
- Enamel / glass lining systems

For the semiconductor industry it is absolutely essential to guarantee that the streams treated within the vessels, piping and fitting systems will stay at the highest possible purity levels. For this industry, levels of purity of part per trillion (and even beyond) are required to ensure the highest possible quality, and to reduce production scrap rates for the user of high purity sulfuric acid. For this reason, any material to be used within this process must ensure an extremely low level of impurities, as well as a low level of leaching of the material used for the piping system into the product. In this particular case, even the use of stainless steel or tantalum would not be viable as these materials would not meet the high demand for product purity. Indeed, no metals are allowed to come into contact with chemicals involved in production of semiconductors, as they would act as ion implants in monocrystalline silicon and change its semiconductor properties in an undesired way. The same would apply to tantalum or enamel-based solutions, which would ultimately not guarantee the need for ultra-high purity values. Likewise, materials like PP or rubber would lead to faster degradation and contamination.

Safety considerations of alternatives would be equivalent those presented for **Application 1.1** since this use would also involve the use of highly corrosive acids like sulfuric acid. The same would apply to economic feasibility of alternatives.

Potential impacts related to substitution

In order to maintain and enhance a competitive semiconductor industry in Europe, there is currently no option to replace the use of fluid systems made from fluoropolymers. Even a slight change in the semiconducting properties, which could be generated due to the use of metal-based materials, would not allow the EU semiconductor manufacturing industry to reach the high standards of efficiency and sophistication that are demanded by the modern downstream user sectors (e.g., telecommunications and electronics).

The semiconductor industry has invested heavily to increase the wafer size during the last 30 years. While foundries used to produce 1-inch wafers in the past, currently common wafer size is 300mm. Larger wafer sizes enable the production of more semiconductors from a single wafer, enhancing productivity and efficiency. By replacing fluoropolymer solutions in this industry, a drastic reduction in product quality would have to be accepted, which would bring the European industry to levels of quality that were acceptable only decades ago (in terms of size, precision and reliability of the articles produced), preventing the possibility to supply to increasingly demanding products such as smartphones, tablets, and personal computers, and thus rendering the European industry as non-competitive in front of companies based in other regions of the world.

According to information from the European Semiconductor Industry Association (ESIA, 2022), in 2021 this industry reached sales for a value of 40.43 billion EUR. Being ranked as the most research and development (R&D) intensive sector by the European Commission (COM), the European semiconductor ecosystem supports approximately 200,000 jobs directly and up to 1,000,000 induced jobs in systems, applications and services in Europe. Overall, micro- and

nano-electronics enable the generation of at least 10% of gross domestic product (GDP) in Europe and the world.

Furthermore, highly efficient semiconductors will play a critical role in the achievement of the objectives of the EU Green Deal, as they are a key enabler of low carbon and energy efficient innovative solutions by optimising energy usage in transportation, manufacturing, consumer products and services. Any negative impact on this industry could seriously hamper the development of such solutions.

Conclusions on the application

For most applications dealing with fluoropolymers, the general principle is that it is the combination of properties they offer that make them highly valued materials. While for semiconductors this principle is still valid, there is one property that clearly stands out, which is the ability of fluoropolymers to grant extremely high level of purity for the aggressive chemicals that are required. Certainly, fluoropolymers add the benefit of also granting high durability and reliability which are critical properties in terms of safety considerations during operations.

Modern (and competitive) microchip technology relies heavily on the possibility to use fluoropolymers in the manufacturing process of semiconductors. Without these materials, the European industry would take a step back of around 30 years, which would leave companies based in the EEA at a clear disadvantage in front of the already dominating industries based in other regions. A ban on the use of fluoropolymers would be in contradiction with the plans expressed by the European Commission to thrive in the global microchip race (European Commission, 2021).

Semiconductors are indispensable in today's modern society, related to consumer electronics and communications. In practice, it is thanks to the availability of microchip miniaturisation that mobile phones have reached the level of (reduced) size and sophistication that enable their functionalities. Removing fluoropolymers from the market would result in loss of these features and make it impossible to maintain the technological levels that have been obtained.

3.3.2. Application 3.2: Use of PTFE, FEP and ETFE in electrical cabling for various industrial sectors

Description of the application

PTFE, FEP and ETFE are used in electrical cabling for various industrial sectors. These fluoropolymers are used because of their exceptional electrical and resistance properties, as well as to provide fire and flame retardancy, which are features required in many industrial applications. In addition, fluoropolymers have a high dielectric strength which means that cables insulated with these materials can be thinner than those manufactured with other materials. On the other hand, due to the dielectric properties, fluoropolymers are widely used for cables and wires for communication facilities as insulators for high-frequency electronics.

LAN cables of category 4 or higher are made with FEP to allow for optimum data transmission properties, which is measured as Velocity of Propagation (VoP).

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Flexibility
- Resistance to high temperature (>200°C)
- Resistance to low temperature
- Resistance to chemicals
- Wide temperature range of operation
- Fire retardancy/smoke suppression
- Electrical insulator (high data transmission range)
- Low arc-tracking
- Barrier properties (low permeation of process media through fluoropolymer liner)

General description of alternatives and comparison with fluoropolymers

Engineering plastics, such as polyvinyl chloride (PVC) or PE combined with halogen free flame retardants (HFFR) could be considered as alternatives, however none of them meet the combination of properties that lead to superior performance of fluoropolymers, such as high flexibility, resistance to harsh chemicals and resistance to high temperatures (>200°C), which are frequently required for many industrial applications.

PEEK and ceramic based cable insulations may also be considered, but again these materials would not bring the combined set of properties that fluoropolymers offer and would not perform under the full set of required situations and process conditions.

A critical property in modern electronics which is required to any material that may be used for data transmission cables is minimum signal disruption. If other plastics such as PE are used in LAN cables, VoP is significantly reduced, resulting in less efficient performance. The use of PE would also result in thicker LAN cables.

Potential impacts related to substitution

While alternative materials could be used in industrial cables under conditions that require minimum performance levels (e.g., moderate temperature ranges, low flexibility needs, absence of harsh chemicals or limited voltage), it is often the case that many industries need to cope with very demanding conditions in relation to those properties. A wide variety of end-sectors depend on availability of cables that are able to perform under harsh conditions of use, from coffee machines to switch pumps placed under water, from data processing cables to control systems in industrial processes.

For example, alternative plastics described earlier will typically have a higher minimum working temperature than fluoropolymers, therefore performance will be significantly reduced particularly in cases where coolants are used to decrease temperature, which is typical in data processing systems. In addition, flame retardants increase dielectric constant and dielectric loss, which reduce data communication rates. The use of alternative plastics combined with other flame retardants will result in weaker data processing and slower signal return, reflecting inferior properties if compared to those obtained with the use of fluoropolymers.

The need to provide additional insulation due to the use of degraded performance by the use of alternatives would result in increased weight and size of cables, which would also be more rigid and brittle. Therefore, electrical installations would become bigger and more complex. Furthermore, performance in high-tech properties such as data transmission via LAN cables would be significantly reduced as well.

Conclusions on the application

Fluoropolymers provide a unique combination of properties that are not met by the alternatives, reaching extreme conditions that cannot be achieved with the use of alternatives. If fluoropolymers are not available in electrical cables, performance of a wide variety of industrial applications would be seriously downgraded, resulting in increased maintenance costs, lower reliability, and eventually higher risks for human health (fires) and the environment (increased replacement of other plastics leading to generation waste).

Ordinary wires are not equipped to handle the high-power consumption and high frequencies of e.g., 5G radios and cells. Fluoropolymers increase 5G reliability by insulating and protecting riser cables from fire and heat and allowing for quick data transmission and flexibility.

Under this situation, many industries based in the EEA would face significant issues to maintain their high levels of performance and efficiency, which could result in a significant decrease of competitiveness of those industries. The example that has been provided on reduced performance of data transfer technologies is illustrative of how European based companies could be challenged by competition in other regions of the world if they were forced to transition to lower performance alternatives.

3.4. Sector of use 4: Automotive and aerospace

3.4.1. Application 4.1: Use of PTFE and FEP in the production of electrical cabling for use in aircrafts

Description of the application

This case is a specific example related to the general case of electrical cables described in **Application 3.2**, describing the use of PTFE, FEP and ETFE in industrial machines.

PTFE and FEP are used in electrical cabling for the aerospace industry (aircrafts, but also outer space vehicles), where there is an essential requirement for high-performance under very demanding conditions. Fluoropolymers offer property retention under a wide range of temperatures and exposure to specialty fuels that may be chemically aggressive.

The aerospace industry also relies on fluoropolymers due to their exceptional electrical properties at high voltage and high signal frequencies and resistance properties, as well as fire and flame retardancy and reduced smoke generation.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength: SPE-J-920-A-0061[4] torsion
- Wear resistance: SPE-J-920-A-0061 wire to wire abrasion
- Mechanical properties: SPE-J-920-A-0061 room temperature bend
- Low coefficient of friction: SPE-J-920-A-0061 Pliability
- Resistance to harsh chemicals: SPE-J-920-A-0061 Resistance to aircraft fluids
- Resistance to high temperature: SPE-J-920-A-0061 accelerated ageing (operating temperature may reach 260°C)
- Resistance to low temperature: SPE-J-920-A-0061 cold bend (operating temperature may reach -70°C)
- Wide temperature range of operation: SPE-J-920-A-0061 Climatic
- Dielectric strength: SPE-J-920-A-0061 High voltage test, spark test, surface resistance, overload resistance, resistance to wet arc tracking, resistance to dry arc tracking
- Fire retardancy/smoke suppression
- Low arc-tracking
- Electrical insulator
- Barrier properties

[4] SPE-J-920-A-0061 refers to specifications for wires to be used in Eurofighter type aircrafts

General description of alternatives and comparison with fluoropolymers

Similar to **Application 3.2**, engineering plastics (such as PVC and PE) combined with HFFR could be considered as alternatives, however as discussed previously these materials will not meet the combination of properties that lead to superior performance of fluoropolymers, which are highly needed in aircrafts. Polymeric materials could give some chemical and electrical protection but would fail to perform under the required set of temperature ranges.

PEEK is able to resist up to 260°C, however this material is significantly rigid which greatly impacts on the design of the electrical systems. On the other hand, chemical resistance and electrical properties are inferior to fluoropolymers.

Ceramics could also be an alternative and provide protection against some (not all) chemicals, but flexibility requirements are again not fulfilled, and they would be significantly heavier.

Potential impacts related to substitution

The aerospace industry requires high insulation performance in aircrafts, this is amplified by the need of higher voltages (>230V) at higher altitudes with partial vacuum conditions and where vibrations can lead to product failure, which is not the case if fluoropolymers are used. Furthermore, cables need to be flexible and resistant to high as well as low temperatures, which can go as low as -70°C; if the flexibility requirements are not met, cables will turn rigid and there could be a breakdown risk that may result in a system failure, thus compromising aircraft safety. In addition, most of the alternatives cannot work at 260°C, this temperature may be reached in aircraft engines where high reliability is critical to guarantee safety during flight. PEEK could be an exception in terms of resistance to higher temperatures but again the lack of other properties like flexibility turns this into a non-viable alternative.

Being fluoropolymers resistant to the action of harsh chemicals, their use in cabling is particularly useful in areas of the aircraft where exposure of the cabling system to specialty fuels that may be chemically aggressive could occur. On the other hand, in the event of a fire incident during flight, fluoropolymers are able to provide fire retardancy and reduced smoke generation suppression properties with better performance compared to alternative materials, which is another critical element to ensure safety of passengers and the crew.

The exceptional dielectric properties provided by fluoropolymers allows for cables insulated with these materials to be thinner than those produced with other materials. Less weight improves the agility and speed of aircrafts and reduces the amount of fuel required.

Conclusions on the application

A typical modern aircraft may contain between 150 and 250 km of cables installed (specific models such as the Airbus 380 have > 500km of installed cables). Aerospace companies use fluoropolymers because they provide outstanding performance under highly demanding environments, which cannot be compromised due to safety issues. High durability and reliability of the materials used in aircrafts are required, this poses significant challenges when

those materials need to withstand temperature variability or chemical attack, while offering sufficient flexibility and other properties such as dielectric strength or flame retardancy. Fluoropolymers are the only materials that offer outstanding properties in relation to those properties, all in one single material type.

If fluoropolymers were to become not available for electrical cables used by the aerospace industry, performance of the aviation in general would be seriously downgraded, resulting in increased maintenance costs, lower reliability, and eventually higher risks for safety of passengers and workers.

In addition to these considerations, it is necessary to highlight that the airspace industry has extremely demanding validation procedures for new materials. The approval could take at least ten years, therefore if changes were to be introduced in the systems used in aircrafts, lengthy and costly procedures for certification would need to be taken into account.

3.4.2. Application 4.2: Use of PTFE in the production of lambda sensor for the automotive industry

Description of the application

PTFE is used in lambda sensor cables due to its resistance to high temperatures and chemicals, dielectric strength, flexibility, and electrical insulator properties. Lambda sensors essentially consist of three parts: wiring, grommet and sleeve. PTFE is used throughout these components with the objective to protect the sensor which is directly exposed to exhaust gases.

In vehicles, lambda sensors adjust the fuel amount that is sent to the engine cylinders by optimizing the air and fuel mixture, which in turn will make the engine work properly. Lambda sensors allow for this control system via measurement of oxygen in exhaust fumes. This is a critical element in cars and vehicles to control the rate of gas emissions by ensuring that the catalytic converter works in an efficient way. Lambda sensors ensure that the car complies with the European regulations on pollution and carbon emissions.

To allow for a better control of emissions, it is common that gasoline injection systems in vehicles feature at least two lambda sensors. The air/fuel mixture is optimized by a control sensor upstream of the catalytic converter. Taking the engine load into consideration, the fuel quantity injected is controlled in a manner that an optimum air/fuel ratio is ensured, thus creating ideal conditions for exhaust-gas treatment at the catalytic converter. In case of rich mixtures, the amount of fuel is reduced. With lean mixtures, it is increased. The second lambda sensor downstream of the catalytic converter (the diagnostic sensor) checks if the control sensor works optimally. If there are any deviations, they can be compensated by the control unit.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical properties (tensile and elongation)
- Resistance to high temperature: ISO 6722 long term heat ageing (operating temperature 280°C)
- Resistance to chemicals: ISO 6722 fluid compatibility
- Resistance to low temperature: ISO 6722 low temperature winding, cold impact
- Weather resistance: ISO 6722 temperature and humidity cycling
- Electrical insulator: ISO 6722 withstand voltage
- Dielectric strength: ISO 6722 withstand voltage
- Fire retardancy/smoke suppression: ISO 6722 resistance to flame propagation

General description of alternatives and comparison with fluoropolymers

Silicon, ethylene propylene rubber (EPR) and ethylene propylene diene rubber (EPDM) could be considered as alternatives, but they are able to operate at maximum temperatures ranging between 150°C and 180°C (specifically, 150°C EPDM, 160°C EPR, and 180°C rubber), therefore

they are not able to work at the required operating temperature of around 250°C, which is frequently encountered in car engines where lambda sensors are installed. In addition to this, alternatives do not meet the mechanical properties (elongation) required by the automotive sector for these critical components.

In addition, EPR and EPDM are resistance to some acids and alkalis, but they are not recommended for petroleum fluids or diester lubricants, products that may eventually become in contact with lambda sensors at some point while in operation.

Potential impacts related to substitution

As mentioned above, alternative materials do not meet the performance required for the adequate functioning of lambda sensor, mainly related to the maximum operating temperature required, which for alternative materials is lower than the maximum temperature that can be achieved with the use of PTFE. This would result in downgraded performance and reduced efficiency to control gas emissions and fuel consumption. This would not be aligned with the decarbonization and sustainability policies that are being promoted by the European Union through the Green Deal.

Alternative materials such as silicon, EDR and EPDM also offer reduced performance on other relevant parameters such as chemical resistance to lubricants or elongation, which are important to ensure adequate fitting and performance in car engines.

Conclusions on the application

Lambda sensors are an essential component that optimizes the functioning of combustion engines to guarantee that gas emissions from vehicles are kept within adequate parameters and fulfil the limits established in the relevant European regulations. The adequate functioning of these components is an essential element to ensure that the objectives to reach net zero carbon emissions by 2050 will be achieved. In order to ensure such adequate performance, PTFE will be required for the production of lambda sensors. While it is expected that combustion engines will be replaced by EVs in the coming years, vehicles based on combustion engines will still be in operation likely until 2050 and, considering the need to provide spare parts for vehicles that will still be operational within approximately 30 years, it can be concluded that PTFE has a key role to play in ensuring the Green Deal objectives in the described application.

3.4.3. Application 4.3: Use of PTFE in the production of control cable liners for the transport industry

Description of the application

PTFE is used in control cable linings for vehicles and aircrafts due to its low coefficient of friction and durability properties, which in combination with some abrasion resistant fillers enable metal wires to slide through the liner as the inner part of cable construction. Control cable liners ensure the well-functioning and safety of vehicles and aircrafts (including spaceships). They are used in many applications such as speedometer cables, hand brake and accelerator cables, gear shift and clutch cables, parking brake and fluid lid opener cables, etc. Control cables are also applied for outdoor power equipment, such as light duty throttle cables or heavy-duty transmission and brake cables. They are even involved in the adequate function of key components related to safety such as wing flaps required to ensure reliability during take-off and landing of aircrafts. Ultimately, these cables are used in any general systems that may require movements in the order of millions of cycles in a lifetime.

These cables need to perform under very demanding and highly variable conditions, e.g., in terms of temperature changes (from cables close to engines to external equipment at high altitude and therefore very low temperatures), resistance to harsh chemicals (fuels and other liquids in vehicles) with no tolerance to failure, situations under which PTFE provides outstanding properties.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (> 40 MPa)
- Wear resistance (>1 million cycles)
- Mechanical properties (elongation break)
- Low coefficient of friction (max 0.2)
- Resistance to chemicals (hydraulic fluids, oils, acidic aqueous solutions)
- Resistance to high temperature (> 250°C)
- Resistance to low temperature (-70°C)
- Wide temperature range of operation
- Fire retardancy/smoke suppression

General description of alternatives and comparison with fluoropolymers

PEEK could be seen as an alternative to PTFE for cable liners. This material offers stability at higher temperatures and can allow for some protection of cables under certain conditions; however, it is not expected to provide the same combination of properties that PTFE offers in one single product.

Potential impacts related to substitution

PEEK is not expected to match the performance required for the lining of control cables intended to be used in the automotive and aerospace industries. Even if additional additives for lubrication were to be used, the results of the application on demand could not be compared with the low coefficient of friction, resistance to chemicals, lifespan, and wide range of operation that PTFE offers, particularly for critical safety systems that need to perform at extremely high cycles in a lifetime. Again, PEEK may proof to be efficient in some cases (e.g., resistance to only some (not all) foreseeable chemical environments in the application, or adequate performance up to +250°C, but not at low temperatures expected in high altitude during flight operation), but not in the broad range of scenarios that can be expected in the automotive and aerospace industries. For this reason, any initiative that could push for replacement of PTFE in control cable liners could create high risk situations for the population, since safety performance of critical transport systems would be downgraded.

Conclusions on the application

Fluoropolymers and in particular PTFE provide a unique combination of properties and remains the best (if not the only) option to facilitate adequate and reliable performance of control systems in land vehicles and aircrafts. If PTFE were not allowed to be used in control cable lining, the performance of these essential components would be seriously downgraded, resulting in a clear compromise to safety of passengers and the population in general. PTFE can be regarded as the top technology option today for these cable liners and removing it from these applications would bring control systems in vehicles to their technological infancy.

Under this circumstance, the whole transportation sector in the EEA, including vehicle and aircraft manufacture, could face an uncertain future and relocation to other countries, mainly in the Americas and the Asia-Pacific region could benefit from technology transfer to guarantee continued availability of highly reliable land vehicles and aircrafts. In addition to the safety considerations, impacts on standards of living of the general population (not only related to massive employment losses in these sectors, but also to affordability of e.g., cars and airplane travel) would need to be carefully evaluated.

3.4.4. Application 4.4: Use of PTFE and ETFE in the production of different auxiliary components for the automotive industry

Description of the application

PTFE and ETFE are used for the manufacture of different parts of car equipment, such as door hinges and seat height adjustment bearings. These parts can be regarded as pivot points which are subject to sporadic demand while cars are running, requiring high reliability and very low friction conditions.

Technical properties required for the material of choice

For these applications, the following properties are relevant for the material of choice:

- Mechanical strength (<12 MPa)
- Tensile strength (>40 MPa)
- Wear resistance (<5E-7 mm^3/Nm)
- Flexibility (E-Modulus <500 MPa)
- Resistance to high temperatures (>250°C)
- Resistance to low temperatures (-30°C)
- Wide temperature range of operation
- Vibration dampening (>0.9)
- Impact resistance (IZOD impact test >8kJ/m^2)

General description of alternatives and comparison with fluoropolymers

Some alternatives that could be considered for these applications are:

- Steel/Steel
- High temperature polymers
- Ultra-high molecular weight polyethylene (UHMWPE)

Steel/steel solutions and high temperature polymers

These alternatives require re-greasing the system in very short time frame (e.g., every two weeks) in order to avoid continued squeaking of the systems. Other high temperature polymers also require additional lubrication either like the steel/steel contact or solid lubricants like PTFE.

High temperature polymers

These polymers are so rigid that a press fit assembly is not possible, which in turn requires additional sealing and causes door drop issues due to wear, because wear particles can easily fall out the contact. Furthermore, in relation to seat-height adjustment bearings, the lack of press fit assembly will make it impossible to remove rattling noises from unoccupied seats, making the car noisier.

UHMWPE

UHMWPE has good mechanical, physical and tribological properties, such as: extreme hardness and durability, good chemical resistance, abrasion resistance, impact resistance, being easy to fabricate, a very low coefficient of friction and being a non-polarity polymer, which would have no additional lubrication requirements. However, UHMWPE causes rigidity issues. In addition, this material has a very low temperature resistance, with a melting point of 125°C -132°C, in contrast with PTFE which has a melting point of 327°C.

Potential impacts related to substitution

For door hinges, good lubrication is essential which can be achieved via the use of fluoropolymer-based systems. Alternatives resulting in higher friction would require significant amount of additional lubrication, this would have to be done via the use of oils which would result in environmental impacts. For example, the use of steel/steel systems in door hinges with frequent re-greasing was a feature of the old (and iconic) Volkswagen Beetle model launched in the 1940s.

From an economic perspective, while the steel-steel contact solution may be cheaper in the creation phase, regreasing efforts should be taken into account when evaluating this possibility. In a broader service life consideration of cars, the final outcome would result in higher costs, particularly if the car owner is not able or willing to take care of the service on his own.

In relation to UHMWPE, it is relevant to note that its low temperature resistance would create significant problems to the car manufacturing industry. This would force the complete redesign of the assembly process of cars (a quite complex one), which involves painting at high temperatures. Doors and hoods would have to be painted separately from the car body and assembled later, in contrast with modern technology (i.e., involving the use of fluoropolymers) which allows for the homogenous painting of the car body together with doors and hoods. This would result in significant impact to the car industry. Indeed, while the UHMWPE solution is also more economic (if focus is placed only on direct comparison one-to-one with the fluoropolymers), the fact that this solution would require major technical changes to the car industry could lead to investments for car manufacturers which could be expected to reach amounts near 100 million EUR.

In addition, alternatives must be tested to check that the performance and safety requirements are fulfilled. The substitution must be also approved by the manufacturers of the different applications. This process takes time, depending on the sector the time frame to consider could be in the range of 5-10 years.

Conclusions on the application

The alternatives previously described will likely result in higher maintenance costs and lower car reliability due to the lower quality of the material replacements. As a result, car production could remain in Europe, but cars produced outside the EEA will be more comfortable, less

noisy and they will require less maintenance. Altogether, the competitiveness of the automotive industry in the EEA will be compromised, as manufacturers based outside the EEA will have opportunities for more cost-effective design solutions.

According to information from the European Automobile Manufacturer's Association (ACEA, 2022), in 2018 the automotive industry was responsible for 12.6 million jobs in the EU, including manufacturing, services and construction. This corresponds to 6.6% of the total EU employment. Direct manufacture of motor vehicles employs 2.6 million people. In terms of trade, a positive balance 76.3 billion EUR was achieved in 2020 in the trade of motor vehicles, with 134.1 billion EUR of exports. The automotive industry contributed to 398.4 million EUR in fiscal income from motor vehicles in 2020 (data from EU14). In the same year, the sector of automobiles and parts invested 58.8 billion EUR in research and innovation related activities.

The use of alternatives would bring certain parts of car technology to systems that were used 50+ years ago. In the event that fluoropolymers may not be available for the application described, it is difficult to assume that consumers would accept a recoil in car quality and comfort, particularly when non-EEA car manufacturers may continue to keep those standards at XXI century levels. Going back to noisy and squeaking car components would be considered a significant disadvantage from a competitive perspective, for a very relevant industry in the EEA.

3.4.5. Application 4.5: Use of FKM for sealing applications in the automotive industry

Description of the application

FKM-based fluoroelastomers are used by the automotive industry in various products such as o-rings, gaskets, shafts, joints, fuel and turbo charger hoses and other connector components that are subject to intense temperature, in order to provide highly reliable sealing systems.

With the development of modern and more fuel-efficient turbochargers involving high pressure direct fuel injection, technical performance required from such sealing systems has reached unprecedented levels. It is imperative that no leakage at high temperatures occurs in vehicles in order to ensure safety for passengers and the surrounding population. Moreover, this energy-efficient, highly powerful and complex engines require durable components that will operate for longer periods without requiring frequent maintenance or replacements.

This case may be expanded to other engine-based means of transport such as aircrafts and ships.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (> 8MPa)
- Wear resistance
- Flexibility
- Low coefficient of friction
- Resistance to harsh chemicals, such as synthetic oils
- Resistance to high temperature (> 200°C)
- Wide range of temperature operation (-40°C to 250°C)
- Barrier properties
- Non-stick properties
- Fire retardancy / smoke suppression

General description of alternatives and comparison with fluoropolymers

Other rubber or elastomeric materials such as acrylic rubber (ACM), ethylene acrylate copolymers (AEM), HNBR, UHMW-PE, Polyoxymethylene (POM), PU, PEEK or EPDM could be suggested as potential alternatives. However, they would fail to provide the same level of efficient performance that FKM-based sealing systems offer. Other elastomeric materials such as ACM, AEM or HNBR have much higher friction coefficients, which is not suited for materials that need to be in constant demand for interacting with other pieces of vehicles while in use. UHMW-PE, POM, PU fail in heat resistance as they cannot withstand the temperature ranges required by car engines. PEEK is too hard to perform adequately in the sealing function of highly demanding engines.

EPDM is a synthetic rubber material that can offer good resistance under certain chemical environments, mainly for outdoor applications. It offers a good range of temperature

resistance (-50°C to 150°C). Although EPDM offers good resistance to diluted acids, ketones and alkalis, it does not perform so well in case of fuels, oils and non-polar solvents. It certainly would not be a suitable choice for the automotive sector, or others in which harsh conditions are expected.

In summary, while there are low-cost alternatives to FKM for certain less demanding (e.g., outdoors) applications, for cases such as car engines where highest standards of chemical and thermal resistance are required, FKM is currently the only reliable option available on the market.

Potential impacts related to substitution

If FKM seals were to be replaced by alternatives from vehicle engines, these systems would become less reliable and subject to increased need for maintenance and replacement, because the alternatives described previously would not perform at an equivalent level. All of them would fail to provide the same technical performance as FKM at least in one key property. FKM is currently the only material available on the market that fulfills all the technical conditions that modern turbocharger engines require to operate vehicles in an efficient way.

Conclusions on the application

FKM seals are a good example of fluoropolymers offering not just one but a combination of different properties that are (all of them required) in high technology applications. While other materials are available on the market, and they could offer equivalent performance under one single property required, they would fail to provide the same performance as FKM sealing systems. This makes those alternatives as not suited to be used for sealing systems in the automotive sector. Beyond increased wear rates, maintenance costs and generation of waste from repairs, the critical trade-off that would be derived from the replacement o fluoropolymers from this application is the fact that safety of passengers and the general population would be compromised due to higher risk of unexpected failure of engine components.

3.5. Sector of use 5: Food and water processing

3.5.1. Application 5.1: Use of modified PTFE, PFA and FEP in the production of systems used for food processing

Description of the application

Modified PTFE is used in membranes and bellows for food and beverage processing systems, but also in many components used by this industry such as baking belts, baking trays, cooking liners etc. In addition, PFA and FEP can also be used for different components in food processing and packaging machines. Because of their superior mechanical and non-stick properties, as well as low coefficient of friction, durability, wide temperature range of operation, and chemical resistance, fluoropolymers are used by the food processing industry when harsh conditions of use are required, or when ultra-high levels of purity and quality are needed. Membranes are used to provide aseptic conditions during handling of food, and bellows are designed to provide a dynamic separation element to protect the product from contamination.

Specific European regulations are in place for materials intended to come into contact with food, with positive lists indicating authorised substances, as well as allowed migration limits.

Fluoropolymers offer the high purity and strictest hygienic requirements that the food industry requires. Those properties are crucial in food processing. Materials must also meet inertness and resistance to high-temperature properties to avoid the migration of hazardous substances into the food that would imply contaminations that could create significant problems related to human health. Furthermore, fluoropolymers allow a unique sealing due to their resistance to chemicals and temperature that provides very precise dosing of the components during the process.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (>30 MPa)
- Wear resistance (min 1E-6 $mm^3/(N{\cdot}m)$
- Mechanical properties (min 3E6 cycles)
- Low coefficient of friction (max 0.2)
- Resistance to chemicals
- Resistance to high temperature (150°C)
- Biocompatibility (food approvals required, e.g., NSF – EU10/2011 and GB4806.1)
- Wide temperature range of operation (0°C to 150°C in several operational conditions)
- Non-stick properties
- Fire retardancy / smoke suppression
- Low bacterial/algae growth

General description of alternatives and comparison with fluoropolymers

Elastomers like EPDM, methyl vinyl silicone rubber (MVQ), or NBR could be considered as alternatives, however they can only be used for a limited life cycle (maximum 20,000 life cycles) so the durability of the application is drastically reduced. On the other hand, the combination of resistance to high temperatures and chemicals are not met at an equivalent level that are achieved with the use of PTFE.

Other materials like PVC, polystyrene or silicon could also be recommended but approval state for food contact, chemical resistance against cleaning agents and performance under changing temperatures are coming as trade-offs.

Potential impacts related to substitution

The substitution of PTFE membranes and bellows with a combination of alternative materials would be expected to result in more frequent replacement of the damaged components. It is estimated that this would be increased by a factor of 150, therefore maintenance costs will be significantly increased as well, in addition this would lead to the generation of more waste since materials would need to be disposed frequently. These repairments also mean production losses, lower reliability, reduced life span and efficiency and a higher risk of food contamination. In contrast, fluoropolymers provide a long-life span to the materials due to their resistance to fatigue.

Membranes and bellows functions to avoid contaminations from the equipment and/or the environment will not be achieved by the alternatives which is a critical point for food safety so human health could be compromised. In addition, it will be quite difficult to obtain the demanding cleaning conditions required by the food industry as the resistance to chemicals of the alternatives are lower than fluoropolymers so again, it would result in health issues. In addition, food and drink streams must not excessively stick to the thermocouples or other food quality sensing devices.

All possible alternatives come with significant shorter lifetime cycles. This requires regular repair cycles for the equipment due to failures, which are costly and produce more waste. For low-cost consumer products this would most likely result in that repair costs are higher than buying new product which results in immense waste and recycling challenges. For higher end products for industrial use, the cost of the final product produced will most likely be higher due to more maintenance and labour cost involved. Even here, the consumer buying the final product (coffee, juice, tomato puree, soups, etc.) will pay the higher price, generating increased inflation in the EU zone in the long term.

Europe would lose competitiveness, especially to Asia-Pacific countries where cost is not high and circular economy is not yet a prioritised topic. More low-cost problems would be imported, and the amount of waste would increase as cheaper products (like household coffee machines) will be disposed instead of putting them into service/repair. Trends will get

removed from circular economy back towards “use and trash – then buy new” as it was the case in the past.

Conclusions on the application

Fluoropolymers provide a unique combination of properties that allow food processing equipment to reach extreme conditions, which is not possible with the use of existing alternatives. If fluoropolymers were not available for use in the food industry, performance of those systems would be seriously downgraded, resulting in increased risk of food contamination or reduced food quality, which could in turn derive into serious health concerns for the general population.

Food and Beverage filling and packing is an extraordinarily relevant industry in EEA, all from dispensing fluids like coffee or juices to breweries or packing equipment. According to FoodDrinkEurope (2022), the EU food and drink industry employs 4.5 million people, generates a turnover of 1.1 trillion EUR and 222 billion EUR in added value, making it one of the largest manufacturing industries in the EU These industries are in need of fluoropolymers as the non-stick properties in combination with chemical resistance makes advanced automation processes (with changing media/fluids and cleaning cycles in between) possible. Reducing these, the EEA will suffer a significant loss in both workforce but even more competitiveness towards other regions like Asia Pacific. Production would most likely be moved out of the EEA if product quality and safety would be downgraded due to the use of alternatives. Standard of living and choice of products would also be reduced, and increased waste generation due to disposal of more frequently replaced elements should also be taken into consideration. While this impact may not be as severe as others related to safety considerations, they should be taken into account as well when evaluating the regulatory future of fluoropolymers.

3.5.2. Application 5.2: Use of PVDF in the production of membranes for water treatment

Description of the application

PVDF is used in the production of hollow fibre membranes used in different subsegments of water ultrafiltration systems. For example, these membranes are relevant at industrial and municipal wastewater treatment plants in which treated water is expected to be returned to waterways (e.g., rivers). They are also used in drinking water at municipal water plants, and also at industrial sites (irrigation in agriculture, cooling towers in process industries, etc.).

Hollow fibre membranes are a class of artificial membranes containing a semi-permeable barrier in the form of a hollow fibre. Originally developed in the 1960s for reverse osmosis applications, hollow fibre membranes have since become prevalent in water treatment, desalination, and other applications[5]. Most commercial hollow fibre membranes are packed into cartridges which can be used for a variety of liquid and gaseous separations.

PVDF filtration membranes are used to filter out contaminants such as pathogens (parasites, bacteria, and viruses), micropollutants (such as pesticides, pharmaceuticals, personal care products, endocrine disruptors and microplastics for drinking water production. A membrane bioreactor (MBR) is a combination of membrane processes like ultrafiltration with a biological wastewater treatment process (activated sludge process).

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength: Tensile strength >45 MPa (ASTM D638).
- Wear resistance: 10 years accelerated test (internal standard test).
- Mechanical properties: Elongation at yield > 25% (ASTM D638); Tensile modulus <2200 MPa (ASTM D638).
- Resistance to harsh chemicals: 1,000,000 ppm·hours to sodium hypochlorite (NaOCl) exposure for membrane cleaning, which is a critical chemical used for removing organic constituents and disinfection.
- Non-stick properties: Resistance to fouling by organic constituents present in surface waters.

PVDF membranes are typically rigorously tested and meet drinking water standards throughout the world. Certifications include: NSF 61 and NSF 419 (USA), KTW (Germany), KIWA (Netherlands), ACS (France), DWI (UK), ICIM (Italy), MOH (China), or KWWA (Korea).

General description of alternatives and comparison with fluoropolymers

PES is the most common material that could be described as a potential replacement for PVDF for the production of membranes intended for water filtration. Other compounds such as PE

[5] https://en.wikipedia.org/wiki/Hollow_fiber_membrane

and PP, or even ceramic based materials may be used in membranes, but PES stands out as the most typical option.

Where one-to-one replacements would not be considered, the only other alternative for water treatment would be to return to clarification methods based on the use of a wide variety of chemicals (e.g., flocculants, coagulants), as well as conventional gravity settling and sand filtration, which is a fairly old technology.

In relation to hollow fibre ultrafiltration membranes, it is critical to distinguish between inside-out type and outside-in type. For inside-out hollow fibre membranes, the feed water is fed to the inside bore of the hollow fibre and the clean water passes through the polymer matrix (the separation barrier) to the outside of the hollow fibre. This type of membrane is used on easier to treat applications (e.g., post treatment of potable water, low turbidity surface water). For inside-out hollow fibre membranes, PES can be used effectively. For outside-in hollow fibre membranes, dirty water is on the outside of the hollow fibre and the clean water is collected from the inside of the hollow fibre. Outside-in hollow fibre membranes are used on higher solids and more fouling feed waters (e.g., industrial applications, wastewater treatment, high turbidity surface water). Due to the challenging applications, outside-in hollow fibre membranes are subjected to more aggressive cleaning, including agitation with air scouring and use of high concentrations of cleaning chemicals (e.g., sodium hypochlorite and acids). For these reasons, outside-in hollow fibre membranes are almost exclusively made from PVDF (The MBR site, 2017).

Potential impacts related to substitution

As previously mentioned in the description of other cases, there are indications that PES may be related to equivalent concern as BPA due to potential endocrine disrupting properties (Kang et al., 2014). In addition to this PES-based membranes are known for exhibiting inferior performance compared to the PVDF equivalent. For example, while PES may provide equal mechanical properties (reaching tensile strength above 45 MPa), its elongation at yield is lower (6% compared to 25%), and the resistance to sodium hypochlorite is limited to 250,000 ppm hour. Their reduced flexibility and chemical resistance will make PES membranes brittle during product life, resulting in broken fibres and reduced life expectancy (5-7 years compared to nearly 20 years duration of PVDF membranes). Furthermore, changing existing PVDF-based systems to PES would require significant engineering studies and equipment changes to make PES membranes work. Because the solutions using PES membranes will be more complex with additional treatment steps, the cost of substitution is expected to be in the range of hundreds of millions EUR for making the necessary retrofits. Additionally, future membrane treatment plants will also be much more expensive to construct if PVDF membranes are no longer available.

The change to filtration systems based on non-membrane solutions would result in the need to use older technologies that imply the use of chemicals and less efficient water treatment processes which could seriously impact the quality of water that could return to humans or the

environment. Indeed, MBR technology using PVDF hollow fibre membranes replaced old conventional gravity settling and sand filtration, and it plays a critical role in providing the advanced wastewater treatment needed to allow municipal wastewater treatment plants to effectively comply with the Urban Wastewater Directive [6] (91/271/EEC), to which the protection of aquatic ecosystems, bathing water, and groundwater are closely related.

Membrane filtration also provides high-quality reclaimed water, helping cities to meet the EU Water Reuse Regulation [7] as well as other legislations fostering the recycling of municipal and/or industrial wastewater. The potential role of treated wastewater reuse as an alternative source of water supply is now well acknowledged and embedded within European and national strategies. Water reuse is a top priority in the Strategic Implementation Plan of the European Innovation Partnership on Water, while maximization of water reuse is a specific objective in the Communication "Blueprint to safeguard Europe's water resources" (COM, 2022).

Many cases exist where membrane filtration was determined to be the best available technology (and in some cases the only viable technology) to protect ecologically sensitive water bodies. Examples include plants in Sweden, with 540 Minimal Liquid Discharge (MLD) and commissioned in 2008, which is the largest MBR in the world, Germany (47 MLD, commissioned in 2003), France (108 MLD, commissioned in 2013) and Belgium (86 MLD, commissioned in 2017).

The annual MBR market is estimated at around 5 billion EUR, solutions costing 50-100% more would result in 2.5-5 billion EUR per year additional investment to meet future wastewater treatment needs. For one single membrane producer in the EU, 1000 jobs would be expected to be lost, including high level manufacturing, engineering, and R&D jobs. Another 500-800 jobs could be lost in other functions within the EEA countries, with revenue losses for one company alone expected in the range of would be 250 - 350 million EUR per year.

Conclusions on the application

Fluoropolymers provide the best solution to allow high quality water ultrafiltration systems. Alternative materials or technologies will either imply the use of potentially hazardous chemicals (PES) or the return to technologies that were used decades ago, involving increased use of chemicals which may remain in water that will later return to the environment. Without this technology, more complex and expensive solutions will have to be employed to provide removal of these contaminants. For many of the more challenging surface water sources impacted by increasing weather events brought on by climate change, good alternative solutions are not feasible in practice.

[6] Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment.
[7] Regulation (EU) 2020/741 of the European Parliament and of the Council of 25 May 2020 on minimum requirements for water reuse

3.6. Sector of use 6: Medical and pharma

3.6.1. Application 6.1: Use of PTFE in the production of equipment to be used in vaccine preparation requiring ultra-high purity media

Description of the application

Similar to **Applications 1.1** and **3.1**, PTFE is used in vessels, pipes, and fitting systems (e.g., diaphragms in valves) for the pharmaceutical industry, with the objective to produce medicines and vaccines, requiring ultra-pure media and sterile conditions. In this industry, most of this equipment is not necessarily based on other materials lined with fluoropolymer, but the fluoropolymers are directly used for tubing and piping systems.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (<10 MPa)
- Flexibility (E-module <500 MPa)
- Resistance to harsh chemicals
- Resistance to high temperature (250°C)
- High flex-life (>5E6 cycles)
- Extremely high product purity

General description of alternatives and comparison with fluoropolymers

Some alternatives that could be considered for these applications are**:**

- PP lining systems
- Rubber lining systems
- Tantalum-based piping
- Stainless steel: V2, V4, 316 L, Hasteloy, Inconel
- Enamel / glass lining systems

Similar to the case of the semiconductor industry (**Application 3.1**), the highest levels of purity of chemicals used in the production of vaccines or other medical products must be guaranteed. For this reason, elements of equipment in contact with chemicals used in the manufacture of these products have to ensure that no impurities will be generated during the process, which could alter the final composition of the medicines or vaccines.

Potential impacts related to substitution

The possible alternative materials listed previously have already been discussed in previous sections and will not be commented further. Due to potential degradation from rubber or other plastic solutions, and to the release of metals or migration of components from enamel elements, the use of these materials would not guarantee the highest purity demands that

the pharmaceutical industry requires, therefore those products could not be regarded as a viable alternative to fluoropolymers in this application.

Conclusions on the application

While fluoropolymers provide an outstanding combination of properties that are relevant for this use, the possibility to grant the highest possible purity levels and sterile conditions makes these materials the only real material of choice for production of vaccines and certain medicines, for which this property is absolutely essential. Failure in achieving this requirement may result in contamination of vessels and on the final vaccines delivered to the population, which would generate not only an obvious health concern, but also social distress and significant issues related to quality controls, tracking of contaminated vessels and eventually removal of a high number of vaccines that could have been marketed before identifying purity issues. In a situation that fluoropolymers would not be available for this use, production of vaccines requiring ultra-high purity conditions may become not viable within the EEA.

According to the European Federation of Pharmaceutical Industries and Associations (EFPIA, 2022), in 2016 the market value of the European pharmaceutical industry was 199,234 million EUR, with a production value of 248,053 million EUR. Investment in innovation for the same year was 33,949 million EUR, and total spending (public and private) on healthcare as a percentage of GDP at market prices of 2016 reached 8.8%. In terms of employment, the pharmaceutical industry contributed to 747,607 jobs, with additional 115,000 jobs focused on pharmaceutical R&D.

Other than the numbers displayed above, the recent crisis related to the Covid-19 pandemic has demonstrated that it is critical for the protection of the European population to keep a strong pharmaceutical sector ready to deal with immediate challenges from an ever-increasing complex health situation.

3.6.2. Application 6.2: Use of PTFE and FPE in the production of implants for the medical device sector

Description of the application

PTFE is used in interventional delivery devices (e.g., cardiovascular grafts, arteries, hernia mesh, stents, ligaments, etc.) due mainly to its inertness, non-toxicity, and biocompatibility properties, which allow for tissue attachment and cell adhesion without adverse reactions, infections, and rejection issues. In addition to that, PTFE coatings are used to enhance anti-friction properties and enable a smooth travel through blood vessels or other parts of the body.

Interventional delivery devices are crucial and, in many cases, the only solution to solve the malfunction or non-efficient behaviour of the human organs which can lead to very serious health issues. Medical devices are essential for saving lives and enhancing the life quality for millions of people who are suffering from certain illnesses.

PTFE etched liners are used as base for the implant construction, whereas the inner diameter of the PTFE is in direct contact with the media applied through the tubing (either inside the body or extraction from the body). For this application, a very low coefficient of friction is required to not disturb the flow and to not collect residue in the liner, which may impact the performance of the medical procedure. In addition, PTFE is able to withstand several sterilization methods. The etched outer surface is needed to bond the PTFE liner stable, yet flexible on another layer of the device construction.

Moreover, it is always necessary to hold all components of the device construction in place. For this functionality, an FEP heat shrink is always needed. FEP is here used for the shrink ratios 1.3:1 or 1.6:1 which are unique for fluoropolymers to be able to give the stability needed for the device.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical properties (moderate stiffness and high ultimate elongation)
- Low coefficient of friction
- Chemical inertness
- Resistance to harsh chemicals (chemical inertness to industrial chemical and solvents)
- Resistance to high temperatures (260°C)
- Resistance to low temperatures (-240°C)
- Weather resistance
- Biocompatibility
- Electrical insulator (high data transmission range)
- Dielectric strength (exceptional, stable with frequency and temperature)
- Barrier properties

- Non-stick/lubricant properties
- Low bacterial/algae growth (negligible moisture absorption)
- Gas exchange properties
- Non-aging characteristics

General description of alternatives and comparison with fluoropolymers

PP is one of the more widely used synthetic plastic materials. It is both strong and flexible, easily cut and can readily be integrated by surrounding tissues. Even though this is the most popular synthetic material on the market, it is associated with many complications, including infection issues.

Other polymers usually used in tubes like PVC, PE, thermoplastic polyurethane (PU/TPE-U), or silicone could be considered as alternatives, but they do not allow for the combination of low friction (without stick-slip), multiple use (cleanability and sterilization), high temperature resistance and dielectric strength (electrical surgery) that the various implant-related applications require.

The life span of alternatives is significantly shorter than that of fluoropolymers, implying a higher probability of failure and as a result a significant risk to human health. Furthermore, the likelihood of replacement is substantially higher as well, resulting in higher levels of waste that will need to be disposed of.

Potential impacts related to substitution

Alternatives do not meet the performance required by interventional delivery devices. The non-use of fluoropolymers would result in a severe decline in the life quality of people, or in the worst-case scenario, an increase in mortality because of the lower efficiency of medical devices and/or the rejection of the implant, therefore human health would be significantly compromised.

European companies manufacturing medical devices would most likely relocate outside of the EEA to other countries where such restrictions do not apply, which could result in an increase in health care tourism. Furthermore, it would have a severe economic impact on the healthcare sector, resulting in increased unemployment and dissatisfaction among the population.

Conclusions on the application

A ban on fluoropolymers for their used in medical devices would be expected to have a great impact on society because the European healthcare sector would be with all likelihood set back more than 50 years in terms of innovation, since the most modern technologies would not be available anymore.

Medical devices are regulated by specific regulations to guarantee human health. Material qualification and registration processes for medical devices are lengthy and costly processes. Depending on the application, approval of medical devices could take up to 12 years. These

procedures often involve significant efforts in terms of testing and changes to existing validated processes. To guarantee the adequate health care, the unique combination of properties offered by fluoropolymers to the interventional delivery devices becomes essential.

For many companies, the procedure to find suitable alternate materials, to re-design the components to accommodate new materials to meet the functional requirements and to change the tools for manufacturability will pose big challenges and make the products economically unviable.

Customers will generally use the most cost-effective solution that meets the needs of the application. It should be considered that the costs and time for research, development, testing, qualifications, and changes to processes would be significant even if suitable alternatives could be identified. Any changes would have to be evaluated, more complex environmental health and safety challenges would be created, and increased costs passed down to customers.

3.7. Sector of use 7: Construction

3.7.1. Application 7.1: Use of PVDF in the production of pipe fittings and manifolds for plumbing in the construction sector

Description of the application

PVDF is used in the production of pipe fittings and manifolds for plumbing systems in buildings, both residential and industrial. PVDF was introduced in the 1990s in this sector, due to its excellent resistance to chemicals and corrosion, resistance to high temperature, high compatibility with many chemical substances, stability, inertness, flame retardant and UV resistance properties. The main applications involve heating systems and sanitary water, related to delivery and transport of both gas and water.

PVDF is non-toxic and its smooth surface does not encourage the growth of microorganisms, therefore this anti-fouling property is helpful to prevent contamination of water or gas.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength
- Wear resistance
- Mechanical properties
- Low coefficient of friction
- Resistance to harsh chemicals
- Resistance to high temperature
- Resistance to low temperatures
- UV resistance
- Wide temperature range of operation
- High limiting oxygen index
- Weather resistance
- Low bacterial / algae growth

General description of alternatives and comparison with fluoropolymers

Brass

Brass was a typical material used for plumbing applications and in fact it can still be found today as a potential alternative. However, PVDF was introduced around 30 years ago to replace brass because it is a lighter material, offers better resistance to attack and is not impacted by corrosion, offering 50+years lifetime for the plumbing installation.

Polypheny lsulfone (PPSU)

PPSU is an alternative material that can be found currently on the market ad may be used for plumbing applications. However, replacement of PVDF with PPSU in plumbing applications

could result in several trade-offs, the most relevant ones being related to compatibility with other materials used in plumbing and reduced lifespan of the materials, along with some foreseeable supply issues.

Potential impacts related to substitution

Even if brass fitting systems are still available for plumbing applications today, it needs to be highlighted that this material is prone to corrosion under certain environments. Because small (yet significant) amounts of lead can be found in certain brass compositions, corrosion of brass-based plumbing materials could lead to release of lead and introduction of this hazardous metal into water systems, which can lead to significant issues from a health and environment perspective. The fact that this material is also heavier than PVDF and would eventually reduce the lifespan of the plumbing installations highlight that it is not a suitable replacement to PVDF fittings and manifold equipment.

In relation to PPSU, it needs to be highlighted that is a polyether composed of bisphenol S (BPS) and 4,4'-dihydroxybiphenyl (DHBP), both of which have been related to potential endocrine disrupting properties (Eckardt et al., 2018). Indeed, PPSU has been associated to generation of BPS during degradation (Li et al., 2022), therefore selection of this material as a component of plumbing installations should be evaluated carefully, particularly as a replacement to PVDF in case of a ban on the use of fluoropolymers, as this could lead to regrettable substitution. PPSU is not resistant to UV radiation and therefore there could be a potential risk of decomposition and release of BPS during normal use of fitting systems produced with PPSU.

PPSU is also considered to be more fragile and not resistant to heat which makes this a less reliable material in comparison to PVDF. More significantly, PPSU is known for not being compatible with the typical glue composition (under a well-known commercial brand) that is frequently used by plumbers in their installations. Introducing PPSU for all plumbing solutions would thus create significant problems down the value chain of plumbing installations, in relation to the need to find alternative materials for sealing fittings and manifolds. In addition, new casts for fitting solutions would have to be developed, brining significant additional costs (approximately 15 million EUR are estimated by one single company) to adapt to new standards having to switch from PVDF to PPSU based fittings.

In addition to this, it needs to be noted that water and gas pipe requirements are regulated by specific regulations, which means that new materials need to be approved for these uses. Such approval procedures may take up to 5 years, with obligations to demonstrate that the alternative is safe for use in water applications. This will involve the need for testing and additional research which can be estimated at about an extra 1 million EUR.

As of today, only two companies are identified as suppliers of PPSU in the EEA. This could point towards a supply issue in the case that replacement of PVDF by PPSU could be imposed due to regulatory restrictions on the use of PVDF, including potential price increases of the

alternative. Currently PVDF is a more expensive product compared to PPSU, but this could change if its use would be imposed in the context of a restriction impact on PVDF.

Companies involved in the production of PVDF based fittings and manifolds may consider taking production of these products outside of the EEA. Individual losses for companies in this sector are estimated at 200 million EUR revenue and 400 jobs terminated.

Conclusions on the application

The consequences of a ban on the use of PVDF in plumbing applications, related to the production of pipe fittings and manifolds for use in sanitary and heating systems (water and gas) could result in significant negative impact for the European society. Looking at alternative materials, the two main options available for substitution currently would entail potential issues human health or the environment, being related to higher corrosion risk from brass (and potential release and uptake of metals like lead in water streams), or to potential degradation of PPSU (e.g., via disposal of systems after end-of-life, or by degradation via exposure to UV radiation) resulting in potential release of hazardous chemicals like BPS. It needs to be noted that PVDF was introduced around 30 years ago as a replacement of brass-based solutions, therefore this change would push the European building sector a few decades backwards in terms of innovation.

Both solutions would bring additional negative situations to the broad value chain related to plumbing, from individual company losses in the range of hundreds of millions of EUR and hundreds of jobs at risk, with relocation of activities outside the EEA, to a need for plumbers to re-evaluate basic materials used in construction, such as typical gluing systems for sealing of fittings and re-shaping of casts for new pieces. This could be related to investments in the range of tens of millions of EUR, which would also include research and testing for verification of materials to be in contact with sanitary water. Relatively long time periods for obtaining approvals to use new materials would have to be foreseen as well.

The lack of availability of fluoropolymers in the plumbing sector will therefore imply a competitiveness decrease of the European companies, due to downgraded performance related to the alternatives not being able to match the combination of properties that PVDF provides. In addition to the negative impact on health and environment, and increased costs related to substitution, more frequent maintenance and increased disposal of materials related to shorter lifespans would need to be considered.

3.7.2. Application 7.2: Use of PVDF in façade and infrastructure protection for the construction sector

Description of the application

PVDF is used in coatings for the construction sector to protect and enhance the durability of critical infrastructure elements, especially for metal-based components. These protective coatings are used in, among others, bridges, pipelines, storage tanks, racks that support solar panels, buildings in housing, heavy industry, and airports.

PVDF is used for this application due to its excellent resistance to chemicals and corrosion, resistance to high temperature, high compatibility with many chemical substances, stability, inertness, durability, flame retardant and UV resistance properties. Its exceptional flexibility allows the use in the complex forming and bending of metal building panels. PVDF is also resistant to high humidity environments, non-toxic, and its smooth surface does not encourage the growth of microorganisms, therefore this anti-fouling property is helpful to prevent stains and dirtiness.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Wear resistance: PVDF meets or exceeds the standards for the building panel industry. AAMA 2605, EU equivalent to ASTM D968).
- Mechanical properties: The superior flexibility of PVDF allows for complex forming and bending of metal building panels AAMA 2605 EU equivalent to ASTM D4145, ASTM D522 and ASTM D2794.
- Resistance to harsh chemicals: EU equivalent to ASTM D1308.
- Weather resistance: Exceptional resistance to UV degradation during exterior exposure AAMA 2605 EU equivalents to ASTM G7, ASTM D2244 colour retention, ASTM D4214 chalk resistance and film erosion.
- Barrier properties: Provides enhanced corrosion and humidity resistance VDA 233-102 EU equivalents to ASTM B117, ASTM D2247 and ASTM D4585.
- Fire retardancy / smoke suppression: Exceptional flame spread resistance and smoke development EU equivalent to ASTM E84.
- Low bacterial / algae growth
- Low refractive index for optical effects: Compared to other coating types, the lower refractive index leads to lower pigment demand for film opacity. The use of less pigment supports sustainability initiatives.
- Other properties: These coatings have less tendency to collect dirt and reduced degradation due to UV exposure. This allows for a graffiti resistant coating. This also allows for the coating to maintain solar reflectance values longer. CRRC-1 Program, ASTM D7897 and ASTM E1918.

General description of alternatives and comparison with fluoropolymers

Silicon-modified polyester, polyurethane or high-performance polyester could be taken into account as alternatives. However, alternatives would potentially reduce the life expectancy of building panels from 40 to 50 years or even more down to 20 to 35 years or less, depending on the alternative technology used and the specific setting.

Potential impacts related to substitution

If alternative materials were to replace PVDF in coating applications for buildings, the reliability of coated surfaces would be expected to decline over time due to the reduced efficiency of such materials. This could lead to compromised safety where the coatings are used to protect elements of the critical infrastructure such as bridges and buildings.

The longer durability of fluoropolymer-based coatings results in a reduced environmental impact and maintenance cost over the lifetime of the building, since maintenance activities will be minimised; less removal and replacement of building panels will be required when PVDF is used in coatings compared to alternatives. The low surface energy and hydrophobicity of PVDF also results in reduced dirt, allowing the structures to remain cleaner for a longer time. Finally, PVDF is also resistant to UV radiation, a property that all the alternatives would not offer. This means that non-fluoropolymer coatings could break down through hydrolysis and photochemical reactions, resulting in increased degradation and reduction of protection objectives.

Conclusions on the application

The architecture and construction industries are not only challenged to build structures that withstand extreme weather conditions, but also maintain the exterior appearance for years to come. Consequently, building design teams are always looking for more durable solutions when envisioning projects that use architectural metal panels. This means they are increasingly turning to architectural metal coatings that offer longevity, lasting colour retention and superior protection from the elements.

It is important to highlight that trade-offs from the use of alternatives to PVDF in this application are not related to appearance or other aesthetics properties, but to safety and integrity of infrastructures, some of which are related to housing (buildings), but also to critical components for mobility (bridges), or even for renewable energy systems (solar panels). The use of high technology fluoropolymer-based coatings allows for enhanced fire protection and longer life of coated surfaces, which in turn reduces the need for material replacement and/or recoating. The reduction in waste and material consumption would be expected to result in lower carbon usage. PVDF is used as the back sheet in most solar panels. Furthermore, the use of painted metal structures is amenable to recycling as many metals such as steel and aluminium are recycled through melting in blast furnaces. In general, it is difficult to reuse or recycle applied organic coatings, but high-temperature incineration would be expected to

result in destruction of the PFAS molecular structure and vapor capture and processing is commonly used during recycling efforts.

The use of high-technology fluoropolymer-based coatings allows for the long life of coated surfaces, which in turn reduces the need for material replacement and/or recoating. The reduction in waste and material consumption would be expected to result in lower carbon usage. The extraordinary resilience of fluoropolymer-based coatings means that relatively little of the material would be expected to be released over the product's lifespan. The erosion of the coated film is minimal. This allows for a life cycle and product warranties of 40 years or more.

It should also be noted that the use of PVDF in the construction sector is limited to industrial applications, and that PVDF-based coatings are generally not available for the general public for use in lower value applications.

The lack of availability of fluoropolymers-based coatings for the construction sector will therefore imply a competitiveness decrease for the European companies, due to downgraded performance related to the alternatives not being able to match the combination of properties that PVDF provides. It would be expected that the sheets for coatings may be produced outside the EEA and/or they will be imported in the case the application would be still needed.

In addition to the negative impact on the environment and increased costs related to substitution, more frequent maintenance and increased disposal of materials related to shorter lifespans would need to be considered.

3.7.3. Application 7.3: Use of PTFE, ETFE, FEP, PFA in the production of sealing systems in compressors used for heating and air conditioning equipment

Description of the application

PTFE, ETFE, FEP and PFA (and their composites) are used in the production of seals, bearings, gaskets, and o-rings. These materials are then used in compressors that are installed mainly in houses for heating and air conditioning purposes. However, there are other applications that could be relevant for this use, for example installations destined for food preservation and maintenance (cooling) of medical products (vaccines, etc.).

The industry referred in this case is typically referred to as Heating, Ventilation, Air Conditioning and Refrigeration industry (HVACR) or Refrigeration, Air Conditioning, and Heat Pump (RACHP) industry.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Mechanical strength (Compressive and tensile strength, ductility, and modulus).
- Wear resistance (Wear rate, including no scuffing/galling, and ability to conform for high-speed sleeve bearings).
- Mechanical properties (Flexural strength, ability to deform/yield slightly to produce adequate sealing).
- Low coefficient of friction: 0.05 maximum dynamic friction coefficient.
- Resistance to harsh chemicals: must not excessively harden, soften, or crack in the presence of pressurized F-gases such as hydrofluorocarbons (HFC) or hydrofluoro-olefins (HFO) or hydrocarbon refrigerants and their oils, such as polyester oil (POE), polyalkylene glycol (PAG), or polyvinyl ether oil (PVE).
- Resistance to high temperature: temperatures of operation may reach 175°C.
- Resistance to low temperatures: certain HVACR applications (helium/cryogenic) can expose polymers to very cold temperatures (<-60C) due to the cooling effect of the refrigerant.
- Wide temperature range of operation: Must not excessively harden, soften, or crack in the presence of refrigerants and oils under large temperature swings (-60°C to 175°C). This temperature range may come from the refrigerant effect as well as the winter ambient outside.
- Electrical insulator: The internal motors, wire insulation, relays, electrical protectors, etc., come in contact with refrigerant and oils and must maintain their insulative properties equivalent to current fluoropolymer material.
- Dielectrical strength.
- Explosive decompression: Due to the large cyclic variation in gas pressure and temperature in normal operation, the polymer must not absorb excess refrigerant with a corresponding fast release causing material “explosion”.

General description of alternatives and comparison with fluoropolymers

Materials such as polyetherimide (PEI), polybenzimidazole (PBI), polyamideimide (PAI) or phenolic resins have been proposed as potential alternatives, however it should be highlighted that these materials have not been fully tested as replacements for fluoropolymers in the application.

Potential impacts related to substitution

None of the alternative materials that have been flagged as potential replacements for fluoropolymers in this application offer the same degree of chemical resistance. In addition, they are expected to offer inferior protection against friction in front of increased compressor power usage, leading to less reliability and service life (bearing failure rate increase, scuffing/galling rate increase), efficiency reduction (refrigerant leakage from less effective sealing causing capacity loss). In the case of flammable refrigerants (which are becoming more common as they are low global warming type refrigerants), leakage would be a safety concern.

Due to the previously mentioned inferior chemical resistance, alternative may lead to increased chemical degradation and higher chances of releases. This could be a safety concern, particularly as the use of flammable refrigerants is increasing, which are considered of lower global warming impact.

Other properties that would be downgraded are ductility, sealing effectiveness, yielding/conformability with bearings, or high temperature tolerance. All of this would make compressors less reliable, less energy efficient, not to mention the need to face higher product costs due to design changes which would likely become necessary.

It important to understand that HVACR systems are very aggressive to polymers in the general sense. HVACR systems are hermetically sealed and normally last 15 or more years. Compression of the refrigerant causes high gas pressure and temperature swings. Temperatures can range from -60°C to 175°C. Under these conditions, the refrigerant can penetrate into the polymer components or coatings and cause several destructive events (brittleness, softness, and explosive decompression). Another unfortunate consequence is that the refrigerant acts like a solvent to some extent and dilutes the oil. Dilution of the oil causes the oil's viscosity to diminish which reduces the oil's ability to effectively lubricate. There are many moving parts inside a compressor and valves and fluoropolymers are used to help reduce friction and keep the refrigerant sealed. So, all these constraints and hardships make the conditions inside an HVACR system very unique and demanding. As a result, these hardships make choosing a polymer type very difficult. There are not many polymers that can withstand this environment. Fluoropolymers are one of the few classes of polymers that work well in these environments because of the combination of many beneficial properties as described earlier and certainly the ones that offer best performance and reliability. They have been approved for use in HVACR systems for many years.

Conclusions on the application

The HVACR industry represents over 30 billion EUR in turnover, over 200,000 direct jobs and millions of indirect jobs. Even a small perturbation in this industry due the unavailability of fluoropolymers would be fairly substantial. This industry plays a vital role in the EU society. It provides critical climate control and ventilation in homes, hospitals, schools, elder care facilities, and most buildings. The HVACR industry creates the environmental conditions necessary for the application by controlling and monitoring temperature, humidity, and air quality.

Electric heat pump compressors (for hot water and air heating) are vital to reduce Europe's reliance on oil and gas. These elements are expected to play a key role in the achievement of the Green Deal goals. Less reliable, less efficient, and shorter lasting heat pump compressors would be a detriment and slow down decarbonisation objectives. Finally, it should be considered that the incorporation of low global warming refrigerants is becoming an increasing trend in the sector. The fact that these refrigerants are flammable requires absolutely efficient sealing systems, which may not be possible if fluoropolymers are not available for this application.

The following are other important applications: transportation and storage of food and other perishables, reach-in food store display cases, walk-in coolers, computer rooms, breweries, liquid desiccant dehumidification, cannabis processing, ice machines, ultra-low temperature/cryogenic freezing, warehouse climate controlled storage, process chillers in industrial plants, indoor farming, shop air drying, dental air compression, ocean refrigeration containers, rail and bus air conditioning (and monitoring), truck/trailer refrigeration, controlled storage of medicines such as vaccines and laboratory specimens, industrial and commercial chillers. Reducing or eliminating HVACR products caused by premature elimination of fluoropolymers would likely cause a global societal crisis.

3.8. Sector of use 8: Cookware

3.8.1. Application 8.1: Use of PTFE in cookware

Description of the application

PTFE is used in cookware (e.g., frying pans and in bakery trays) due to its long-lasting non-stick performance. The main positive effects resulting from this use are related to safety (preventing metal migration into food), improved health conditions (less oil being used, less burned food), sustainability (less food waste due to burned food, longer life-time of articles which are as well easier to clean, resulting in lower carbon footprint due to less water and detergent usage for cleaning) and hygiene (articles are easier to clean).

It is relevant to highlight that decomposition of PTFE is expected at a temperature of 350°C. Above 260-270°C, slight degradation of PTFE coatings may begin. However, most food will be burned before reaching any of those temperature levels, in fact decomposition of frying oil starts at 180°C, with the Maillard reaction (browning of food) starting at 140°C. Therefore, it is not expected that any decomposition of PTFE would be involved in the cooking process.

It is the case that in the curing process of cookware (not in the end use by consumers), coatings are heated up to 420°C for a short time. Any release of volatile materials (which would in any case be minimal) will be collected and absorbed by abatement techniques that are currently present at any production facility.

Technical properties required for the material of choice

For this application, the following properties are relevant for the material of choice:

- Resistance to harsh chemicals (those that may be used for cooking but also for cleaning purposes)
- Resistance to high temperature
- Barrier properties
- Non-stick properties

General description of alternatives and comparison with fluoropolymers

Ceramic materials can be used as an alternative to coat cookware. The use of non coated stainless-steel articles for coating can also be used but these will obviously not provide the desired non-stick properties.

Potential impacts related to substitution

Non-stick properties of ceramic coated cookware are nowhere near to the levels that PTFE provides. This means that replacement needs to occur more frequently, which will result in higher cost for consumers. Furthermore, this solution is not valid in industrial kitchen appliances (e.g., cooking robots) which require very high performance. For this sector, no viable alternatives are considered to be available.

According to the Federation of European manufacturers of Cookware and cutlery (FEC), there are currently 600 million pieces of coated cookware in EU households. Assuming a replacement of coated cookware every 4 years, this results in 150 million pieces of coated cookware being sold in Europe on a yearly basis.

Conclusions on the application

PTFE shows unique long lasting non-stick performance not met by other metals or coating materials up to now.

It needs to be highlighted that PTFE is known as being a non-toxic material. The main concern related to the use of PTFE in cookware was the use of other PFAS surfactants as polymerisation aids during the manufacturing process, where small concentrations of such surfactants may remain in the final PTFE coat and thus be released during the use phase of cookware. However, industry has taken significant steps over the last years to remove the use of those surfactants. It is expected that in the near future, all PTFE grades may be available on the market without involving PFAS in the manufacture. The result of this will be that cookware will be coated with a non-hazardous material that contains no remaining of any other substance of concern. It would therefore be questionable that a non-hazardous product should be banned from applications in which it provides significant benefits to society, related not only to comfort levels, but also to safety and improved health conditions. Indeed, even before such technical developments occurred, release of such PFAS from coated cookware was nevertheless regarded as being improbable, as stated by the German Institute for Risk Assessment (BfR, 2019), which wrote that “toxicologically relevant migration of PFOA (one of the PFAS of highest concern) from non-stick coated cookware is unlikely to happen if the production is done under ‘Good Manufacturing Practice’”.

in 2017, the Danish Consumer Council THINK Chemistry selected 16 frying pans from the Danish market. These products were tested for the release of unwanted fluorine substances. In the test, the frying pans were first washed. They were then filled with olive oil and put in the oven at 200 degrees for 30 minutes. The olive oil was then tested for the content of 22 specific fluorine substances. It was also tested for so-called total organic fluorine, which is a broad term for fluorine substances. No release of fluorine substances was found in any of the frying pans. However, the test shows that the frying pans tested did not release these substances to food. If frying pan material contains fluorine substances in their non-stick coating, the substances are therefore well-bound in the pan's material (Danish Consumer Council, 2017).

4. Conclusions

The case studies described in this report are just a small sample of the many applications in which fluoropolymers are used. However, they can be considered as a good representation of the many key properties that fluoropolymers offer to a wide number of industrial sectors, and which enable highly valuable benefits that end-users in Europe enjoy.

Fluoropolymers are currently irreplaceable for many critical applications, and existing potential alternatives would be associated with significant trade-offs that could compromise safety of workers, general population, or the environment, either due to direct hazardous properties of the alternative, or by downgrading performance of key applications. As of today, it is not anticipated that viable alternatives offering equivalent performance could be developed in the near future.

Fluoropolymers were first discovered and developed in the late 1930s. Since then, many innovative processes have been developed which involve the use of these high-value materials. This has enabled sophisticated and high-performance technological systems that have resulted in the quality standards that the modern society has achieved. Fluoropolymers were frequently introduced in existing industrial sectors to improve safety and reliability conditions, replacing less efficient materials. Under a situation in which fluoropolymers may no longer be available and downstream users would be forced to switch to alternatives, a relevant number of applications could be pushed backwards 50 years or more, in terms of technologies that would have to be used. Clear examples of this would be the manufacture of semiconductors at modern technical standards, or the development of innovative green energy techniques.

On top of this, some of those applications are key enablers of strategic objectives that the European Union has established, in terms of energy and decarbonization (as indispensable components in lithium batteries or green hydrogen production), or related to innovative technology, such as data processing systems. Ultimately, the contribution of fluoropolymers to safety in many systems related to the chemicals industry, vehicles such as cars or airplanes, processing of water and food, or production of vaccines and medicines highlight the important contribution of these materials to the European society. While human safety and environmental protection, as well as contribution to development of clean energy sources have been highlighted as key benefits derived from the use of fluoropolymers, their contribution to the competitiveness of the European industry should also be taken into account. In fact, all the respondents to the questionnaire expressed concerns that a situation in which fluoropolymers may no longer be available for the specific application described could result in strong negative impact to many sectors and eventually relocation of a large number of stakeholders involved in the value chain of fluoropolymers. 100% of the replies obtained in the survey underlined the possibility that Europe would become a net importer of articles and goods manufactured with the aid of fluoropolymers in other regions of the world

that may continue to allow the use of these substances, in an ever increasingly competitive environment.

The vast majority of fluoropolymers have been proven to be polymers of low concern. Furthermore, industry continues to make progress to remove the use of other (small molecule-) PFAS as processing aids in their manufacture of fluoropolymers. In parallel, increasingly effective abatement techniques are able to adequately control industrial emissions. All of these initiatives, coupled to the high value that fluoropolymers bring to the progress, competitiveness, safety, protection, and well-being of the modern European society, suggest that the benefits of the continued use of fluoropolymers would largely outweigh potential risks (if any), related to the manufacture, use and disposal of fluoropolymers. In summary, it appears evident that any regulatory initiative that could impact fluoropolymers should look at establishing mechanisms that would ensure that these materials will continue to be available for the many critical industrial sectors in which they are currently used.

The case studies described have been grouped depending on the sector of use involved, with a description of the specific application in which the fluoropolymers are handled. It should be noted that frequently, the combination of properties offered by fluoropolymers could make the description of one case expandable others. For example, the combination of high range of operating temperature with resistance to harsh chemical environments is relevant for sectors such as the chemical processing industry, food and water treatment, semiconductors, or pharmaceuticals. Therefore, specific cases for those sectors have been described, which are equivalent between each other in terms of describing the benefits that fluoropolymers offer for the application, as well as in relation to the potential alternatives. While this can be clearly seen in some of the cases described in this report, in other situations only one specific example has been provided, however this does not preclude that the application may be relevant for other industrial sectors. For example, the use of fluoropolymers in seals and gaskets has only been described for the chemical process industries, however fluoropolymer-based seals and gaskets are also critical for sectors such as transport of dangerous goods, automotive or aerospace industry (e.g., in safety components such as wing flaps in aircrafts). In any case, the specific cases described should be taken as a small representation of the vast spectrum of applications in which fluoropolymers can be used in the modern society.

5. References

ACEA, 2022. The Automobile Industry. Pocket Guide 2021/2022. *European Automobile Manufacturers' Association*. Available at: https://www.acea.auto/files/ACEA_Pocket_Guide_2021-2022.pdf#page=6. Last access: June **2022**.

BfR, 2019. Available at: https://www.bfr.bund.de/cm/343/neue-gesundheitsbezogene-richtwerte-fuer-die-industriechemikalien-pfos-und-pfoa.pdf. Last access: July **2022**.

Bloomberg NEF, 2021. Electric Vehicle Outlook. Available at: https://about.bnef.com/electric-vehicle-outlook/. Last access: June **2022**.

Danish Consumer Council (2017). Available at: https://kemi.taenk.dk/test/test-kemi-i-stegepander. Last access: July **2022**.

Eckardt, M., Greb, A. and Simat, T.J. Polyphenyl sulfone (PPSU) for baby bottles: a comprehensive assessment on polymer-related non-intentionally added substances (NIAS). Food Additives & Contaminants: Part A. Volume 35, **2018** - Issue 7.

EFPIA, 2022. Data Centre of the Pharmaceutical Industry. *European Federation of the Pharmaceutical Industries and Associations*. Available at: https://www.efpia.eu/publications/data-center. Last access: June **2022**.

ESIA, 2022. European semiconductor market in December 2021. *European Semiconductor Industry Association*. Available at: https://www.eusemiconductors.eu/sites/default/files/uploads/ESIA_WSTS_PR_2112.pdf. Last access: June **2022**.

ESIA, 2021. European semiconductor market in December 2021. *European Semiconductor Industry Association*. Available at: https://www.eusemiconductors.eu/sites/default/files/uploads/ESIA_WSTS_PR_2012.pdf. Last access: June **2022**.

Eurochlor, 2022. Mercury Cell Process. Available at: https://www.eurochlor.org/about-chlor-alkali/how-are-chlorine-and-caustic-soda-made/mercury-cell-process/. Last access: June **2022**.

European Commission, 2022. A Water Blueprint – taking stock, moving forward. Available at: https://ec.europa.eu/environment/water/blueprint/index_en.htm. Last access: June **2022**.

European Commission, 2021. Inside the future: Europe's plan to thrive in the global microchip race. Available at: https://ec.europa.eu/commission/commissioners/2019-2024/breton/announcements/inside-future-europes-plan-thrive-global-microchip-race_en. Last access: June **2022**.

Findaboutplastics, 2020. Available at: https://www.findoutaboutplastics.com/2020/05/design-properties-for-engineers.html. Last access June **2022**.

FoodDrinkEurope, 2022. Data and trends of the European Food and Drink Industry in 2021. Available at: https://www.fooddrinkeurope.eu/resource/data-trends-of-the-european-food-and-drink-industry-2021/. Last access: June **2022**.

FPG, 2022a. Fluoropolymers vs. Side chain fluorinated polymers. *Fluoropolymers Product Group. Plastics Europe.* Available at: https://fluoropolymers.plasticseurope.org/application/files/3516/3913/1778/Fluorpolymers_vs._side_chain_fluorinated_polymers_final.pdf. Last access: June **2022**.

FPG, 2022b. Update of market data for the socioeconomic analysis (SEA) of the European fluoropolymer industry. *Fluoropolymers Product Group. Plastics Europe.* Available at: https://fluoropolymers.plasticseurope.org/application/files/1216/5485/3500/Fluoropolymers_Market_Data_Update_-_Final_report_-_May_2022.pdf. Last access: June **2022**.

FPG, 2021. Regulatory Management Option Analysis on Fluoropolymers. *Fluoropolymers Product Group. Plastics Europe.* Available at: https://fluoropolymers.plasticseurope.org/application/files/5416/5104/8333/20211104_FP_RMOA_Final_3.pdf. Last access: June **2022**.

FPG, 2017. Socio-economic Analysis of the European Fluoropolymer Industry – Executive Summary. *Fluoropolymers Product Group. Plastics Europe.* Available at: https://fluoropolymers.plasticseurope.org/application/files/7816/1167/4026/Final_SEA_Fluoropolymers_summary2017_3.pdf. Last access: June **2022**.

Henry, B.J., Carlin, J.P., Hammerschmidt, J.A., Buck, R.C., Buxton, L.W., Fiedler, H., Seed, J. and Hernandez, O. A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers. *Integr Environ Assess Manag*. **2018**: 316-334.

Hydrogen Council, 2021. Hydrogen Insights: A perspective on hydrogen investment, market development and cost competitiveness. Available at: https://hydrogencouncil.com/wp-content/uploads/2021/02/Hydrogen-Insights-2021.pdf. Last access: June **2022**.

Hydrogen Europe, 2022. Direct communication.

Hydrogen Roadmap Europe, 2019. A Sustainable Pathway for the European Energy Transition. Available at: https://www.fch.europa.eu/sites/default/files/Hydrogen%20Roadmap%20Europe_Report.pdf Last access June **2022**.

JRC, 2014. Best Available Techniques (BAT) Reference Document for the Production of Chlor-alkali. *Joint Research Centre Science and Policy Reports*. **2014**. Available for download at:

https://publications.jrc.ec.europa.eu/repository/handle/JRC91156

Kang, J.S., Choi, J.S., Kim, W.K., Lee, Y.L., and Park, J.W. Estrogenic potency of bisphenol S, polyethersulfone and their metabolites generated by the rat liver S9 fractions on a MVLN cell using a luciferase reporter gene assay. *Reprod. Biol. Endocrinol*. **2014**; 12: 102.

Korzeniowski S.H., Buck R.C., Newkold R.M., El kassmi A., Laganis E., Matsuoka Y., Dinelli B., Beauchet S., Adamsky F., Weilandt K., Soni V.K., Kapoor D., Gunasekar P., Malvasi M., Brinati G., and Musio S. A. Critical Review of the Application of Polymer of Low Concern Regulatory Criteria to Fluoropolymers II: Fluoroplastics and Fluoroelastomers. *Integr Environ Assess Manag.* **2022** *(in-press)*.

Li, Y., Liu, Y., Liu, S., Zhang, L., Shao, H., Wang, X., and Zhang, W. Photoaging of Baby Bottle-Derived Polyethersulfone and Polyphenylsulfone Microplastics and the Resulting Bisphenol S Release. *Environ. Sci. Technol*. **2022**, 56, 5, 3033–3044.

Mesothelioma, 2017. How asbestos invaded the chlorine industry. Available at: https://www.mesothelioma.com/blog/how-asbestos-invaded-the-chlorine-industry/. Last access: June **2022**.

OECD, 2009. Data analysis of the identification of correlations between polymer characteristics and potential for health or ecotoxicological concern. *Organisation for Economic Co-operation and Development*. Available at: http://www.oecd.org/chemicalsafety/risk-assessment/42081261.pdf. Last access: June **2022**.

Ruf, Y., Baum, M., Zorn, T., Menzel, A., and Rehberger, J. Fuel Cells Hydrogen Trucks – Heavy duty's High Performance Green Solution. Available at: https://www.fch.europa.eu/sites/default/files/file_attach/FCH%20HDT%20-%20Study%20Report_final_vs.pdf. Last access: June **2022**.

The MBR Site, 2017. The material question - choosing MBR membrane materials. Available at: https://www.thembrsite.com/blog/choosing-mbr-membrane-materials/. Last access: June **2022**.

Annex I: Questionnaire for downstream users of fluoropolymers

1. **Please provide identification information of your company in the EEA[1] and the relevant contact person.**

Company Name	
Country	
Contact person name	
Role	
Telephone number	
e-mail address	

2. **Please indicate at least 3 examples of major applications using fluoropolymers that are relevant to your business, and the industries in which they are used.**

   For an overview of possible industry & sector of use, please refer to Annex I. If the application of interest is not found in the Annex, please describe it.

Case #	**Description of application**	**Fluoropolymers used (see list below)**	**Industries involved**
Case 1			
Case 2			
Case 3			

List of (major) fluoropolymers that will be covered in this questionnaire.

Abbreviation	**Name**	**CAS #**
PTFE	Polytetrafluoroethylene	9002-84-0
PFA	Perfluoroalkoxy polymer	26655-00-5 / 31784-04-0
FEP	Fluorinated ethylene propylene	25067-11-2
FKM	Vinylidene fluoride-hexafluoropropylene copolymer	9011-17-0
ETFE	Ethylene tetrafluoroethylene	25038-71-5 / 68258-85-5
PVDF	Polyvinilidene fluoride	24937-79-9

[1] EEA: European Economic Area = EU + Iceland, Liechtenstein, and Norway. It is expected that all the replies to the following questions refer to this economic area.

3. **Please indicate which of the following technical properties are relevant for the applications listed in question 2 (more than one selection is possible).**

   If possible, please indicate any technical requirements that may be relevant to justify the importance of the use of fluoropolymers, including units of properties. For example, "a minimum value of xx Pa for mechanical strength is required for the product to perform in Case 1".

Case 1

Category	Technical property	Relevant to application	Specification & Measurement standard
Durability	Mechanical strength		
	Wear resistance		
	Mechanical properties (e.g., flexibility)		
	Low coefficient of friction		
Inertness – stability	Resistance to harsh chemicals		
	Resistance to high temperatures		
	Resistance to low temperatures (e.g., cryogenic properties < 50°C)		
	Wide temperature range of operation		
	Weather resistance		
	Biocompatibility		
	High limiting oxygen index		
Functionality	Electrical insulator (high data transmission range)		
	Ionic conductivity		
	Piezoelectric properties		
	Dielectric strength		
	Barrier properties		
	Non-stick properties		
	Optical clarity		
	Fire retardancy / smoke suppression		
	Low bacterial / algae growth		
	Low refractive index for optical effects		
	Other (please specify):		

Case 2

Category	Technical property	Relevant to application	Specification & Measurement standard
Durability	Mechanical strength		
	Wear resistance		
	Mechanical properties (e.g., flexibility)		
	Low coefficient of friction		
Inertness – stability	Resistance to harsh chemicals		
	Resistance to high temperatures		
	Resistance to low temperatures (e.g., cryogenic properties < 50°C)		
	Wide temperature range of operation		
	Weather resistance		
	Biocompatibility		
	High limiting oxygen index		
Functionality	Electrical insulator (high data transmission range)		
	Ionic conductivity		
	Piezoelectric properties		
	Dielectric strength		
	Barrier properties		
	Non-stick properties		
	Optical clarity		
	Fire retardancy / smoke suppression		
	Low bacterial / algae growth		
	Low refractive index for optical effects		
	Other (please specify):		

Case 3

Category	Technical property	Relevant to application	Specification & Measurement standard
Durability	Mechanical strength		
	Wear resistance		
	Mechanical properties (e.g., flexibility)		
	Low coefficient of friction		
Inertness – stability	Resistance to harsh chemicals		
	Resistance to high temperatures		
	Resistance to low temperatures (e.g., cryogenic properties < 50°C)		
	Wide temperature range of operation		
	Weather resistance		
	Biocompatibility		
	High limiting oxygen index		
Functionality	Electrical insulator (high data transmission range)		
	Ionic conductivity		
	Piezoelectric properties		
	Dielectric strength		
	Barrier properties		
	Non-stick properties		
	Optical clarity		
	Fire retardancy / smoke suppression		
	Low bacterial / algae growth		
	Low refractive index for optical effects		
	Other (please specify):		

4. **Please indicate a list of potential non-fluoropolymer alternatives [2] (second best alternatives) for the applications listed in question 2.**

Case #	Potential alternatives to fluoropolymers that could be considered as alternatives
Case 1	
Case 2	
Case 3	

5. **Please explain possible trade-offs that could be expected when alternatives to fluoropolymers are used in these applications. Use the following guidance for completion.**

- Amount of product used: how much fluoropolymer is used per year, and how much alternative would be required? If total volumes cannot be reported, please state ratio (e.g., if double amount of alternative would be required, please state 1/2 in the non-fluorinated alternative column.
- Property comparison: how will the main technical function of the manufactured products be impacted if alternatives are used instead of fluoropolymers?
- Combination of functionalities: how will the use of an alternative compare in relation to the combination of technical functions that fluoropolymers bring to manufactured products?
- Overall performance: what will be the ultimate impact on the manufactured products if fluoropolymers were to be replaced with the alternatives?
- Safety & reliability: will there be any impact to the overall safety of the manufactured products (and those further down in the value chain)? If yes, please describe.
- Application life: will the service life of the manufactured products be different if alternatives are to be used in the relevant application? If yes, please describe.
- Circularity: would there be any impact in the contributions of the sector to the circular economy if alternatives to fluoropolymers were used? If yes, please describe.
- Decarbonisation: would there be any impact in the contributions of the sector to a green energy transition? If yes, please describe.
- (Eco)toxicity comparison: how would the alternatives compare to fluoropolymers from a hazard perspective?
- Other: if you can identify additional relevant criteria, please specify, and describe expected impact.

[2] The principle to follow is that there is always a possibility to substitute, therefore indicating that there are no alternatives for a specific application is not a valid reply; there will be opportunities in following questions to describe why an alternative is not considered to be ideal. Alternatives cannot be other fluoropolymers or fluorinated products (e.g., PFAS).

Case 1		
Criteria	**With Fluoropolymer**	**With non-fluorinated alternatives**
Amount of product used:		
Property comparison:		
Combination of functionalities		
Overall performance		
Safety & Reliability		
Application life		
Circularity		
Decarbonisation		
(Eco)toxicity comparison		
Other (please describe):		

Case 2		
Criteria	**With Fluoropolymer**	**With non-fluorinated alternatives**
Amount of product used:		
Property comparison:		
Combination of functionalities		
Overall performance		
Safety & Reliability		
Application life		
Circularity		
Decarbonisation		
(Eco)toxicity comparison		
Other (please describe):		

Case 3		
Criteria	**With Fluoropolymer**	**With non-fluorinated alternatives**
Amount of product used:		
Property comparison:		
Combination of functionalities		
Overall performance		
Safety & Reliability		
Application life		
Circularity		
Decarbonisation		
(Eco)toxicity comparison		
Other (please describe):		

6. **In a hypothetical case that fluoropolymers were not available for use in the EEA, and you were forced to use alternative products, do you think that the application would continue? Or could it be expected that technology would be transferred outside the EEA? Please justify your answer, including potential impacts down in the value chain.**

Case 1	
Case 2	
Case 3	

7. **Please indicate the expected socio-economic impact that should be expected if fluoropolymers were no longer available for these applications, and industry was forced to use alternative products.**
   When providing your replies, please consider the impact (if relevant for each case) of potential technological downgrades resulting from the use of alternatives, particularly since the EEA's economic strength is based on developing and supplying high technology across the globe.

   - Economic impacts: based on your knowledge of the value chain, what could be the consequences to be expected for end-use applications in the EEA if fluoropolymers were to be replaced by non-fluorinated alternatives? If available, quantitative data (real or estimated) would be highly valuable, particularly related to impacts on revenue, GDP and/or jobs that could be lost (direct and indirect); if this is not available, a qualitative estimate based on your experience could also be valuable.
   - Societal impacts: in which way would society be affected, e.g., which products or services would be impacted, and how, if fluoropolymers were no longer available for the specific application under discussion? What would be the consequences for the EEA's position in terms of technological competitiveness compared to other regions globally?

Case 1	
Economic impacts:	
Societal impacts:	

Case 2	
Economic impacts:	
Societal impacts:	

Case 3	
Economic impacts:	
Societal impacts:	

8. **Please provide any additional information that you believe could be relevant to defend the continued use of fluoropolymers in the EEA.**

Annex II: Main fluoropolymers covered in this report

Abbreviation	Name	CAS #
PTFE	Polytetrafluoroethylene	9002-84-0
PFA	Perfluoroalkoxy polymer	26655-00-5 / 31784-04-0
FEP	Fluorinated ethylene propylene	25067-11-2
FKM	Vinylidene fluoride-hexafluoropropylene copolymer	9011-17-0
ETFE	Ethylene tetrafluoroethylene	25038-71-5 / 68258-85-5
PSEPVE	Sulfonated tetrafluoroethylene	31175-20-9
PVDF	Polyvinilidene fluoride	24937-79-9

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POSITION PAPER

Fluoropolymers: an outlier in the PFAS class of substances

Final report

Date

18 July 2022

Executive Summary

Fluoropolymers are frequently confused with other chemicals that belong to the PFAS group of substances. While fluoropolymers meet the chemical and structural conditions set in the broad definition of PFAS, their properties and range of applications are very different not only from the short-chain or long-chain non-polymeric PFAS that have been cause of concern due to their toxic properties for human health or the environment, but they are also very different from other polymeric PFAS like perpolyfluoroethers or side-chain fluorinated polymers.

In addition to their clearly defined and differentiated structure, existing scientific data shows that fluoropolymers are biologically stable and chemically inert, negligibly soluble in water, non-bioavailable, non-bioaccumulative, and non-toxic. Furthermore, their range of applications is different from the other polymeric PFAS, since fluoropolymers are mainly used in industrial applications.

This report highlights the main differences between fluoropolymers, perfluoropolyethers and side-chain fluorinated polymers, highlighting how those differences justify considering fluoropolymers as chemicals posing no relevant risk for human health or the environment. While the first three Sections intend to explain such differences in a way that will be easy to understand for any reader, Section 4 goes slightly deeper in technical justifications of the contrast between these families of chemicals. Since one of the most critical differences, particularly between fluoropolymers and side-chain fluorinated polymers is the potential of degradation, both during normal conditions of use as well as under ambient conditions in the natural environment (which is negligible in the case of fluoropolymers) a technical Annex with data on information available for fluoropolymers has been added.

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1. Introduction

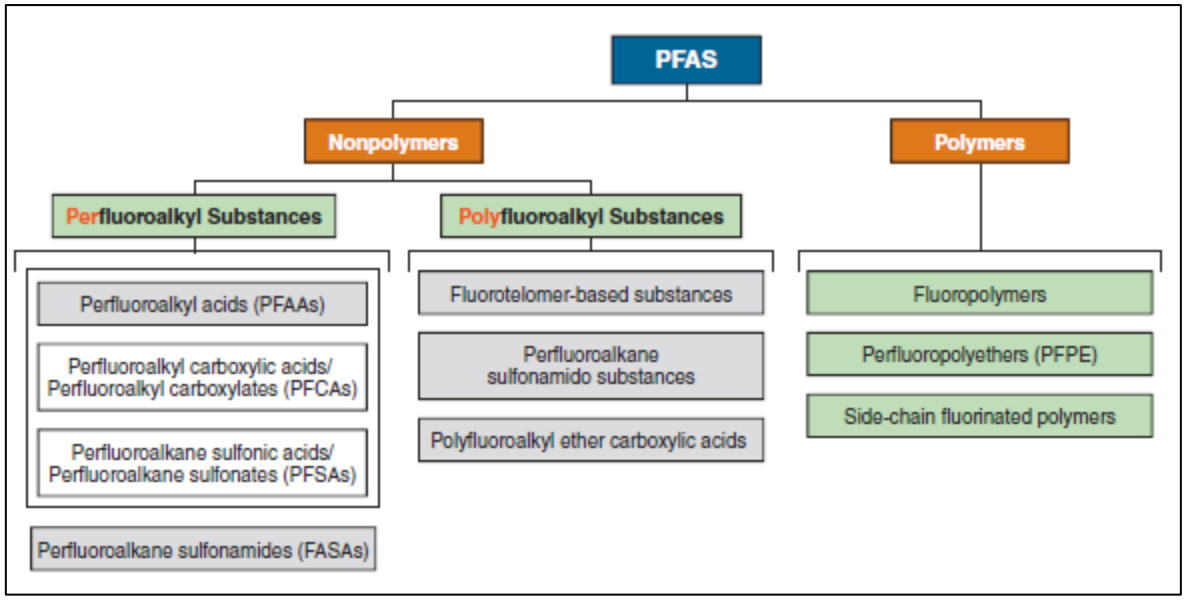
A restriction proposal under the REACH Regulation[1] on per-and polyfluoroalkyl substances (PFAS) is currently under development, in order to limit the risks to human health and the environment from their manufacture and use. Fluoropolymers (FPs), which are high molecular weight polymers with unique properties (Korzeniowski et al., 2022; Henry et al., 2018), are a separate family within the PFAS group, and could therefore be adversely impacted by this restriction even though the vast majority of FPs meet the condition of Polmers of Low Concern (PLC).

In this paper, the position of FPs inside the broad group of PFAS will be defined, and the difference between FPs and other types of polymeric PFAS, namely side-chain fluorinated polymers (SCFPs) and perfluoropolyethers (PFPEs), will be highlighted.

2. Where do fluoropolymers fit within the PFAS group?

PFAS are a group of 4,730 (OECD, 2018) different highly fluorinated synthetic (man-made) substances, both polymeric and non-polymeric, although other sources increase the number to approximately 9,000 chemicals (NIOSH, 2022). Due to the large number of chemicals pertaining to this group, and the wide variability of composition and properties, PFAS can be divided in different families. A summary of the structure of the PFAS group is displayed in **Figure *1*Error! Reference source not found.** (ITRC, 2020).

Figure 1. Structure of families in the PFAS group



[1] Regulation (EC) No 1907/2006

As seen in **Figure 1**, FPs are part of the PFAS group and, for this reason, they are candidates to be included in the scope of the restriction proposal. However, because of their different chemical structure and properties, they need to be considered as a separate family within the group, clearly distinct not only from the non-polymeric PFAS, but also from the other polymeric PFAS. These differences are relevant not only in terms of grouping, but more importantly also in relation to the risk for human health and the environment that will be derived from their manufacture and use.

3. Why should fluoropolymers be considered different from other PFAS?

FPs should be considered a separate class under the PFAS group, which can be differentiated from other PFAS on the basis of their nature, structure, uses and applications, as well as from the point of view of safety and environmental impacts.

The polymeric nature of FPs

The term polymer is derived from the Greek roots “poly” (many) and “mer” (part) and this popularly defines these substances as long-chain materials made up of many simple parts (Jensen, 2008). More scientifically, a polymer is defined as a molecule of high relative molecular mass (macromolecule), the structure of which essentially comprises the multiple repetitions of units derived from molecules of low relative molecular mass, known as monomers (IUPAC, 2022).

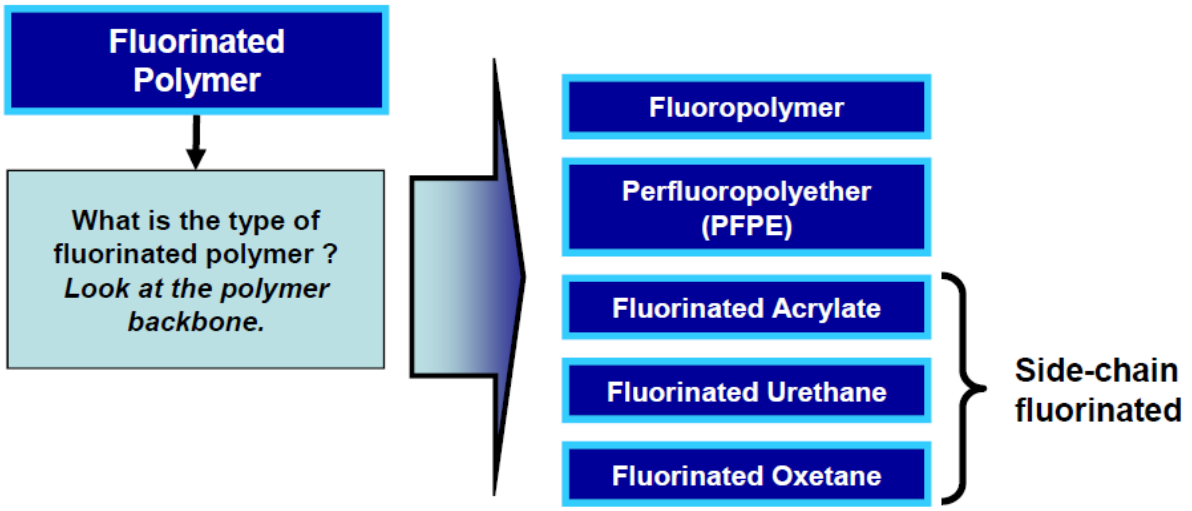
In the case of FPs, this macromolecule is a long chain (backbone) of thousands of connected carbon atoms (C) to which fluorine atoms (F) are bound (FPG, 2022).

For this reason, this family of synthetic polymers can be easily differentiated from the non-polymeric PFAS, which are also based on chains of C atoms, but which are much shorter than those of polymers (chain length between 2 and 13 C atoms).

The structure of FPs

FPs are the only polymeric PFAS in which F is directly attached to C in a carbon polymeric backbone. This fact differentiates FPs from the other polymeric PFAS, in which F is directly attached to C in another type of polymeric backbone (polyether), or F is directly attached to C in a side chain and not to the carbon polymeric backbone (SCFPs). This is displayed in **Figure 2** (Wahlström et al., 2021).

Figure 2. Types of polymeric PFAS based on their structure.



Use and applications.

FPs are mostly used in industrial applications due to their unique set of material properties. They are solid materials, and the main applications are the production of plastic and rubber elements which are later used in a wide variety of industrial sectors such as pharmaceutical and medical products and devices, renewable energy, telecommunications, electronics and semiconductors, automotive and aerospace, food and water processing, architecture and building, and chemical process industries (Glüge et al., 2020; Banerjee et al., 2017).



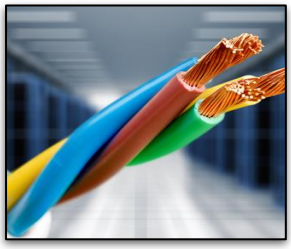
Pharmaceutical



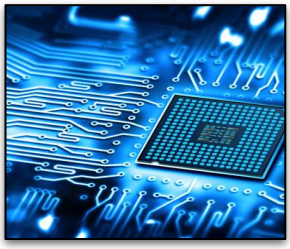
Medical devices



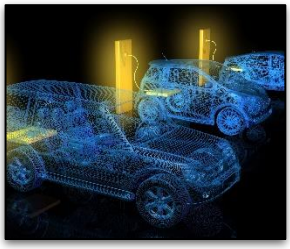
Renewable energy



Telecommunications



Electronic and semiconductors



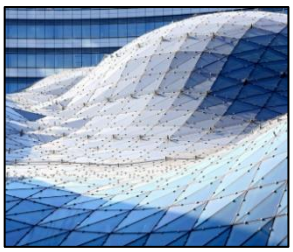
Automotive



Aerospace



Food and water processing



Architecture and building



Chemical processing

In contrast, the other polymeric PFAS such as SCFPs are focused predominantly on consumer applications due to their surface properties. The main application is the surface protection of textile, apparel, leather, carpets, and paper (Glüge et al., 2020). The Danish EPA (2013) highlighted that around 50% of the use of SCFPs is found in textile applications such as carpets and carpet care products. The main industrial sectors of use are cosmetics, nonwovens, carpets, textiles, food and packaging, and firefighting foams. In relation to PFPEs, while these are mainly used as lubricants in specific industrial sectors, certain consumer applications related to surface protection are also relevant (Fiedler et al., 2020). These differentiated polymeric PFAS can be liquids, greases, or dispersions in water.



Cosmetics



Nonwovens



Carpets



Textiles



Food packaging



Firefighting foams



Lubricants

Environmental considerations and degradation to small PFAS molecules.

FPs and PFPEs do not degrade to small PFAS molecules that may be mobile or bioaccumulative, under intended use conditions or under environmental conditions at the end-of-life phase of their applications. This is due to the strength of the C-F bond, the high molecular weight, and the lack of water solubility or volatility, (Fiedler et al., 2020; Danish EPA, 2013).

On the contrary, depending on the type of side chain included in the structure, the SCFPs can potentially lead to the formation of non-polymeric PFAS substances as a result of degradation under environmental conditions (Fiedler et al., 2020; Danish EPA, 2013).

Safety considerations.

The main FPs meet the conditions set out by the OECD (2009) to be regarded as Polymers of Low Concern (PLC) because they are biologically stable and chemically inert in presence of virtually any chemical, negligibly soluble in water, non-bioavailable, non-bioaccumulative, and non-toxic (Henry et al., 2018). While this original research was limited to four FPs, additional work has demonstrated that approximately 96% of the FPs available on the market meet the PLC criteria (Korzeniowski et al., 2022).

For other polymeric PFAS, their behaviour against the PLC criteria is currently unknown. Furthermore, the fact that they are mainly used in consumer applications could be linked to potential higher risk compared to the case of FPs, which are mainly used in industrial sectors.

4. Key differences between fluoropolymers and other polymeric PFAS

4.1. Structural comparison

Attending to the structure of the macromolecules, the polymeric PFAS can be grouped in the following three main categories (COM, 2020):

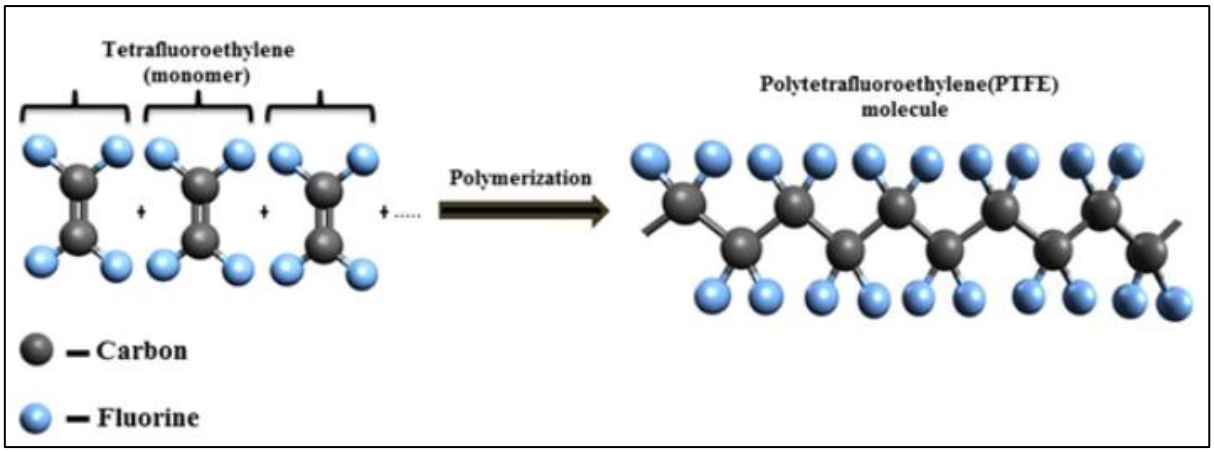
- FPs: have a carbon polymer backbone with F directly attached to C in the backbone.
- PFPEs: have a polyether polymer backbone, in which repeating monomer contains a carbon-oxygen (C-O) bond, with F directly attached to C in the backbone.
- SCFPs: have a carbon polymer backbone with fluorinated side chains directly attached to C in the backbone. In this case, F are not directly attached to C in the backbone.

Fluoropolymers

FPs are polymers with F directly attached to their carbon backbone that are manufactured by (co)polymerisation of olefinic monomers. In order to obtain a FP, it is necessary that at least one of these monomers contains a F bond to one or both of the olefinic C atoms, so that the carbon-only polymer backbone with F directly bonded to it can be generated (Henry et al., 2018). The exceptionally strength of the C-F bond in FPs generates their unique, high value properties (Banerjee et al., 2017).

Figure 3 (Dhanumalayan et al., 2018) shows the polymerization process and the final structure of polytetrafluoroethylene (PTFE), the most important FP in terms of production and use.

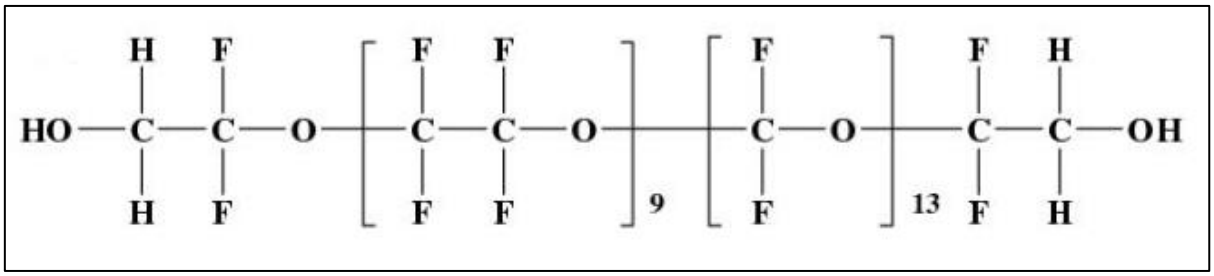
Figure 3. Chemical structure of PTFE.



Perfluoropolyethers

PFPEs are long-chain polymers that consist of a polyether polymer backbone composed of C, O, and F, in which F and O are strongly bonded to C. The chemical structure is shown in **Figure 4** (Lee et al., 2006).

Figure 4. Chemical structure of PFPE.

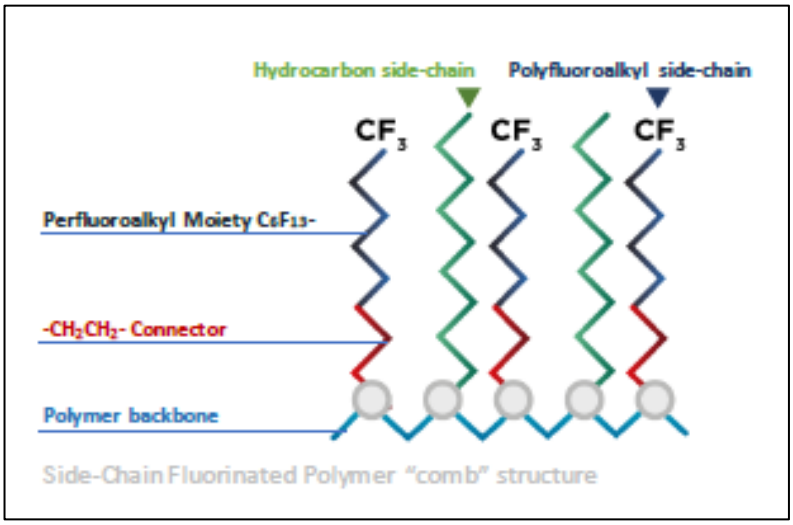


Side-chain fluorinated polymers

SCFPs constitute a diverse type of polymeric PFAS substances. They are fluorotelomer based products of polymeric nature, both long and short chain (FPG, 2017). The fluorinated side-chain moieties are produced by the telomerization or electrochemical fluorination process, in such a way that the fluorinated side chains are attached to the polymer backbone by a spacer moiety and a linking group (Fiedler et al., 2020). The final structure, which can be seen in **Figure 5** is a hydrocarbon polymer backbone with a polyfluoroalkyl side chain bound to the backbone that contains a perfluoroalkyl moiety as well as side chains that have no fluorinated

carbons. The polymer has a comb structure where some of the tines (aka teeth) are a side chain with the perfluoroalkyl moiety while other side chains contain hydrocarbon functionality, not fluorine (FPG, 2022).

Figure 5. Chemical structure of SCFP.



4.2. Safety considerations

Fluoropolymers

Due to their unique properties, initially four FPs have been classed as PLC according to the OECD criteria, given that they have been proven to be biologically stable and chemically inert in presence of virtually any chemical, negligibly soluble in water, non-bioavailable, non-bioaccumulative, non-toxic and resistant to degradation (Henry et al., 2018). The four FPs are:

- polytetrafluoroethylene (PTFE)
- fluorinated ethylene propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers (PFA)

However, according to a recent study (Korzeniowski et al., 2022) the PLC classification can be extended to at least 96% of the commercial FPs available on the market worldwide, due to their physio-chemical, biological, toxicological, and ecotoxicological properties.

Furthermore, the main uses of FPs are related to industrial applications. Industrial use is considered per definition as non-dispersive as this use can take place at only a few numbers of sites and/or involve few users. Also, the safety & waste disposal requirements in the industrial environment are more stringent than in other uses, such as consumer uses.

Perfluoropolyethers

PFPEs are mainly used as lubricants in specific industrial sectors, however consumer applications related to surface protection are also relevant (Fiedler et al., 2020).

Side-chain fluorinated polymers

SCFPs are used as surface protectors in textile, apparel, leather, carpets, and paper. These are open and dispersive uses where many consumers come into contact with the SCFPs-containing products (Glüge et al., 2020).

4.3. Relevant uses of application

Fluoropolymers

According to the bibliography, out of the 4,730 substances included in the PFAS category (OECD, 2018), only 256 are commercially relevant (Buck et al., 2021). In the case of FPs, only 38 substances are currently available on the market, out of the 267 compounds that are currently identified. This means that commercial FPs only represent 0.8% of the PFAS universe, but they represent 14.8% of the PFAS with commercial relevance. This is due to the unique properties of these materials and their high performance.

FPs are extremely stable, solid specialty materials used in a wide range of sectors: transport, chemicals and power, cookware, electronics and semiconductors, food and pharma, textiles, architecture, medical applications, renewable energies, and consumer articles (FPG, 2017). Also, FPs play an important role in the development of new materials for advanced applications in aeronautics and aerospace, building industries, petrochemicals, automotive industries, Li-ion batteries, high performance membranes, textile treatment, wires and cables, and microelectronics (Banerjee et al., 2017).

It is relevant to note that FPs are used when other materials fail to satisfy minimum performance criteria as per global standards. As example, FPs have been used in the production of electrical cables for airplanes due to their unique combination of properties (high insulation, resistance to high voltages, flexibility at very low and high temperatures, fire retardancy, chemical resistance to specialty fuels, low weight), that ensure safety for passengers and crew during flight. Usually being a higher price option, FPs are only used when other materials fail to provide critical properties (or combination of properties) that are absolutely necessary under certain conditions (e.g., resistance at extreme temperature ranges and under very corrosive environments).

Perfluoropolyethers

8 of the polymeric substances that are currently in the market are PFPEs (Buck et al., 2021), which represents 0.2% of the PFAS universe and 3.1% of the PFAS with commercial relevance.

PFPEs are used as functional fluids, surfactants, and surface protection products (Buck et al., 2011). The main use of PFPEs is as lubricants in many industrial sectors, such as aerospace (Jones W.R., 1994), aviation, automotive, pharmaceutical and medical applications, process

equipment, semiconductors and electronics (Huskey 2005). Also, they are marketed as surface treatments for natural stone, metal, glass, plastic, textiles, leather, and paper and paperboard treatment for food-contact applications (Buck et al., 2011).

The main uses of PFPEs are industrial, but some consumer uses related to the surface protection have to be considered. PFPEs are available as liquids or greases (Fiedler et al., 2020).

Side-chain fluorinated polymers

In the case of the SCFPs, only 6 substances are commercially relevant (Buck et al., 2021). This represents 0.1% of the PFAS universe and 2.3% of the PFAS with commercial relevance. They are frequently marketed as polymer dispersions in water (FPG, 2022).

SCFPs have surface properties (FPG, 2022) and, for this reason, they are used as surface protectors to provide water, oil, and stain repellence to textiles, apparel, leather, carpets, nonwovens, and paper, and soil release properties (Glüge et al., 2020; FPG, 2017).

4.4. Key properties

Fluoropolymers

FPs have material properties, which include durability, mechanical strength, inertness, thermal stability in foreseeable use conditions, and resistance to chemical, biological, and physical degradation (Henry et al., 2018). Also, they are non-wetting, non-stick, and highly resistant to temperature, fire, and weather.

These properties are attributable to the very strong C-F bonds, the strongest bond between C and any other atom, making them highly stable. C atoms alone form the FP backbone, each surrounded by an envelope of F atoms.

The main properties of FPs are (Henry et al., 2018):

- very high molecular weight (>100 000 Da)
- high thermal, chemical, photochemical, oxidative, hydrolytic, and biological stability
- low flammability
- low dielectric constant
- resistance to degradation
- negligible residual monomers and low molecular weight oligomer content
- limited low molecular weight leachables
- no reactive functional groups of concern in the structure

Perfluoropolyethers

PFPEs are a special class of materials, mainly used as lubricants and functional fluids, which can be used in different applications because of their versatility. However, they show some different features compared with FPs, such as low surface tension and radiation resistance to gamma ray (Huskey, 2005).

Side-chain fluorinated polymers

SCFPs are mainly used as surface protector due to the high level of repellence to harmful chemicals, oils, blood and bodily fluids, etc. This behaviour is directly related to their surface properties, such as low surface tension and low surface free energy, and non-fouling behaviour (Honda et al., 2005).

4.5. Outcome from potential degradation processes

Fluoropolymers

FPs are substantially different from the other polymeric PFAS in terms of potential emissions due to degradation during intended use or under environmental conditions.

FPs generally display a high molecular weight, they show no degradation under their intended use nor under ambient conditions typically found in the natural environment, little to no water solubility or volatility, and therefore would not be expected to degrade to lower molecular weight PFAS (Fiedler et al., 2020; Danish EPA, 2013). Also, they do not lead to the formation of long-chain PFAS as a result of degradation (COM, 2020).

Perfluoropolyethers

Regarding degradation, according to literature sources, PFPEs exhibit a similar behaviour to FPs (COM, 2020; Fiedler et al., 2020; Danish EPA, 2013). Specifically, because the repeating units of the PFPEs contain only 2 or 3 perfluorinated C atoms per O atom, their degradation cannot lead to the formation of long-chain PFAS (Buck et al., 2011).

Side-chain fluorinated polymers

The linking group in the structure of the SCFPs can be susceptible to cleavage, depending on the structure of each material, resulting in loss of the fluoroalkyl side chain. Thus, SCFPs can ultimately be a source of perfluoroalkyl acids (PFAAs), such as PFOA, PFOS, perfluorobutanoic acid (PFBA), perfluorohexane sulfonic acid (PFHxS), or perfluorohexane carboxylic acid (PFHxA), and so forth, unless there is stability data to prove otherwise. It means that, under environmental conditions, SCFPs can degrade to these non-polymer PFAS (Fiedler et al., 2020; Danish EPA, 2013), which are well known due to their effects on human health and the environment.

Annex I at the end of this report provides further information on the fact that FPs do not degrade during normal use or under intended environmental conditions.

5. Conclusions

Fluoropolymers are a well-defined and distinct family of substances inside the PFAS group that show unique combination of properties, which are not shared by other members of these large group of chemicals. Although they pertain to the polymeric PFAS, they are clearly different from other fluorinated polymeric materials (specifically perfluoropolyethers and side-chain fluorinated polymers) due to:

- Unique combination of properties, which make them highly valuable in extremely demanding applications.
- No degradation potential, since they do not degrade to small PFAS molecules during the intended use or under ambient conditions in the natural environment.
- Safety considerations, since they are not toxic, not bioaccumulative, and have insignificant human health impact.
- Environmental considerations, as non-soluble, non-mobile substances with insignificant environmental impact.
- Main uses related to industrial applications.

Due to their chemical structure (carbon backbone with polyfluoroalkyl side chains bound to it), side-chain fluorinated polymers can degrade to hazardous non-polymeric PFAS during the intended use or under environmental conditions at the end-of-life phase of their applications. Moreover, these substances are used mainly at the consumer level, which is considered an open and dispersive use. Therefore, side-chain fluorinated polymers could develop effects on human health and the environment that would never be exhibited by fluoropolymers.

In the case of perfluoropolyethers, degradation potential during the use phase is limited and therefore, potential risks related to their use are expected to be limited.

On the other hand, the vast majority of fluoropolymers fulfil the criteria to be considered as Polymers of Low Concern: they are high molecular weight polymers, have narrow molecular weight distribution, and have negligible oligomer content and organic and inorganic leachables. Data show that fluoropolymers have thermal, chemical, photochemical, hydrolytic, and biological stability. However, the behaviour against the Polymer of Low Concern criteria of side-chain fluorinated polymers and perfluoropolyethers is currently unknown.

Based on these differentiating properties, mainly related to the specific chemical structure of fluoropolymers (carbon backbone with F atoms directly bonded to C atoms), it is possible to conclude that fluoropolymers are a separate family of substances inside the PFAS group, even compared with the other fluorinated polymeric materials. Therefore, they should be also treated separately from other PFAS in relation to regulatory initiatives.

6. References

Banerjee S., Tawade B.V., Ladmiral V., Dupuy L.X., MacDonal M.P., and Améduri B. Poly(fluoroacrylate)s with tunable surface hydrophobicity via radical copolymerization of 2,2,2-trifluoroethyl α-fluoroacrylate and 2-(trifluoromethyl)acrylic acid. *Polymer Chemistry*, 2017, 8, 1978.

Buck R.C., Korzeniowski S.H., Laganis E., and Adamsky F. Identification and classification of commercially relevant per- and poly-fluoroalkyl substances (PFAS). *Integrated Environmental Assessment and Management.* Volume 17, Number, pp. 1045–1055. **2021**.

Buck R.C., Franklin J., Berger U., Conder J.M., Cousins I.T., de Voogt P., Jensen A.A., Kannan K., Mabury S.A., and van Leeuwenkk S.PJ. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integrated Environmental Assessment and Management*. Volume 7, Number 4, pp. [redacted].

COM, 2020. Scientific and technical support for the development of criteria to identify and group polymers for Registration/Evaluation under REACH and their impact assessment. *European Commission.* June **2020**.

Danish EPA, 2013. Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances. *The Danish Environment Protection Agency*. Part of the LOUS review, Environmental Project No. 1475, **2013**.

Dhanumalayan E., Joshi G.M. Performance properties and applications of polytetrafluoroethylene (PTFE) - a review. *Advanced Composites and Hybrid Materials*. **2018**.

Fiedler H., Kennedy T., and Henry B.J. A critical review of a recommended analytical and classification approach for organic fluorinated compounds with an emphasis on per- and polyfluoroalkyl substances. *Integrated Environmental Assessment and Management*. Volume 17, Number 2, pp. [redacted].

FPG, 2022. Fluoropolymers vs. Side chain fluorinated polymers. *Fluoropolymers Product Group. Plastics Europe.* Available at: https://fluoropolymers.plasticseurope.org/application/files/3516/3913/1778/Fluorpolymers_vs._side_chain_fluorinated_polymers_final.pdf. Last access: May **2022**.

FPG, 2017. Understanding FluoroTechnology. *Fluoropolymers Product Group. PlasticsEurope.* **2017**.

Glüge J., Scheringer M., Cousins I.T., DeWitt J.C., Goldenman G., Herzke D., Lohmann R., Carla A., Ng C., Trieri X., and Wangj Z. An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environmental Science: Processes & Impacts*, **2020**, 22, 2345.

Henry B.J., Carlin J.P., Hammerschmidt J.A., Buck R.C., Buxton L.W., Fiedler H., Seed J., and Hernandez O. A Critical Review of the Application of Polymer of Low Concern and Regulatory

Criteria to Fluoropolymers. *Integrated Environmental Assessment and Management*. Volume 14, Number 3, pp. [redacted].

Honda K., Morita M., Otsuka H., and Takahara A. Molecular aggregation structure and surface properties of poly(fluoroalkyl acrylate) thin films. *Macromolecules* **2005**, 38, 5699-5705.

Huskey, 2005. Applications and benefits of perfluoropolyether (PFPE) lubricants. *HUSK-ITT Corporation*. **2005**.

ITRC, 2020. Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS). *Interstate Technology Regulatory Council (ITRC)*. **2020**.

IUPAC, 2022. What are polymers? International Union of Pure and Applied Chemistry. Available at: https://iupac.org/polymer-edu/what-are-polymers/. Last access: May **2022.**

Jensen W.B. The origin of the polymer concept. *Journal of Chemical Education*. **2008**.

Jones W.R. Properties of perfluoropolyethers for space applications. NASA Technical Memorandum 106616. *National Aeronautics and Space Administration*. **1994**.

Korzeniowski S.H., Buck R.C., Newkold R.M., El kassmi A., Laganis E., Matsuoka Y., Dinelli B., Beauchet S., Adamsky F., Weilandt K., Soni V.K., Kapoor D., Gunasekar P., Malvasi M., Brinati G., and Musio S. A. Critical Review of the Application of Polymer of Low Concern Regulatory Criteria to Fluoropolymers II: Fluoroplastics and Fluoroelastomers. *Integrated Environmental Assessment and Management.* **2022**.

Lee J., Chun S.W., Kang H.J., and Talke F.E. The effect of UV stabilizer on the photo degradation of perfluoropolyether lubricants used in hard disk. *Tribology Letters*. 28. [redacted].

NIOSH, 2022. The National Institute for Occupational Safety and Health (NIOSH). Per- and polyfluoroalkyl substances (PFAS). Available at: https://www.cdc.gov/niosh/topics/pfas/default.html. Last access: May **2022**.

OECD, 2018. Toward a new comprehensive global database of per- and polyfluoroalkyl substances (PFASs). Series on Risk Management No. 39. *Organisation for Economic Co-operation and Development*. **2018**.

OECD, 2009. Data analysis of the identification of correlations between polymer characteristics and potential for health or ecotoxicological concern. Available at: http://www.oecd.org/chemicalsafety/risk-assessment/42081261.pdf. Last access: May **2022**.

Wahlström M., Pohjalainen E., Yli-Rantala E., Behringer D., Herzke D., Mudge S.M., Beekman M., de Blaeij A., Devilee J., Gabbert S., van Kuppevelt M., Zare Jeddi M., Gabrielsen P., and Trier X. Fluorinated polymers in a low carbon, circular and toxic-free economy. Technical report. Eionet Report. *European Topic Centre Waste and Materials in a Green Economy. European Environment Agency*. **2021**.

Annex I: Degradation of fluoropolymers

Thermal degradation

In addition to the chemical structure, the key difference between FPs and SCFPs is their degradation potential. Fluoropolymers are inert and stable substances, and no degradation is expected under normal use.

Thermal degradation of FPs can be evaluated by means of Thermogravimetric Analysis (TGA). This analytical technique allows to determine the thermal stability of the material along with the fraction of volatile components and the thermal degradation by monitoring the weight variation occurred when a sample is heated at a constant rate.

An assessment of the thermal degradation of some FPs has been performed by running a TGA analysis under ambient atmospheric. The results are shown in Table 1 and Figures 6 to 11.

By assessing several FPs, the main conclusions that can be established are the following:

- Degradation of FPs does not occur at temperatures lower than maximum temperatures attained by these fluoropolymers during processing or end-use.
- Degradation of FPs starts at temperatures (Onset point) significantly higher than standard maximum temperatures of processing.
- FPs get destroyed completely below 650°C without leaving any residue. It is pertinent to note that most municipal incinerators operate above 800°C resulting in complete destruction of FP applications at their end of life.
- A negligible amount of weight loss is observed during the processing temperatures of FPs. These are mainly due to the moisture variations and elimination of the residual additives as surfactants or initiators, which are not PFAS substances.

Table 1. Summary of Thermogravimetric Analysis

Fluoropolymer	Melting point (°C)	Standard max T during processing (°C)	Onset point (°C)	Offset point (°C)
PTFE (suspension powder)	327	360-375	529	600
PTFE (emulsion type)	327	360-375	529	594
PFA	310	350-360	510	575
FEP	260	325-350	500	629
FKM	-	230	388	601
PVDF	166	180-220	449	571

Figure 6. TGA analysis of Polytetrafluoroethylene (PTFE) suspension powder

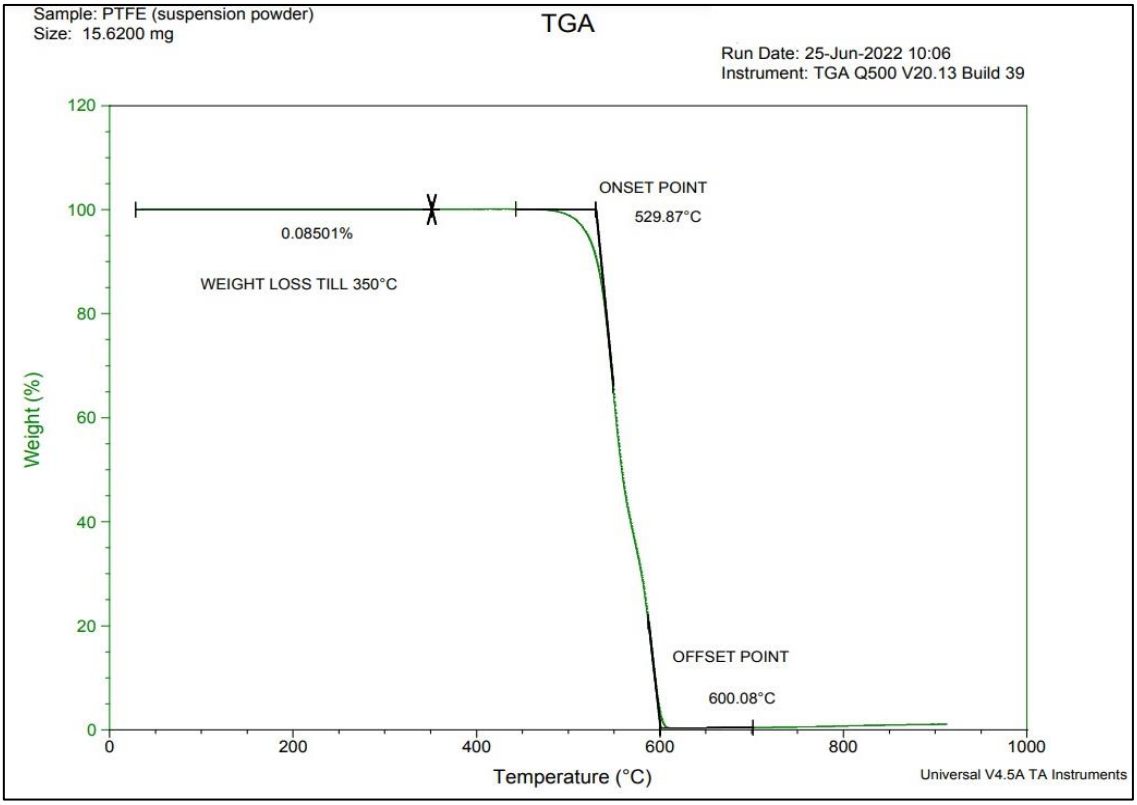


Figure 7. TGA analysis of Polytetrafluoroethylene (PTFE) emulsion powder

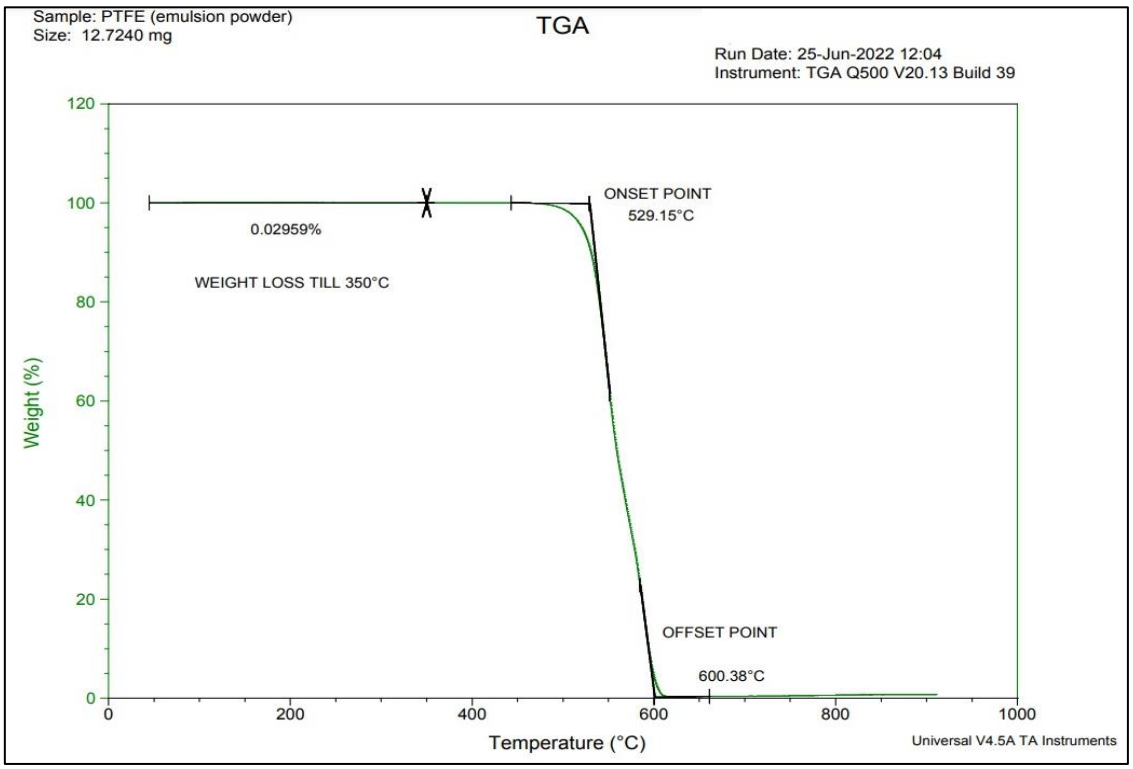


Figure 8. TGA analysis of Perfluoroalkoxy alkane (PFA)

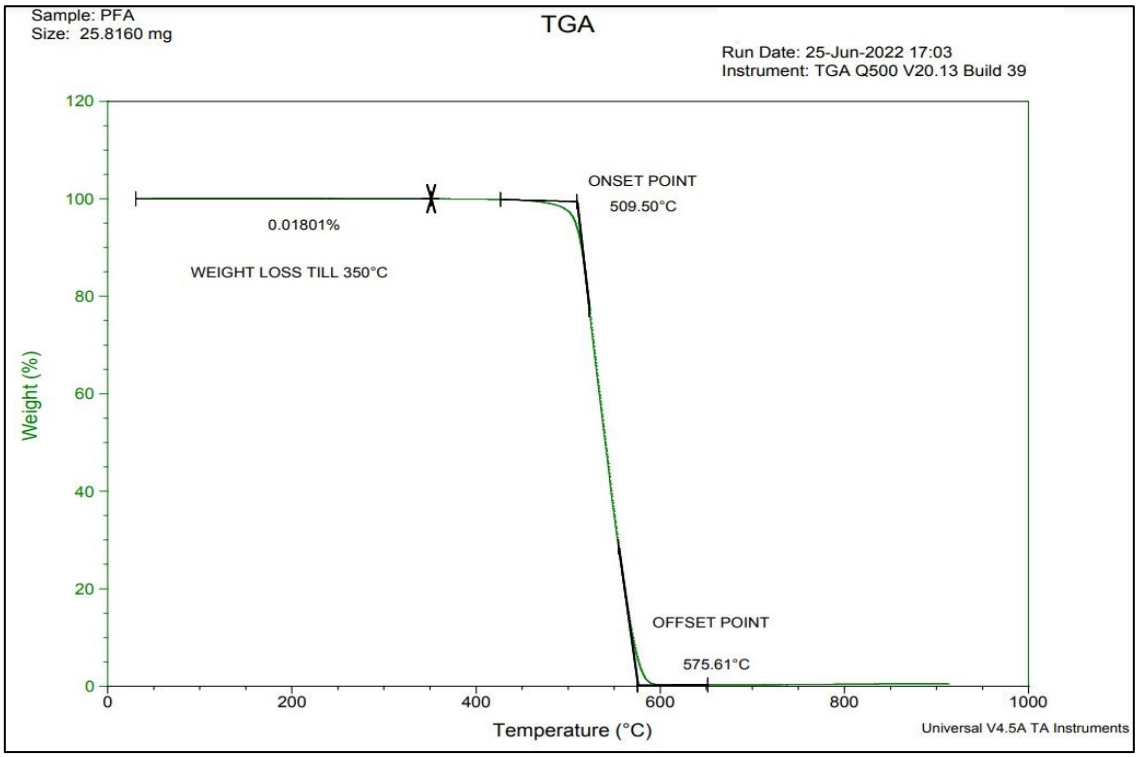


Figure 9. TGA analysis of Fluorinated ethylene propylene (FEP)

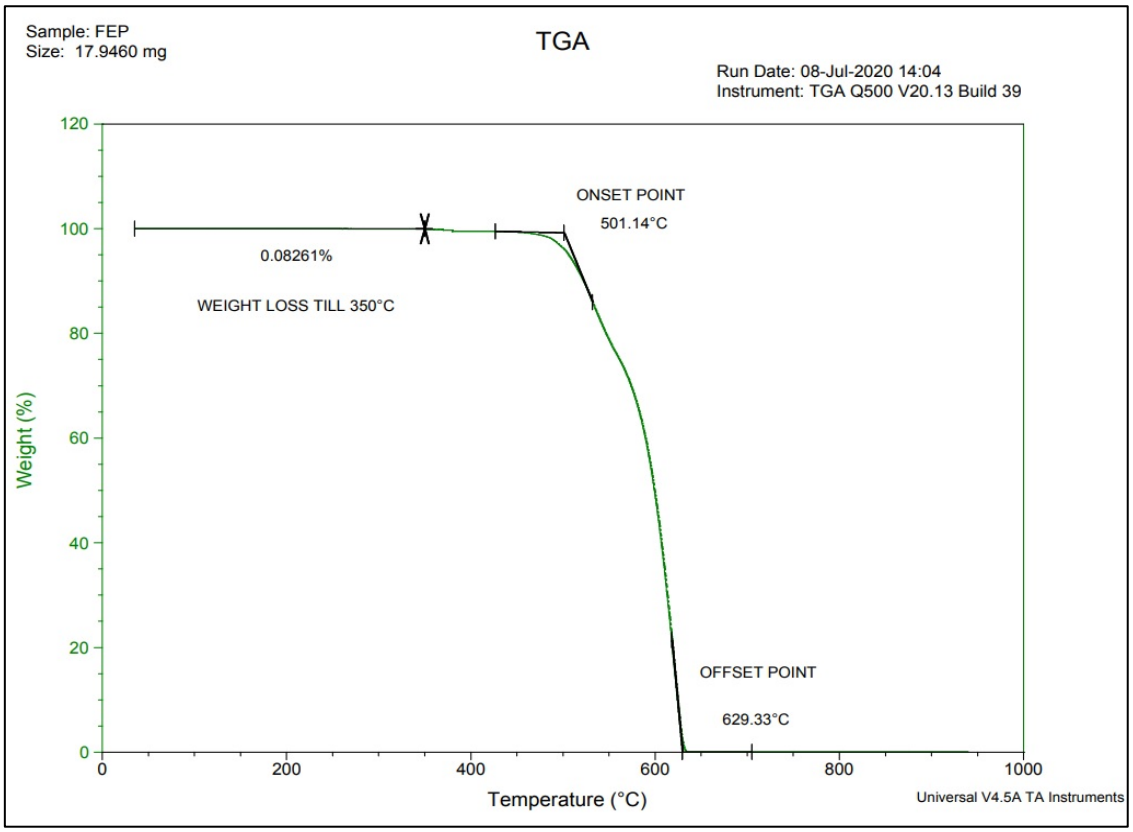


Figure 10. TGA analysis of Polyvinylidene difluoride (PVDF)

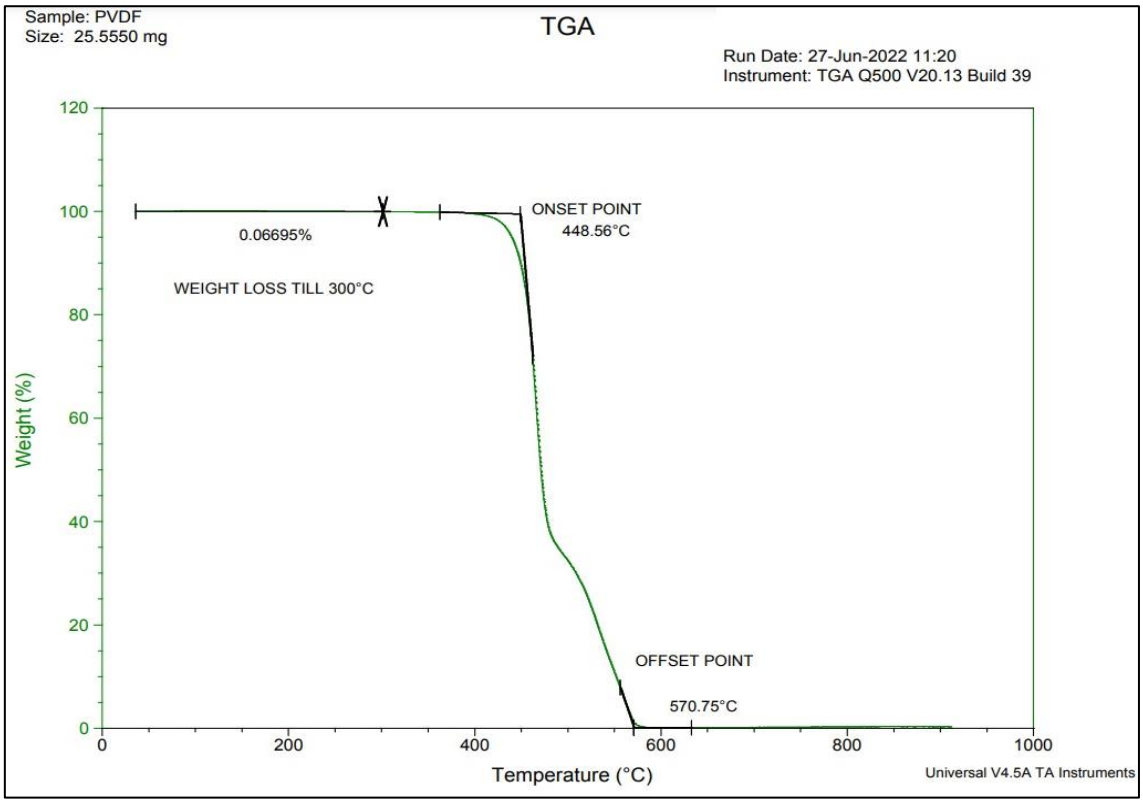
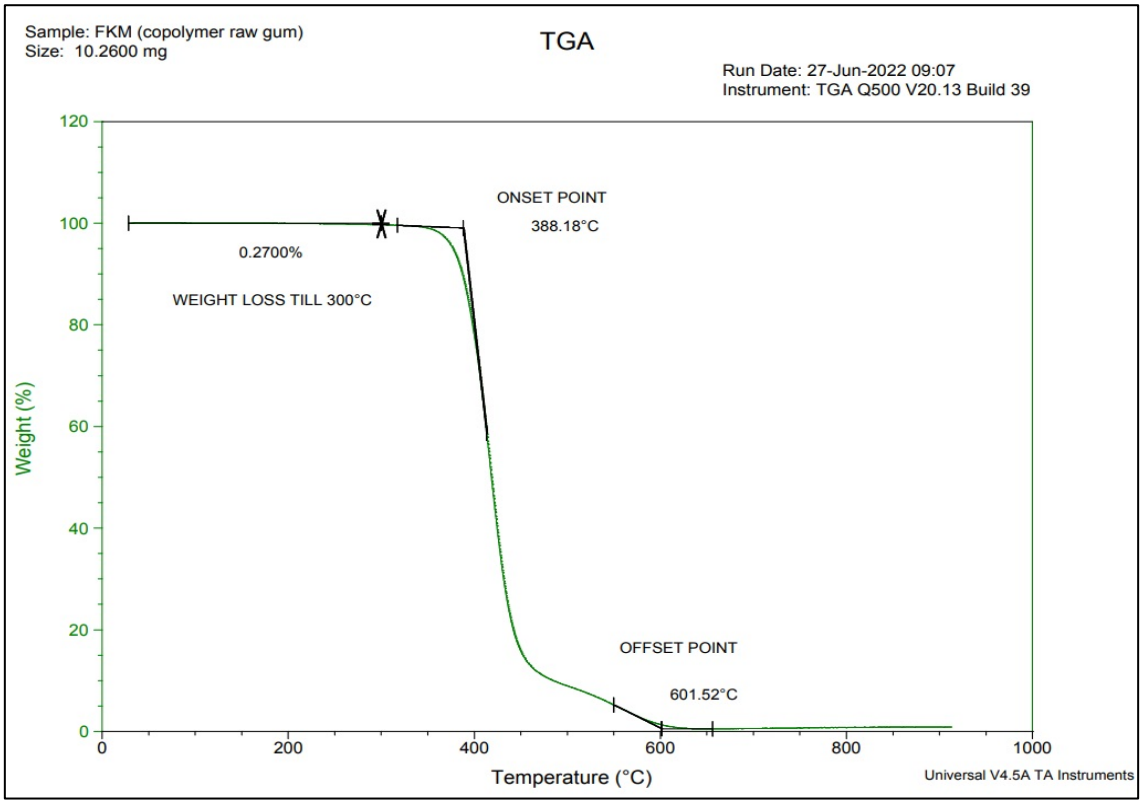


Figure 11. TGA analysis of Vinylidene fluoride-hexafluoropropylene copolymer (FKM)



Environmental degradation

Polymer degradation is a change in the properties of the polymer, such as tensile strength, colour, shape, and molecular weight, or of a polymer-based product under the influence of one or more environmental factors, such as heat, light, chemicals, or any other applied force. Degradation is often due to a change in the chemical and/or physical structure of the polymer chain, which in turn leads to a decrease in the molecular weight of the polymer.

During application many FP-based products are used in open environment. Polymers can be degraded by action of UV radiation and humidity. To understand effect of environmental condition (Sunlight, rain and humidity) over PTFE, an FP manufacturer has conducted a study to observe effect on mechanical properties of PTFE when kept in open environment.

For this study, Granular PTFE as well as PTFE Fine Powder have been analysed. Granular PTFE is manufactured using suspension polymerization while PTFE Fine Powder is manufactured using emulsion polymerization method, which ends up in different processing methods and applications. For Granular PTFE, resin is compression moulded into hollow billets and skived into 0.5 mm sheet, while, for PTFE Fine Powder, powder is compression moulded into 1.75mm thick disks and kept in open environmental condition at terrace to see effect of different environmental parameter such as sunlight, rain and humidity on PTFE.

After every 3 months samples were drawn out and their mechanical properties, such as tensile and elongation, were tested to check for any depletion of properties or polymer degradation as a result of harsh weather conditions under which they had been kept.

For the measurements, Tinius Olsen equipment was used with the following parameters: initial Jaw separation-22mm; sample shape- Dumbbell; strain rate – 50mm/min.

For this project, environmental conditions in the relevant region such as average temperature, monthly temperature variation, average rainfall and monthly rainfall variation were taken into consideration. For Granular PTFE, the study was developed between 1 August-2011 and 1 May 2021, and for PTFE Fine Powder, the study was started on 29 October 2021 and is still on-going. All the analysis is conducted according to ASTM standards for PTFE. The main results are shown in Figures 12 to 15.

The most relevant conclusions are as follows:

- No significant change in mechanical properties is observed.
- No significant amount of weight loss was observed; maximum approximately 0.5% weight loss is related to moisture variations and elimination of residual additives or surfactants, which are not PFAS substances.
- It is evident that PTFE is highly inert in nature and does not degrade by the action of environmental condition like sunlight, rain and humidity.

Figure 12. Effect of environmental conditions on Granular PTFE - tensile strength

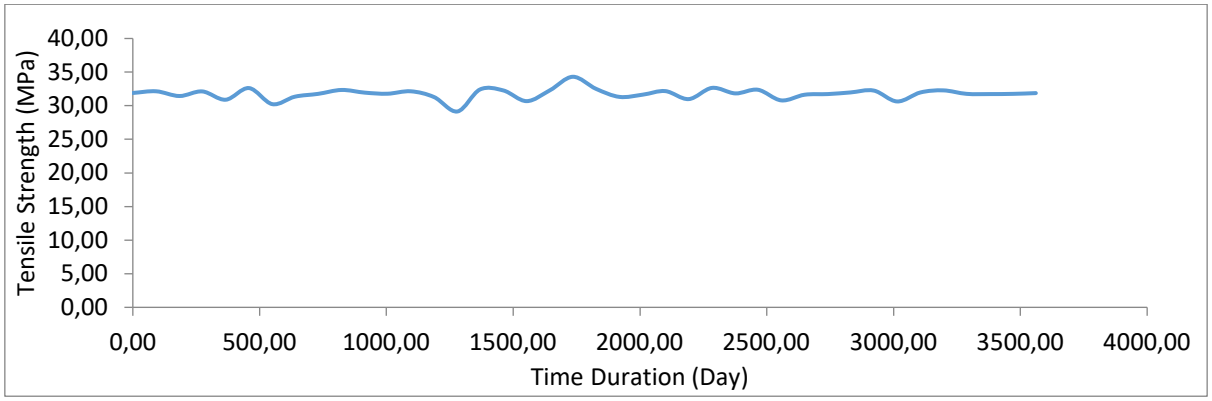


Figure 13. Effect of environmental conditions on Fine Powder PTFE - tensile strength

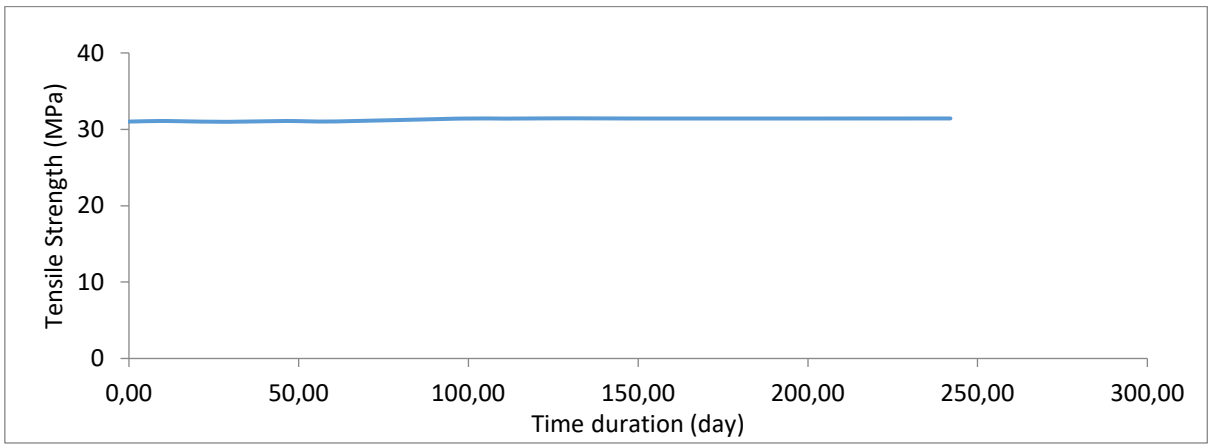


Figure 14. Effect of environmental conditions on Granular PTFE - elongation

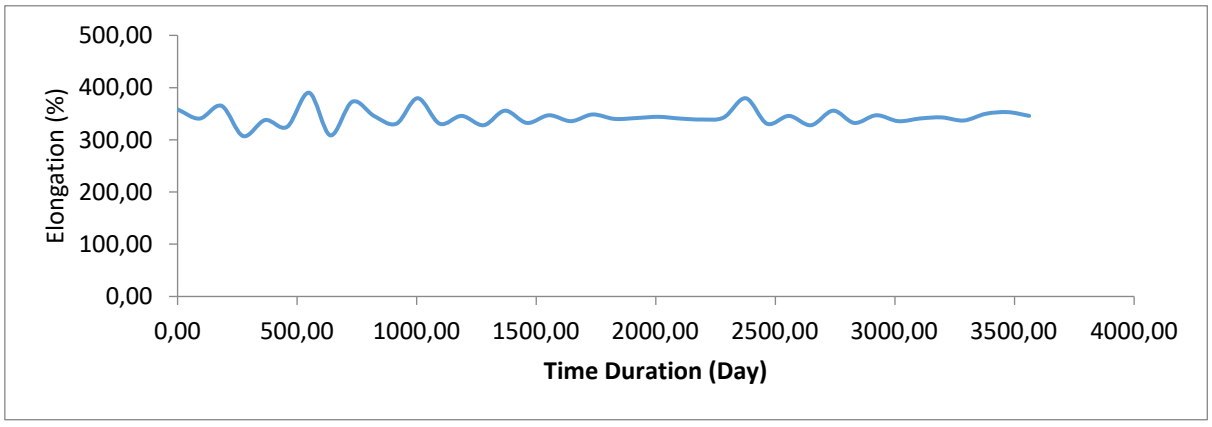
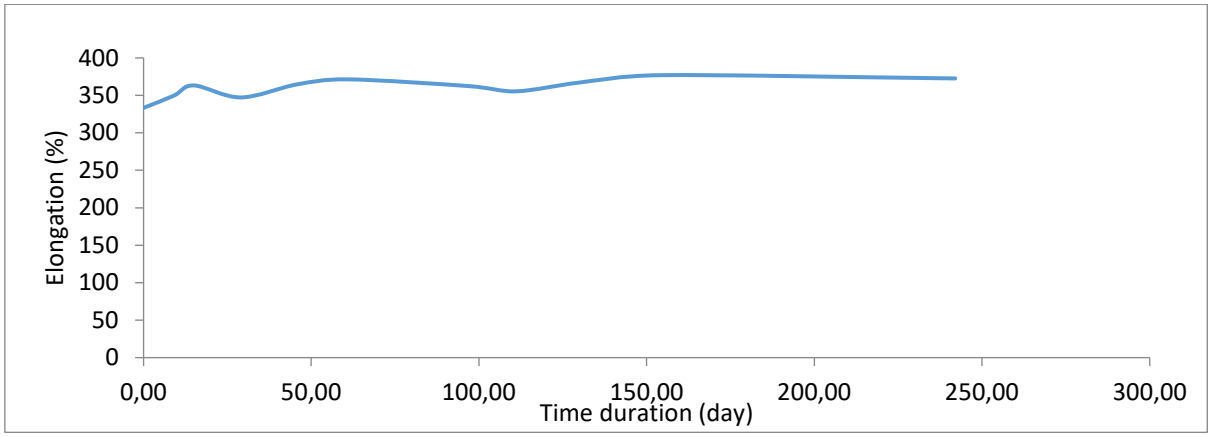


Figure 15. Effect of environmental conditions on Fine Powder PTFE - elongation



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Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle



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IOMC

INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS

A cooperative agreement among **FAO, ILO, UNDP, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD**

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Executive Summary

Per- and polyfluoroalkyl substances (PFASs) comprise a class of synthetic compounds that have attracted much public attention since the early 2000s, when the persistence, hazards and ubiquitous occurrence of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) started to be reported and recognized. Since then, research and risk management measures have expanded from these two PFASs to a wide range of PFASs. To date, research has primarily focused on understanding the identity, life cycle, hazard, occurrence and exposure, and risk of non-polymeric PFASs. This has informed development of many risk management measures at the national and international level. To ensure the sound management of the entire class of PFASs, it is equally important to understand polymeric PFASs, which include side-chain fluorinated polymers (SCFPs), fluoropolymers and perfluoropolyethers (Buck et al., 2011; Fiedler et al., 2019).

This report summarizes efforts by the OECD/UNEP Global PFC Group, between July 2021 and April 2022, in synthesizing publicly available scientific and technical information on the life cycle of SCFPs, which are polymers with a non-fluorinated polymer backbone and with substructures that meet the OECD PFAS definition (hereafter referred to as “PFAS moieties”) on the side chains.

The report provides a comprehensive overview on the chemical identities of SCFPs that have been on the global market, including a non-exhaustive list of 103 SCFPs and 42 monomers (Chapter 2). Based on the generic chemical structures identified, these SCFPs can be categorized according to the types of PFAS moieties present on the side chains, including n:2 fluorotelomers ($C_nF_{2n+1}CH_2CH_2-$), perfluoroalkanesulfonyl fluoride (PASF)-derivatives [$C_nF_{2n+1}S(O)_2-$], perfluoroalkanoyl fluoride (PACF)-derivatives [$C_nF_{2n+1}C(O)-$; $C_nF_{2n+1}CH_2-$] and perfluoropolyethers (PFPEs; containing a moiety such as $-CF_2-O-CF_2-$ in the fluorinated side chains), with varied fluorinated carbon chain lengths. Another way of categorizing the SCFPs can be according to the structural repeating units in the polymer backbone, with some simplifications, including acrylates {e.g., $[-CH_2-CH(C(O)OR_F)-]_n$}, ethoxylates {e.g., $[-O-CH_2-CH_2-]_n$}, oxetanes {e.g., $[-CH_2-C(CH_3)(CH_2OCH_2R_F)-CH_2-O-]_n$}, silicones {e.g., $[-Si(CH_2CH_2R_F)-O-Si(CH_2CH_2R_F)-]_n$} and urethanes {e.g., $[-NH-C(O)-O-]_n$}, where R_F is used to represent a fluorinated carbon chain moiety. In this report, the four chapters on the life cycle of different SCFPs are separated according to structural repeating units in the polymer backbone, specifically: acrylates and urethanes (Chapter 3), oxetanes (Chapter 4), silicones (Chapter 5), and ethoxylates (Chapter 6). In each chapter, the analysis focuses on the production and use of respective SCFPs, presence of other PFASs in the commercial formulations, degradation of SCFPs during use and end-of-life treatment, environmental releases of SCFPs, and other PFASs present in the commercial formulations, followed by a summary of critical knowledge and data gaps and options for a way forward. Chapter 7 focuses on overarching conclusions and recommendations. The key messages of chapters 3-6 are summarized at the start of each chapter. The report comes with an Annex comprising five spreadsheets providing information on: substances identities, use information, PFAS-impurity studies, degradation studies and SCFP release.

Compared to many non-polymeric PFAS, SCFPs and their known and unknown degradation products have received comparatively little attention from scientists and regulators, despite their manifold industrial uses and high volumes, their propensity to release non-polymeric PFAS, and their potential environmental and health impacts.

Overall, a wide range of information on the chemical identities of SCFPs, other PFASs present therein, historical and ongoing production and use, degradation of SCFPs, and release of SCFPs and associated non-polymeric PFASs is identified in the public domain and has been synthesized in this report.

Despite the many knowledge and data gaps identified, the following can be concluded from the information synthesized here: A wide range of SCFPs have been produced and used in many different applications, with at least some SCFPs at high volumes (up to tens of thousands of tonnes/year). Many non-polymeric PFASs may be present in the commercial SCFP formulations, sometimes at percentage levels. During the production, use and disposal of SCFPs and SCFP-treated products, substantial amounts of SCFPs and associated non-polymeric PFASs may have been released. It is well expected that SCFPs can degrade and form non-polymeric PFASs, including PFCAs and/or PFSAs, in the environment and biota. Thus, many SCFPs are acting as long-term significant sources to the global burden of non-polymeric PFASs including PFCAs and PFSAs.

Concerted action by all stakeholders is needed to address SCFPs in an efficient and effective manner. This includes identifying, making funding available and conducting research on those critical knowledge and data gaps that are most relevant for soundly regulating/managing SCFPs in different jurisdictions, building on the gaps identified in the respective chapters above. When addressing critical knowledge and data gaps, to increase efficiency, the following concerted action may be taken: (i) investigating additional information that is available in safety data sheets and patents (but was not actively searched and considered in this analysis due to time and resource constraints); (ii) working with manufacturers to enable open access to information that has been generated by them (and made available to specific regulators), but has not been made publicly available; and (iii) regularly gathering newly available public information and synthesizing them to further increase the knowledge base on SCFPs.

In parallel to action on critical knowledge and data gaps, concerted action may be taken to develop, facilitate and promote national and international stewardship programmes and regulatory approaches to reduce emissions of SCFPs and related PFASs and to work toward global elimination, where appropriate and technically feasible.

List of Acronyms

CAS	Chemical Abstracts Service
CASRNs	CAS Registry Numbers
CDR	Chenical Data Reporting
EU	European Union
FASAs	Perfluoroalkanesulfonyl amides
FASEs	Perfluoroalkanesulfonyl amidoethanols
FCN	Inventory of Effective Food Contact Substance Notifications
FTAcs	Fluorotelomer acrylates
FTCAs	Fluorotelomer carboxylic acids
FT-ethers	Fluorotelomer ethers
FTOs	Fluorotelomer olefins
FTOHs	Fluorotelomer alcohols
FTOH-aces	Fluorotelomer alcohols acetates
FTUCAs	Fluorotelomer unsaturated carboxylic acids
ICCM	International Conference on Chemicals Management
IUR	Inventory Update Reporting
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
N.A.	Not available
OECD	Organisation of Economic Co-operation and Development
PACF	Perfluoroalkanoyl fluoride
PASFs	Perfluoroalkanesulfonyl fluorides
PDMS	Polydimethylsiloxane

PFAIs	Perfluoroalkyl iodides
PFASs	Per- and polyfluoroalkyl substances
PFCAs	Perfluoroalkylcarboxylic acids
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFPEs	Perfluoropolyethers
PFSAs	Perfluoroalkanesulfonic acids
PMTFPS	Polymethyltrifluoropropylsiloxane
POSF	Perfluorooctanesulfonyl fluoride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SCFPs	Side-chain fluorinated polymers
SDS	Safety data sheets
SPIN	Substances in Preparations in Nordic Countries
t	Tonnes
UN	United Nations
UNEP	United Nations Environment Programme
US	United States
US EPA	US Environmental Protection Agency
US FDA	US Food & Drug Administration
yr	Year

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1 Background, motivation and scope

The OECD/UNEP Global PFC[1] Group was established to respond to the Resolution II/5 adopted at the second session of the UN International Conference on Chemicals Management (ICCM 2) in 2009, which calls upon intergovernmental organizations, governments and other stakeholders to "consider the development, facilitation and promotion in an open, transparent and inclusive manner of national and international stewardship programmes and regulatory approaches to reduce emissions and the content of relevant perfluorinated chemicals of concern in products and to work toward global elimination, where appropriate and technically feasible". Further work on this resolution was reaffirmed in Resolution III/3 adopted at ICCM 3 in 2012 noting that a significant need remains for additional work to support implementation of Resolution II/5. This report is prepared within the framework of the Group. For more details on the Group and its work, see the OECD PFAS web portal (https://oe.cd/2M9).

This report summarizes recent efforts by the Group between July 2021 and April 2022 in synthesizing publicly available scientific and technical information on side-chain fluorinated polymers (SCFPs), a subset of per- and polyfluoroalkyl substances (PFASs)[2]. It focuses on the life cycle of SCFPs, including production and use, presence of other PFASs in the commercial formulations, degradation of SCFPs during use and end-of-life treatment, and environmental releases of SCFPs and other PFASs present in the commercial formulations. In brief, this report provides a comprehensive overview on the identities of SCFPs that have been on the global market (Chapter 2), on the life cycle of acrylate and urethane SCFPs (Chapter 3), of oxetane SCFPs (Chapter 4), of silicone SCFPs (Chapter 5), and of ethoxylate SCFPs (Chapter 6), and a brief summary (Chapter 7). The report comes with a separate Annex comprising five spreadsheets providing information on: substances identities, use information, PFAS-impurity studies, degradation studies and SCFP release.

PFASs comprise a class of synthetic compounds that have attracted much public attention since the early 2000s, when the persistence hazards and ubiquitous occurrence of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) started to be reported and recognized. Since then, research and risk management measures have expanded from these two PFASs to a wide range of PFASs.

In general, PFASs can be divided into two categories: non-polymeric and polymeric ones. To date, research has primarily focused on understanding the identity, life cycle, hazard, occurrence and exposure,

[1] "PFCs" here refer to "per- and polyfluorinated chemicals", and not to "perfluorocarbons". As stated below, "per- and polyfluorinated chemicals" was a term commonly used before the term "per- and polyfluoroalkyl substances" was recommended by Buck et al. (2011). As it is part of the Group official name, it remains unchanged.

[2] Following OECD (2021), this report uses the acronym "PFASs" for "per- and polyfluoroalkyl substances" as stated in Buck et al. (2011), and its corresponding singular form "PFAS" refers to either a perfluoroalkyl or polyfluoroalkyl substance. It is noted that there is a notion of using "PFAS" as the acronym for both the singular and plural forms. This report does not make any recommendation to address this notion. Readers may decide which acronym they would use.

and risk of non-polymeric PFASs, particularly perfluoroalkylcarboxylic acids (PFCAs), perfluoroalkanesulfonic acids (PFSAs), and some of their well-known non-polymeric precursors derived from fluorotelomers and perfluoroalkanesulfonyl fluorides (PASFs) such as fluorotelomer alcohols (FTOHs) and perfluoroalkanesulfonyl amides/amidoethanols (FASAs/FASEs)[3]. This has informed development of many risk management measures at the national and international levels.[4]

To ensure the sound management of the entire class of PFASs, it is equally important to understand polymeric ones, which include SCFPs, fluoropolymers, and perfluoropolyethers (Buck et al., 2011; Fiedler et al., 2019). In this spirit, the Global PFC Group have identified understanding of the life cycle of polymeric PFASs as a work priority. This is a first synthesis report on polymeric PFASs, focusing on SCFPs—defined as polymers with a non-fluorinated polymer backbone and with substructures that meet the OECD PFAS definition[5] (hereafter referred to as "PFAS moieties") on the side chains.[6]

SCFPs are of particular interest because many of them can act as a long-term significant source of non-polymeric PFASs such as PFCAs and/or PFSAs in the environment as a result of the following three factors: historical and likely ongoing high production volumes and widespread use, presence of (high levels of) other non-polymeric PFASs in the commercial formulations, and ability of releasing PFAS moieties on the side chains over time (these three factors are elaborated below). This has resulted in the inclusion of related SCFPs in regulatory actions in many jurisdictions when addressing some PFCAs and PFSAs.[7] For example, the recent listing of PFOA, its salts and PFOA-related compounds under the Stockholm Convention includes SCFPs that meet the definition, "PFOA-related compounds which, for the purposes of the Convention, are any substances that degrade to PFOA, including any substances (including salts and polymers) having a linear or branched perfluoroheptyl group with the moiety (C_7F_{15})C as one of the structural elements" (Stockholm Convention, 2019; POPRC, 2021).

In addition, certain SCFP formulations have been applied in a way that can result in direct human exposure to monomers and their reaction products, causing adverse effects on human health. For example, upon inhalation of sprays containing 6:2 fluorotelomer silanes for surface treatment during application, the hydrolysis products of 6:2 fluorotelomer silanes may cause serious acute lung injury (e.g., Nørgaard et al. 2010, 2014). This has led to the restriction of (3,3,4,4,5,5,6,6,7,7,8,8-tridecafluorooctyl)silanetriol and its

[3] These well-known non-polymeric PFCA/PFSA precursors are also common degradation intermediates of many other PFASs including certain SCFPs, which are elaborated in the sections below.

[4] https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/riskreduction/

[5] PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS (OECD, 2021).

[6] This is derived from the commonly accepted SCFP definition in Buck et al. (2011)—polymers that "do not have perfluorinated or polyfluorinated polymer backbones, but are composed of variable composition backbones with polyfluoroalkyl (possibly perfluoroalkyl) side chains". Other definitions of SCFP exist, e.g., "side-chain fluorinated polymers contain a nonfluorinated polymer backbone, off of which fluorinated side chains branch." by ITRC (https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/#2_2_3_1). The definitions agree with each other, but only have some different wordings for describing the PFAS moieties on the side chains.

[7] Note that degradation intermediates themselves may be toxic and have long lifetime in biota and humans, see, e.g., Kabadi et al. (2020) and Rice et al., (2020).

mono-, di- or tri-O-(alkyl) derivatives from their use in spray products under the European Union (EU) REACH regulation[8] and in Switzerland.[9]

This report aims to provide an overview of existing scientific and technical information on SCFPs, focusing on their identities and life cycle, and with a particular goal to map the existing landscape and highlight critical knowledge and data gaps. It builds primarily on a review of peer-reviewed scientific literature, regulator reports and databases, and technical documents published by companies. It is intended to be comprehensive, but not exhaustive. For instance, due to time and resource constraints, an active search and analysis of patents and safety data sheets (SDS) was not conducted for this report. Also, not all critical knowledge and data gaps are captured in this report, particularly unknown ones.

[8] Annex XVII to REACH, Entry 73 (https://echa.europa.eu/documents/10162/2906fed0-12ab-9593-23a1-72efd611fe70), including the following condition of restriction: *1. Shall not be placed on the market for supply to the general public after 2 January 2021 individually or in any combination, in a concentration equal to or greater than 2 ppb by weight of the mixtures containing organic solvents, in spray products.*

[9] https://www.fedlex.admin.ch/eli/cc/2005/478/en#lvl_d4e267/lvl_d4e268/lvl_3

2 Identities of Side-Chain Fluorinated Polymers on the Global Market

Chapter summary:

- A wide range of SCFPs and their monomers have been commercialized since the 1950s. Many of them have information on their generic chemical structures in the public domain, whereas for some others, only ambiguous descriptions are identified.
- The generic chemical structures of SCFPs allow for grouping them according to the types of PFAS moieties present on the side chains and/or the structural repeating units in the polymer backbone. Such grouping can, to a certain extent, inform about, e.g., their possible impurities, use patterns, and degradation mechanisms, which are elaborated in the following chapters.
- CASRNs and CAS names alone cannot be used to identify unique SCFPs (in other words, the same CASRN and CAS name can be used for different SCFPs with the same generic chemical structures, but different structural details such molecular-weight ranges and distribution).
- However, limited to no information is available on additional structural details of most commercial SCFPs, e.g., molecular-weight ranges and distribution, molecule parts other than the monomers or structural repeating units, and percentage compositions of individual monomers. This impedes the ability to more precisely assess environmental behavior and thus risks of individual SCFPs.
- Nevertheless, existing information shows that chemical identities, including molecular weight and PFAS moiety content in the molecular structure, can vary considerably across different types of SCFPs and across different SCFPs within the same type.
- Future efforts may further investigate technical datasheets from companies and patents, and work with manufacturers to have in-depth understanding of the chemical identities of commercial SCFPs, including by making existing measurements publicly available and by measuring commercial formulations. Such efforts can start with the SCFPs that are still in commerce and with high production volumes. Efforts are also needed to collect and make such information publicly available in an easily accessible manner (including development of unique identifiers other than CASRNs and CAS names).

A wide range of SCFPs have been commercialized since the 1950s. Aiming to capture a comprehensive overview of the SCFP diversity on the market, Table S1 in the Annex (an Excel sheet file provided separately) provides a non-exhaustive list of 103 SCFPs and 42 monomers, including information sources, Chemical Abstracts Service Registry Numbers (CASRNs), CAS names, synonyms (if available), molecular formula (if available), previously used CASRNs (if relevant), types of PFAS moieties and structural repeating units, fluorinated carbon chain length, CASRNs of the related PFAS monomers, and registration status in various national/regional chemical inventories. They were identified by a brief search of the OECD 2018 PFAS List, regulatory databases,[10] scientific literature,[11] technical documents published by companies and SciFinder.[12] These identities served as a basis for the search of production and use information discussed in the later sections.

2.1. General categorization of SCFPs

In most cases, the generic chemical structure(s) can be identified, ranging from homopolymers to co-polymers with one or more types of non-fluorinated co-monomers. In several other cases, the generic chemical structure(s) cannot be identified or cross-referenced from multiple sources because only ambiguous trade/trivial names or descriptions are available. For example, the substance with EC No. 458-200-2 is registered with the name "[No public or meaningful name is available]" under the EU REACH, while its Substance Infocard[13] provides a figure of some vague structures without explanation.

Based on the generic chemical structures identified, these SCFPs can be categorized in different ways. One way is according to the types of PFAS moieties present on the side chains, including primarily n:2 fluorotelomers ($C_nF_{2n+1}CH_2CH_2-$),[14] PASF-derivatives [$C_nF_{2n+1}S(O)_2-$], perfluoroalkanoyl fluoride (PACF)-derivatives [$C_nF_{2n+1}C(O)-$; $C_nF_{2n+1}CH_2-$[15]] and perfluoropolyethers (PFPEs; containing a perfluorinated ether moiety such as $-CF_2-O-CF_2-$ in the fluorinated side chains),[16] with varied fluorinated carbon chain lengths.

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[10] Sources: the Inventory of Effective Food Contact Substance (FCS) Notifications by the United States Food & Drug Administration (https://www.cfsanappsexternal.fda.gov/scripts/fdcc/?set=FCN); EU REACH registered substances (https://echa.europa.eu/information-on-chemicals/registered-substances); US EPA CDR database (https://chemview.epa.gov/chemview/)

[11] Sources: Dinglasan-Panlilio and Mabury (2006; https://pubs.acs.org/doi/10.1021/es051619%2B), Frömel and Knepper (2010; https://www.sciencedirect.com/science/article/pii/S0045653510006491), Wang et al. (2013; https://doi.org/10.1016/j.envint.2013.08.021), Wang et al. (2014A; https://doi.org/10.1016/j.envint.2014.04.013).

[12] Sources: two Solvay's presentations on Fluorolink®, a search of the brand names "PolyFox" (provided in Buck et al., 2011), "Zonyl" and "Capstone" in SciFinder.

[13] https://echa.europa.eu/substance-information/-/substanceinfo/100.104.618

[14] Historically, fluorotelomer manufacturers have also produced other types of fluorotelomers, such as [$(CF_3)_2CF-(CF_2CF_2)_n-CH_2CH_2-$] (Wang et al., 2014A), which might have also been made into SCFPs.

[15] For example, one monomer CASRN 3934-23-4 (2-Propenoic acid, 2-methyl-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl ester, $C_7F_{15}CH_2OC(O)C(CH_3)=CH_2$) was synthesized by 3M from PFOA that was derived from perfluorooctyl fluoride (Bank et al. 1994); therefore, such compounds are categorized as PACF-based derivatives here. Despite not being derived from the telomerization process, such PFASs have sometimes been termed as "n:1 fluorotelomers" in literature for readability. Future work may consider to identify more proper terminology for this PFAS group.

[16] Other types of PFAS moieties present on the side chains include perfluoroalcohols ($C_nF_{2n+1}O-$) (see Table S1) or a vinylene-intercepted polyfluorinated side chain [e.g., $-(CF_2)_6-CH=CH-(CF_2)_5CF_3$] (Shirai et al. 2021).

The SCFPs can also be categorized according to the structural repeating units in the polymer backbone, with some simplifcations, including acrylates[17] {e.g., $[-CH_2-CH(C(O)OR_F)-]_n$}, ethoxylates {e.g., $[-O-CH_2-CH_2-]_n$},[18] oxetanes {e.g., $[-CH_2-C(CH_3)(CH_2OCH_2R_F)-CH_2-O-]_n$}, silicones {e.g., $[-Si(CH_2CH_2R_F)-O-Si(CH_2CH_2R_F)-]_n$} and urethanes[19] {e.g., $[-NH-C(O)-O-]_n$}, where R_F is used to represent a fluorinated carbon chain moiety.

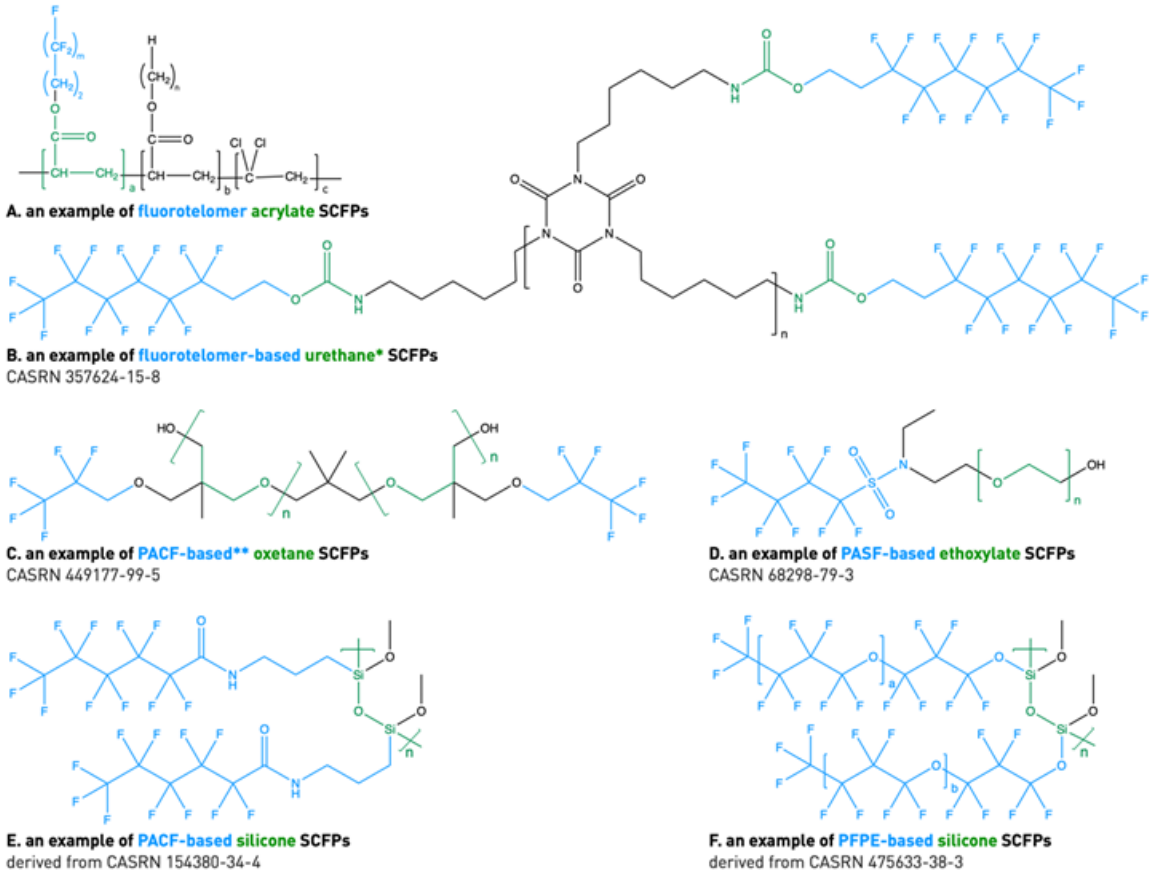
Examples of different types of SCFPs are illustrated in Figure 2.1. The two categorization methods bring different benefits. For example, categorization according to the types of PFAS moieties present on the side chains can inform about synthesis routes, possible impurities, and PFAS degradation products, whereas categorization according to structural repeating units in the polymer backbone can inform about possible use areas, possible impurities, degradation mechanisms, and so on. Depending on the exact purposes, readers may select either way of categorization, or a combination of both. In this report, the following four chapters on the life cycle of different SCFPs are separated according to structural repeating units in the polymer backbone, specifically: acrylates and urethanes (Chapter 3), oxetanes (Chapter 4), silicones (Chapter 5), and ethoxylates (Chapter 6).

[17] The term “acrylates” here also include methacrylates.

[18] Note that ethoxylates are different from other SCFPs, with often only one PFAS side chain connecting to the end of the polymer backbone. Given their polymer backbones $[(-OCH_2CH_2-)_n]$ are non-fluorinated, they are listed as SCFPs here.

[19] The term “urethanes” here include polyurethanes and related chemistry (such as polyallophanates and polyisocyanurates).

Figure 2.1. Examples of different types of side-chain fluorinated polymers. Blue colour highlights PFAS moieties, and green colour highlights structural repeating units in the polymer backbone.



2.2. Detailed structural information for individual SCFPs

As highlighted in Wang et al. (2021), for SCFPs and other polymers, individual CASRNs and chemical names often cover a wide range of substances with different compositions (such as different molecular-weight ranges, and numbers and types of functional groups) that may have distinct hazardous properties, environmental fate, bioaccessibility, degradation potential and implications for risk management. Therefore, it is important to have additional structural details of individual SCFPs such as molecular weight-ranges and distribution, molecule parts other than monomers or structural repeating units, and percentage compositions of individual monomers.

Currently, such additional structural details are sometimes available in the public literature (including technical datasheets provided by companies), but are scattered and often with limitations. For example, two biodegradation studies reported additional information on the chemical compositions of two commercial acrylate and urethane SCFPs, respectively (see Table 2.1; Russell et al., 2008 and 2010); however, due to a lack of CASRNs or other identifiers, such information cannot be linked to the SCFPs in Table S1. Further, the structural details of two commercial fluorotelomer-based ethoxylate SCFPs have

been reported by an analytical study and a biodegradation study: Zonyl FSO-100−with the perfluorocarbon chain length being between 2 and 14 carbon atoms and the degree of ethoxylation being between 0 and about 15 (Dinglasan-Panlilio and Mabury, 2006); and Zonyl FSH−with the perfluorocarbon chain length being at least between 4 and about 12 carbon atoms and the degree of ethoxylation being between 0 and at least 18 (Frömel and Knepper, 2010). In addition, Solvay reported the structural details of three PFPE-based ethoxylate SCFPs in one presentation (Solvay, no date (n.d.)), which were coincidentally identified during the preparation of this synthesis report.

Additional structural details can be identified in patents, but possibly in wide ranges. For example, Washington et al. (2015A) looked into two patents of fluorotelomer-based acrylate polymers and noted that the mass % of fluorotelomer in the polymers ranged from 79% to 85% in one patent and from 40% to 75% in the other. It is generally unknown how individual patents are translated into commercial practices (Freilich and Ouellette, 2019).

Further efforts have also been made by scientists to analytically determine compositions in commercial SCFPs. For example, Chu and Letcher (2014) measured a Scotchgard pre-2002 formulation and a Scotchgard post-2002 formulation, and detected one composition[20] in each formulation. Later, this analytical information was used to detect the presence of these compositions in different environmental media as an indicator of environmental fate and releases of the corresponding formulations (more details are elaborated in Section 3.4 below). Such analytical studies are so far limited, partially due to limited access by scientists to commercial formulations and analytical standards (Ng et al. 2021).

Therefore, it is generally challenging to capture an overview of the data availability of structural details for commercial SCFPs on the global market. Nevertheless, based on existing information, the chemical identities, including molecular weight and PFAS moiety content in the molecular structure, can vary considerably across different types of SCFPs and across different SCFPs within the same type.

Table 2.1. Additional structural details on the chemical compositions in commercial SCFP formulations reported in peer-reviewed scientific studies. N.A. = not available

References	Russell et al. (2008)	Russell et al. (2010)
SCFP type	Fluorotelomer-based acrylate polymer (Figure 2.1 A)	Fluorotelomer-based urethane polymer
Molecular weight	M_n = 40 000 Daltons*	M_n or M_w = 3 500 Daltons**
Fluorine content	10.095 weight%	10 weight%
SCFP weight% in the formulation	23–24%	23%
SCFP particle size in the formulation	100–300 nm	100–300 nm

* Here the authors used a number-average molecular weight (Mn), which is defined as the total weight of the molecules divided by the total number of molecules.

** Here it is not clear whether the authors referred to a number-average molecular weight (Mn) or a weight-average molecular weight (Mw), as both terms were mentioned for the same value in the Supporting Information of the study. A weight-average molecular weight depends not only on the number of molecules present, but also on the weight of each molecule. It can be calculated as $\sum w_i M_i$, where w_i is the weight fraction of polymer with molecular weight M_i. A

[20] They were able to detect mass spectral peaks at *m/z* 1315.0591 and 1634.3120 in each formulation, respectively. However, the authors did not report more details, except that the former mass peak contains a $[C_8F_{17}SO_2N(C_2H_5)]^-$ ion and the latter contains a $[C_4F_9SO_2N(CH_3)]^-$ ion.

weight-average molecular weight is larger than or equal to the corresponding number-average molecular weight for any given polymer.

2.3. Summary of critical knowledge and data gaps related to the chemical structure of SCFPs

A) In multiple cases in Table S1, the generic chemical structures of a given SCFP or its monomer(s) cannot be identified, even though their corresponding CASRNs were identified; such information gap impedes our understanding of these SCFPs (e.g., which non-polymeric PFASs may be released). Ways in which the information is lacking include: (i) Only the trade names were assigned to the CASRNs without further details, e.g., CASRNs 949581-65-1 (Scotchgard PM-3622), 940891-99-6 (Scotchgard PM-490), 923298-12-8 (Scotchgard PM-930) and 1224842-54-2 (Unidyne TG-5521); and (ii) the assigned CAS name is ambiguous, e.g., CASRN 328389-91-9 [Propanoic acid, 3-hydroxy-2-(hydroxymethyl)-2-methyl-, polymers with 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane and reduced Me esters of reduced polymd. oxidized tetrafluoroethylene, compds. with triethylamine].

B) CASRNs and CAS names alone cannot be used to identify unique SCFPs (in other words, the same CASRN and CAS name can be used for different SCFPs with the same generic chemical structures, but different structural details such molecular-weight ranges and distribution). Therefore, apart from the generic chemical structures of any given SCFPs, additional structural information is needed for studies and assessments of their hazardous properties, environmental fate, bioaccessibility, degradation potential, and implications for risk management, such as the molecular-weight range and distribution of the SCFP, the fluorine content, the molecular percentage of individual co-monomers, and how the co-monomers are connected (e.g., by providing a reaction scheme if available). In the public literature, additional structural information was identified for some commercial SCFPs; however, such information is scattered and often with limitations (e.g., due to a lack of CASRNs or other identifiers, reported information cannot be linked to specific SCFPs listed in Table S1). Analytical studies can help to measure the structural details of individual SCFPs, but such studies are generally challenging due to a lack of access by scientists to commercial formulations and analytical standards.

2.4. Options for a way forward

To address these two gaps, future efforts may further investigate technical datasheets from companies and patents, and work with manufacturers to better understand the chemical identities of commercial SCFPs, including by making existing measurement results publicly available and by measuring commercial formulations. To increase efficiency, priorities may be first given to those SCFPs that are still in commerce and with high production volumes. Efforts are also needed to collect and make such information publicly available in an easily accessible manner, e.g., via the OECD PFAS Web Portal, the OECD eChemPortal and/or work under the Stockholm Convention[21]; such efforts may engage the cheminformatics community, as unique identifiers other than CASRNs and CAS names would be needed for identifying unique SCFPs. This can greatly enable a better understanding of the environmental fate and degradation behaviour of

[21] The Secretariat of the Stockholm Convention, in consultation with the POPs Review Committee, has developed an indicative list for PFOA, its salts and PFOA-related compounds, including PFOA-related SCFPs, covered under the listing under the Stockholm Convention. It is expected that an indicative list of PFHxS, its salts and PFHxS-related compounds will be prepared if those chemicals are listed under the Stockholm Convention. For more details, see the Stockholm Convention webpage (www.pops.int).

individual SCFPs (which can vary greatly, given the large range of molecular weights and the mass percentage of PFAS moieties in the polymer reported for a few commercial SCFPs as outlined above), and estimation of generation and releases of non-polymeric PFASs from individual SCFPs. In parallel, a logical maximum percentage of PFAS moieties could be developed based on literature review (including patents) and stakeholder consultation, as a precautionary approach for estimating non-polymeric PFAS releases from SCFPs.

3 The Life Cycle of Acrylate and Urethane SCFPs

Chapter summary:

- Historically, many acrylate and urethane SCFPs containing *long-chain* PFAS moieties on the side chains (hereafter referred to as "*long-chain*" SCFPs) were produced in significant amounts, jointly on the scale of thousands of tonnes or more per annum (which were at least one order of magnitude higher than the production volumes of many non-polymeric PFASs including those used in fire-fighting foams). Currently, many long-chain acrylate and urethane SCFPs have been replaced by short-chain ones, while some long-chain ones may still be used (details unknown due to confidentiality). Despite limited information (due to no reporting requirements, confidentiality, etc.), it can be concluded that short-chain acrylate and urethane SCFPs are still being produced jointly on the scale of thousands of tonnes or more per annum.
- Acrylate and urethane SCFPs have been mainly used as surface protectors to impart water- and oil-repellency and soil-resistance to fabrics, textiles, and apparel articles (both for industrial pre-market treatment, or professional/consumer aftermarket treatment), and food contact paper and paperboard. Some acrylate and urethane polymers may also be used as fluorosurfactants in products such as fire-fighting foams, inks, and paints, lacquers and varnishes.
- Considerable amounts (up to 5 weight%) of other non-polymeric PFASs may be present in commercial formulations. They may originate from unreacted starting materials and reaction intermediates, contaminants from the raw materials, degradation products, and reaction byproducts. They may also be monomeric PFASs intentionally left in the formulations to keep the acrylate and urethane particles suspended in the formulations.
- Acrylate and urethane SCFP degradation may follow two main degradation mechanisms: direct cleavage of PFAS moieties from the side chains (e.g., hydrolysis of the ester bond), and breakdown of the polymer carbon–carbon backbone to form small oligomeric species which subsequently undergo ester bond cleavage.
- While existing degradation studies agree well on the degradation mechanisms, historical studies have reported a wide range of degradation half-lives, ranging from less than 1 year to over a thousand years. Some of these large variations observed are caused by experimental artefacts, which can be and were minimized/eliminated in more recent studies (where the degradation half-lives of two commercial fluorotelomer-based acrylate SCFPs were measured to be several decades).

Meanwhile, the variations observed also partially reflect the true variability of several parameters that may impact degradation, including molecular size of SCFPs, specific surface area of SCFP particles, substrate, temperature, pH values, and humidity. Such variability cannot be minimized/eliminated. Therefore, degradation half-lives of acrylate and urethane SCFPs in the environment and biota will remain to some extent uncertain. Nevertheless, it can be concluded that these SCFPs will degrade and thus serve as a long-term source of non-polymeric PFASs once released in the environment.

- In contrast to abiotic and biotic degradation, little is known about the fate of SCFPs during municipal waste incineration of SCFP-treated articles, and whether this would be a significant source of non-polymeric PFASs into the environment.
- Upon application for surface treatment, both SCFPs and other PFASs present in the formulations may partially be released via air, wastewater and/or solid waste, and partially transferred onto treated articles, which may be released during the subsequent processing, use and disposal. Due to various uncertainties and unknowns, the contribution of acrylate and urethane SCFPs to PFASs in the environment and biota is unclear. But it is likely significant, particularly in the long term, given the large volumes produced and used. Future efforts may collect further information and reduced the uncertainties to reach more precise estimates.

Given the similarities between acrylate and urethane SCFPs in many aspects in terms of use patterns, presence of other PFASs in the commercial formulations, and degradation mechanisms, they are jointly analysed and described in this chapter.

3.1. Historical and ongoing production and uses

Most acrylate and urethane SCFPs and acrylate SCFP monomers identified in Table S1 have been registered for production and use in many jurisdictions, but mostly with unknown commercial status[22]. Table 3.1 summarizes the production/import volumes of various acrylate and urethane SCFPs, containing various types of PFAS moieties with varied chain length on the side chains, as reported in the EU, in the United States (US), and in the Nordic Countries (Denmark, Finland, Norway and/or Sweden). Many are available in large tonnage ranges (e.g., >454 to <4540 tonnes/year), and many others have been claimed as confidential business information and sealed from the public. Therefore, these data are discussed together with other information identified in peer-reviewed scientific literature as follows.

Historically, acrylate and urethane SCFPs were the major SCFPs produced. Until the early 2000s, PASF-based SCFPs were mainly derived from perfluorooctanesulfonyl fluoride (POSF), i.e., long-chain C_8-based SCFPs.[23] Based on the then major producer–3M's reporting, it was estimated that prior to 2002, about

[22] The listing in most national/regional chemical inventories indicate whether the substances have been produced or used in the respective jurisdiction, but do not indicate whether they are currently being produced or used.

[23] Long-chains refer to perfluorocarboxylic acids (PFCAs) with carbon chain lengths C8 and higher, including perfluorooctanoic acid (PFOA); perfluoroalkane sulfonic acids (PFSAs) with carbon chain lengths C6 and higher,

55% of POSF (up to ca. 2400 tonnes in 2000) were used to produce different types of SCFPs (see Figure S8 in the Supplementary Data of Wang et al. 2014A); and a majority were made into acrylate (likely up to about 20% of POSF) and urethane (likely 23–32% of POSF) SCFPs. As a comparison, 3M reported that its estimated global production of POSF-derivatives for fire-fighting foams was about 150 tonnes in 2000, about 3% of 3M's total global production POSF-derivatives at that time (3M, 2000). Based on public records, the same study also estimated that after 2002 following 3M's global phase out, POSF-based SCFPs were (mostly) discontinued in Japan, Western Europe and the US, while Chinese manufacturers started large-scale production of POSF-based SCFPs in 2002, with a production volume of up to ca. 120 tonnes POSF-equivalent per year, and presumably discontinued most of this production after 2008. However, it is possible that some POSF-based acrylate SCFPs are still being produced and used. For example, the use of CASRNs 68298-62-4 and 68867-62-9 in some Nordic countries in 2019 has been reported, though it is unclear at what levels and for which purposes due to confidentiality (see Table 3.1).

Since 2002, POSF-based SCFPs in many applications such as textiles have largely been replaced by C_4 perfluorobutanesulfonyl fluoride (PBSF)-based SCFPs, i.e., short-chain ones (Wang et al. 2013, 2014A). The current production volumes of PBSF-based acrylate and urethane SCFPs are largely unknown, but are still on a significant level. For example, two PBSF-based acrylate SCFP monomers are registered in the EU with the production/import tonnage band of ≥110 to <1100 tonnes/year (see Table 3.1).

Similarly to PASF-based derivatives, most (80%) of the n:2 fluorotelomers manufactured by Asahi, Clariant, Daikin and Dupont were made into SCFPs (up to 7200 tonnes PFAI-equivalent in 2006), as reported by the "Telomer Research Program" in 2002 to the US Environment Protection Agency (EPA). At that time, n:2 fluorotelomers were produced as mixtures of different chain lengths with long-chain 8:2 and 10:2 as main components (Wang et al. 2014A). Since 2006, the major global fluorotelomer manufacturers have stepwise replaced mixture fluorotelomers with predominantly short-chain 6:2 fluorotelomer (>99%) and the transition was completed by 2015 (Wang et al., 2013; US EPA, n.d.). However, the use of two long-chain fluorotelomer-based acrylate SCFPs (CASRNs 142636-88-2 and 70969-47-0) and one long-chain fluorotelomer-based acrylate monomer (CASRN 27905-45-9) in some Nordic countries in 2019 has been reported (see Table 3.1). It is possible that CASRN 70969-47-0 was produced before the transition, given the long shelf-life of fire extinguish agents, in which it is used (see below). For CASRNs 142636-88-2 and 27905-45-9, it is unclear whether they were produced before or after the industrial transition, as no details are provided in the SPIN database.

Unlike for PASF-based derivatives, a break-down of the production of n:2 fluorotelomer SCFPs on the basis of SCFP types is not publicly available, but at least n:2 fluorotelomer acrylate SCFPs have been and are still being produced in large quantities, on the scale of hundreds to thousands of tonnes per annum (for examples, see acrylate SCFP monomers–n:2 fluorotelomers in Table 3.1).

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including perfluorohexanesulfonic acid (PFHxS) and perfluorooctanesulfonic acid (PFOS); and, precursors of these substances (https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutpfass/).

Table 3.1. Production/import volumes of acrylate and urethane SCFPs and their monomers in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting); and in the EU reported in the REACH dossiers. n.d. = no date; t = tonnes; yr = year.

CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import mass reported
Acrylate SCFPs			
101896-32-6	n:2 fluorotelomers	unclear	**EU:** confidential (n.d.)
817203-49-9	n:2 fluorotelomers	6	**EU:** confidential (n.d.)
1071022-26-8	n:2 fluorotelomers	6	**SPIN:** 0.6 t + confidential (2012–2019)
1793072-86-2	n:2 fluorotelomers	6	**SPIN:** confidential (2016)
142636-88-2	n:2 fluorotelomers	8;10;12	**US:** <454 t/yr in 2012–2015 **SPIN:** confidential (2011–2019)
70969-47-0	n:2 fluorotelomers	6;8;10;12;14;16;18	**US:** <227 t in 2005, 57.9 t in 2011, <454 t/yr in 2012–2015 **SPIN:** 64.7 t + confidential (2001–2019)
304012-61-1	n:2 fluorotelomers	6;8;10;12	**SPIN:**confidential (2008–2016)
479029-28-2	n:2 fluorotelomers	6;8;10;12	**SPIN:** confidential (2004–2011)
1078712-88-5	n:2 fluorotelomers	2;4;6;8;10;12;14;16;18	**US:** 15.6 t in 2011
53515-73-4	PACF-derivatives	7	**SPIN:** confidential (2000–2003)
1017237-78-3	PASF-derivatives	4	**US:** <454 t/yr in 2012–2015 **SPIN:** confidential (2011, 2014–2019)
425664-29-5	PASF-derivatives	4	**SPIN:** confidential (2008–2019)
819069-72-2	PASF-derivatives	4	**SPIN:** confidential (2006–2007)
162568-17-4	PASF-derivatives	8	**SPIN:** confidential (2000–2015)
68298-61-3	PASF-derivatives	7;8	**SPIN:** confidential (2000)
68298-62-4	PASF-derivatives	7;8	**SPIN:** confidential (2000–2019)
68555-90-8	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68329-56-6	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68555-92-0	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2017)
68586-13-0	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68586-14-1	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68649-26-3	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
68867-62-9	PASF-derivatives	4;5;6;7;8	**US:** >4.54 to <227 t in 2001 **SPIN:** confidential (2000–2019)
127133-66-8	PASF-derivatives	4;5;6;7;8	**SPIN:** confidential (2000–2003)
Acrylate SCFP monomers			
1228350-17-1	n:2 fluorotelomers	6	**EU:** =1 to =10 t/yr (n.d.)
17527-29-6	n:2 fluorotelomers	6	**EU:** =100 to <1000 t/yr (n.d.) **US:** >4.54 to <227 t/yr in 1989, 1997 & 2001, confidential in 2011, <454 t in 2012, >454 to <908 t/yr in 2013–2015 **SPIN:** confidential (2000, 2004–2010)
2144-53-8	n:2 fluorotelomers	6	**EU:** =1000 to <10000 t/year (n.d.) **US:** >4.54 to <227 t in 1985, confidential in 2011, >454 to <4540 t in 2012, >272 to <454 t in 2013, >454 to <4540 t/yr in 2014 and 2015 **SPIN:** confidential (2003–2019)
27905-45-9	n:2 fluorotelomers	8	**US:** >4.54 to <227 t/yr in 1989 and 1997, >227 to <454 t in 2001, >454 to <4540 t in 2005, confidential in 2011, >45.4 to <227 t in 2012, <454 t/yr in 2013–2015 **SPIN:** confidential (2000, 2004–2019)

17741-60-5	n:2 fluorotelomers	10	**US:** >4.54 to <227 t/yr in 1989, 1997 and 2001, >454 to <4540 t in 2005, confidential in 2011, >45.4 to <227 t in 2012, <454 t/yr in 2013–2015 **SPIN:** confidential (2000, 2004–2005)
34395-24-9	n:2 fluorotelomers	12	**US:** >4.54 to <227 t/yr in 1989, 1997 and 2001, <227 t in 2005, <454 t/yr in 2012–2015 **SPIN:** confidential (2000, 2004–2005)
34362-49-7	n:2 fluorotelomers	14	**US:** >4.54 to <227 t/yr in 1989, 1997 and 2001, <227 t in 2005, <454 t/yr in 2012–2015 **SPIN:** confidential (2004–2005)
85631-54-5	n:2 fluorotelomers	6;8;10;12	**EU:** =10 to <100 t/yr (n.d.) **SPIN:** confidential (2000–2012)
352-87-4	PACF-derivatives	1	**EU:** =1 to <10 t/yr (n.d.) **SPIN:** confidential (2008–2009, 2015–2017)
355-93-1	PACF-derivatives	4(1H)	**EU:** =10 to <100 t/yr (n.d.)
67584-55-8	PASF-derivatives	4	**EU:** =100 to <1000 t/yr (n.d.) **US:** >4.54 to <227 t/yr in 1985, 1989, 1993 and 1997, confidential in 2011, <454 t/yr in 2012–2015 **SPIN:** confidential (2000–2019)
67584-59-2	PASF-derivatives	4	**EU:** =10 to <100 t/yr (n.d.) **SPIN:** confidential (2000–2017)
212335-64-3	PASF-derivatives	4	**US:** confidential in 2011, <454 t/yr in 2012–2015
3063-94-3	Unclear*	1	**EU:** =0 to <10 t/yr (n.d.)
Urethane SCFPs			
357624-15-8	n:2 fluorotelomers	6	**SPIN:** confidential (2011–2014)
118102-37-7	n:2 fluorotelomers	6;8;10;12	**SPIN:** confidential (2000–2014)
118102-38-8	n:2 fluorotelomers	6;8;10;12	**SPIN:** confidential (2000–2014)
68990-40-9	n:2 fluorotelomers	2;4;6;8;10;12;14;16	**SPIN:** confidential (2000–2003)
135228-60-3	n:2 fluorotelomers	4;6;8;10;12;14;16;18	**SPIN:** confidential (2003–2016)
144468-32-6	n:2 fluorotelomers	4;6;8;10;12;14;16;18	**SPIN:** confidential (2000–2010)
162491-88-5	n:2 fluorotelomers	Unclear	**SPIN:** confidential (unclear)

Both acrylate and urethane SCFPs have been used in a wide range of applications, which are divided into several major use areas and separately described below. Similar to the production volumes, use information reported to the SPIN database has mostly been claimed as confidential business information (see Table S2). Furthermore, although some data were reported by 3M in the past (see Figure S8 in the Supplementary Data of Wang et al. 2014A), it is generally unknown how much acrylate and urethane SCFPs have been used in which applications.

Fabrics, textiles, and apparel articles

To date, a wide range of commercial SCFP products have been used to treat fabrics, textiles, and apparel articles to impart water- and grease-repellency and soil-resistance, usually applied in combination with hydrocarbon water-repellent adjuvants, resins, and/or monomeric PFASs that demonstrate some synergistic effects (Bank et al., 1994). These SCFPs include many acrylate (e.g., CASRN 68298-62-4) and urethane[24] (e.g., 3M Scotchgard Fabric Protector; 3M, 2018) SCFPs. They can also be a mixture containing both acrylate and urethane SCFPs (e.g., Teflon Advance Carpet Protector), as reported by Dinglasan-Panlilio and Mabury (2006). In these SCFPs, nonfluorinated co-monomers serve the functions of extending fluorine efficiency, providing functionality to enhance durability, and/or modifying the hand feel of the treated fabric (Bank et al. 1994). The treatments of textiles can be done both pre-market by manufacturers,

[24] Urethane SCFPs, typically based on the reaction of fluorinated diol intermediates with diisocyanates, were particularly used for the treatment of 100% cotton and cotton-blend textiles (Bank et al., 1994).

and aftermarket by professional services and consumers (3M, 1999). For more examples and technical details, see Table S1, 3M (1999) and Bank et al. (1994).

Food-contact paper and paperboard

Many acrylate and urethane SCFPs have been used as an oil- and water-resistant agent in paper and paper board. As such, these SCFPs can prevent the paper material from soaking up fats and water, with the applications particularly targeting fatty foods especially those intended to be heated in packaging or stored for an extended period, and as moisture barriers (OECD, 2020). These SCFPs can be used either by the addition to the pulp during paper production (internal sizing), or as a surface treatment to the paper (external sizing) (Uehara et al., 2021; OECD, 2020). More technical details on the internal and external sizing, including respective advantages and disadvantages can be found in OECD (2020).

Currently, 15 fluorotelomer-based acrylate[25] and 1 PFPE-based urethane SCFPs are listed on the US Food & Drug Administration (FDA)'s Inventory of Effective Food Contact Substance Notifications (FCN) database[26] for such uses. Additional information on the concentration limits for using SCFPs in making the food-contact paper and paperboard in the US can be found in the US FDA FCN database.[27] Furthermore, several major manufacturers have reached agreement with the US FDA to voluntarily phase out their sales of 6:2 fluorotelomer-based SCFPs for use in food contact applications in the US by 2023 (see Table S2; US FDA, n.d.).

Others

One acrylate SCFP (CASRN 70969-47-0) has been reported as fluorosurfactants in fire-fighting foam formulations (e.g., Solberg 1x3 ATC, Sigma AFFF; Solberg, n.d.; Sigma, n.d.) that are used in extraction of crude petroleum and natural gas, manufacture of coke and refined petroleum products, and wholesale trade (except of motor vehicles and motorcycles) (see Table S2; US EPA, 2016; SPIN, n.d.). CASRN 68298-62-4 has been reported for use in the following application areas with no further details available (likely as fluorosurfactants): paints, lacquers and varnishes; reprographic agents; adhesives and binding agents; printing inks; and glossing agents (see Table S2; SPIN, n.d.).

[25] The number here counts different salts of a SCFPs as different SCFPs. If different salts of a SCFP would be counted as one SCFP, there would be 11 distinct fluorotelomer-based acrylate SCFPs.

[26] https://www.cfsanappsexternal.fda.gov/scripts/fdcc/?set=FCN

[27] Further US-FDA generated documents on the chemistry and exposure, toxicology, and environmental impacts of the PFASs that were approved by US FDA for food contact substances between 2002 and 2016 can be found at https://www.edf.org/sites/default/files/EDF-PFAS-FOIA-FCN-Chemistry-Memos.pdf.

3.2. Presence of other PFASs in the commercial formulations

Commercial acrylate and urethane SCFP formulations are generally available in the form of aqueous dispersion of SCFP particles (Russell et al. 2008, 2010; Uehara et al. 2021; Washington et al. 2014). A range of non-polymeric PFASs have been detected in several fluorotelomer-based commercial acrylate and urethane SCFP formulations (see Table S3), including perfluoroalkyl iodides (PFAIs), PFCAs, and fluorotelomer acrylates (FTAcs), alcohols (FTOHs), alcohol acetates (FTOH-aces), carboxylic acids (FTCAs), ethers (FT-ethers), olefins (FTOs) and unsaturated carboxylic acids (FTUCAs).

The levels of non-polymeric PFASs may vary considerably across commercial formulations (see Table S3). One study reported residuals at the level of over 5 weight % of the solids in one fluorotelomer-based commercial formulation tested (see Table S1 of Washington et al. 2014). 3M reported that most of its PASF-based formulations for industrial applications typically contain monomer residuals at 1 percent or lower levels, though it is not clear whether the 1 percent or lower levels referred to the ratio of non-polymeric PFAS residuals to the SCFP content in dispersions or to the total dispersion mass (3M, 1999). In another two PASF-based commercial urethane SCFP formulations, no non-polymeric PFASs were detected (Chu et al. 2014; Letcher et al. 2020); however, this result may be an artefact.[28]

The detected non-polymeric PFASs can be grouped into four categories based on origins (by comparing to the general synthesis routes of SCFPs; see Figure 3.1), with some belonging to more than one category: (i) unreacted raw materials and reaction intermediates used in the synthesis (e.g., PFAIs, FTOHs, FTAcs); (ii) impurities from the starting materials (e.g., PFOA)[29]; (iii) degradation products of the unreacted raw materials and reaction intermediates (e.g., FTAcs → FTOHs → FTCAs, FTUCAs, and PFCAs; Young and Mabury, 2010, Liu and Avendaño, 2013, and Evich et al., 2022) and SCFPs (see Section 3.3 below); and (iv) reaction byproducts of PFASs in the previous three categories (e.g., 8:2 FTOH → 8-8 ether; 8:2 FTOH + PFOA → 8-2-8 ester)[30].

In addition to being impurities from the starting materials and synthesis in the formulations, some non-polymeric PFASs (e.g., FTOHs) can also be intentionally left at significant levels in commercial formulations as dispersants to keep the SCFP particles suspended in the aqueous phase.

Commercial formulations are applied to materials such as textiles and pulp whereby the SCFP particles are strongly adsorbed and, in some cases, chemically bound to the material surface, and the rest application suspension is discharged to wastewater (Russell et al. 2008, 2010; Uehara et al. 2021; Washington et al. 2014). Thus, during application of commercial formulations, PFAS impurities therein are partially released (via air, wastewater and/or solid waste; Heydebreck et al., 2016), and partially transferred onto products (for examples of the detection of some non-polymeric PFASs in SCFP-treated products, see Table S3). The levels of PFAS impurities released and remaining in treated products may be highly

[28] The non-detection could be due to several reasons: (i) the dilution that the concentration of SCFPs was estimated to be <3% in the formulations (i.e., at least about an order of magnitude lower than the other studies), resulting in the PFAS impurity levels below the detection limit; (ii) possible key compounds such as FASEs (Wang et al., 2014A) were not monitored; and/or (iii) the analytical methods used in that particular study are not effective for capturing non-polymeric PFASs, particularly those that are still co-associated with the polymer (Larsen et al. 2006; Washington et al. 2009, 2014). Washington et al. (2014) provides a solid analytical workflow for measuring levels of PFAS other than the SCFPs in the commercial formulations.

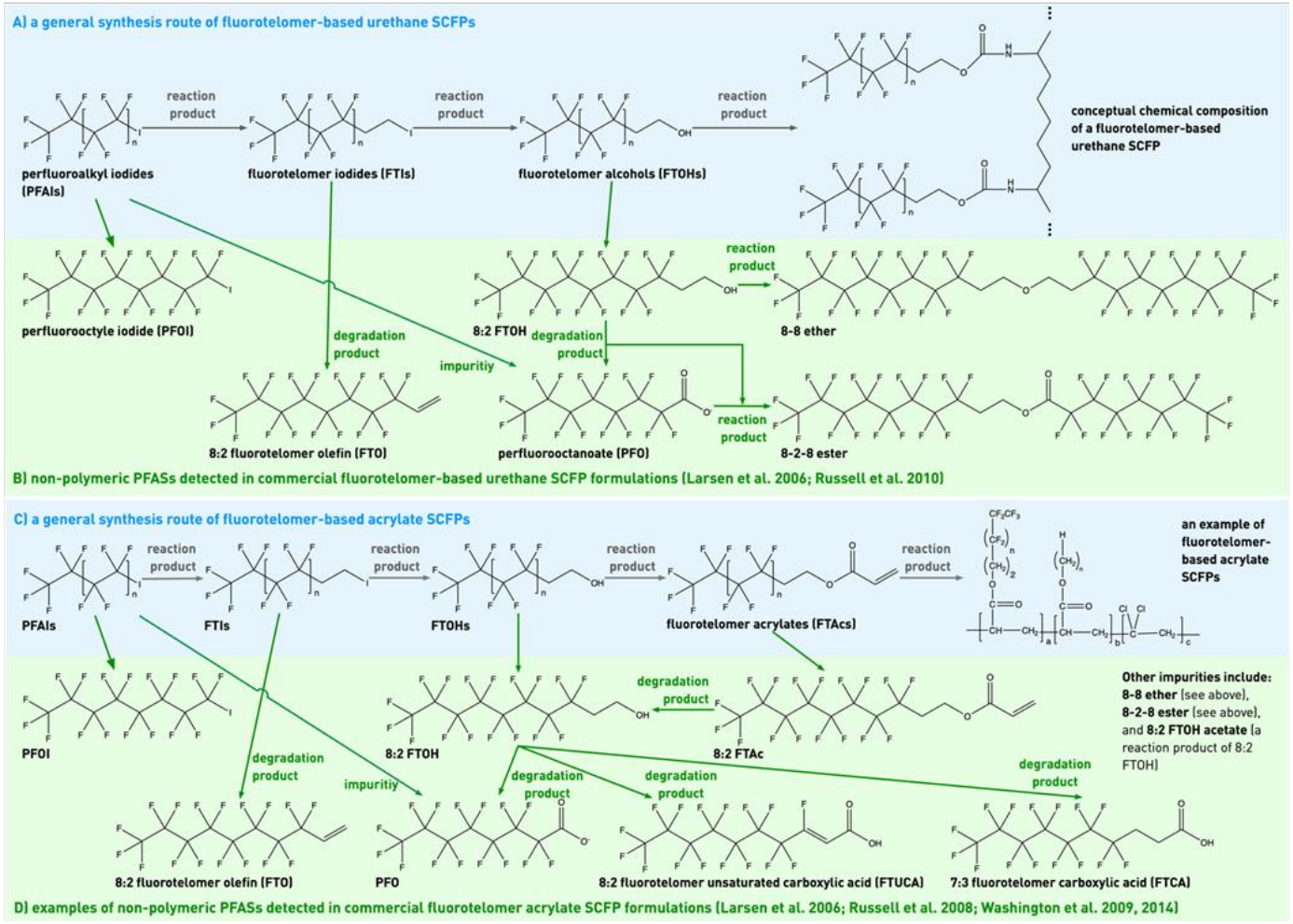
[29] PFOA was detected in the perfluoroalkyl iodides (PFAIs) starting material for synthesizing fluorotelomers; for more details, see the Supplementary Data of Wang et al. (2014A).

[30] The acronyms “8-8 ether” and “8-2-8 ester” are taken from the original publications. Future terminology may harmonized them in the same manner as “8:2 FTOH” for “8:2 fluorotelomer alcohol”.

variable, depending on the processes and control measures.[31] No mass balance studies of the fate and distribution of non-polymeric PFAS during application of commercial SCFPs are identified.

[31] Some patents describe flash drying, e.g., at 127 ℃, is included in the application of SCFPs. When Washington et al. (2014) dried a commercial SCFP at 127 ℃, the PFAS impurities dropped 2- to 3-orders of magnitude to constant concentrations within about 10 minutes.

Figure 3.1. A comparison of detected non-polymeric PFASs to the general synthesis routes of commercial fluorotelomer acrylate and urethane SCFPs.



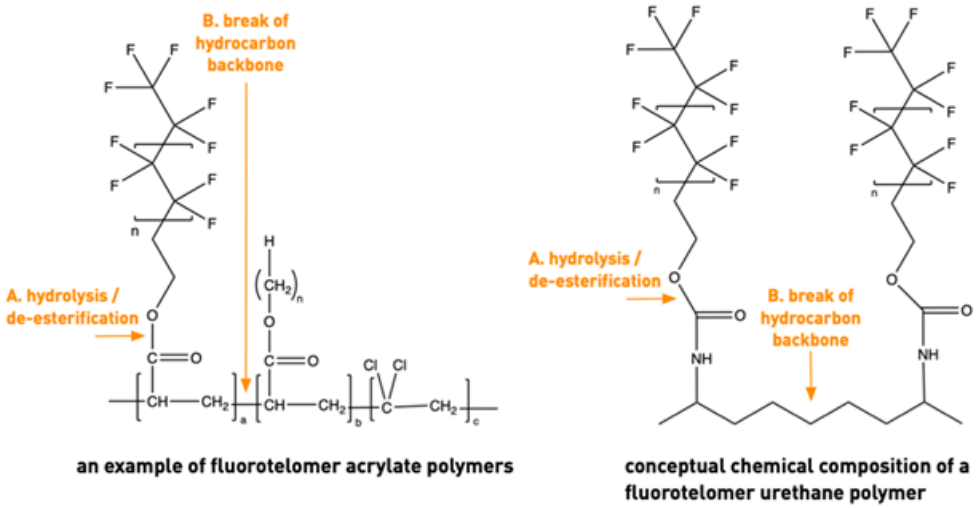
3.3. Degradation of SCFPs during use and after end-of-life

Acrylate and urethane SCFP degradation may follow two main degradation mechanisms (see Figure 3.2): A) direct cleavage of PFAS moieties from the side chains (e.g., hydrolysis of the ester bond); and B) breakdown of the polymer carbon−carbon backbone to form small oligomeric species which subsequently undergo ester bond cleavage (Russell et al. 2008, 2010).

Existing degradation studies have shown that the PFAS moieties may be released during abiotic or biotic degradation (i.e., the occurrence of the mechanism A), which can then subsequently further degrade and form PFCAs and/or PFSAs in the environmental and biota following rather well-characterized degradation pathways of non-polymeric PFASs [which have been well synthesized in Young and Mabury (2010), Liu and Avendaño (2013) and Evich et al. (2022)].

These studies did not show whether the mechanism B also occurred, whereas a recent study by Schellenberger et al. (2022) detected release of SCFP-containing microplastic fibres from functional textiles during washing, suggesting the mechanism B may occur during certain conditions (which may be learned from the research field of microplastic formation in the future).

Figure 3.2. Schematic illustration on two main degradation mechanisms of acrylate and urethane SCFPs.



While existing degradation studies agree well on the degradation mechanisms, historical studies have reported a wide range of degradation half-lives[32] (see Table 3.2), ranging from less than 1 year, to a couple of years, to decades to roughly a century, to over a thousand years. These large variations are partially caused by limitations in the experimental design of some previous studies (e.g., whether non-polymeric PFAS residues were all removed; Larsen et al., 2006, Washington et al., 2009, Washington et al. 2015B). In other words, some of the large variations observed are caused by experimental artefacts, which can be and were minimized/eliminated in more recent studies (where the degradation half-lives of two fluorotelomer-based acrylate SCFPs were measured to be several decades; Washington et al., 2015A and

[32] Note that the degradation half-lives here refer to the initial degradation step(s) of cleaving PFAS moieties from the polymer backbone.

2015B). More technical details and discussion on this possible source of error, as well as a recommended analytical workflow to minimize/eliminate it, can be found in Washington et al. (2014).

At the same time, the variations observed also partially reflect the true variability of several parameters that may impact degradation, including 1) molecular size of SCFPs (only three studies reported, with the number/weight-average molecular weight ranging from nearly 3000 Dalton to 40,000 Dalton, which can influence, e.g., bioavailability); 2) specific surface area of SCFP particles (which can influence areas available for degradation; Washington et al. 2009); 3) substrate (as hydrophobicity may well be diminished when water can come through the substrate and result in hydrolysis / de-esterification without or with less interference from the side chains, see Figure 3.2); 4) temperature, 5) pH values (shorter degradation half-lives with increasing alkalinity above pH = 8; Washington et al. 2015B), and 6) humidity (the same SCFP degraded more slowly when it was dry in comparison to when it was water-submerged; Washington et al. 2015A,B). Such variability cannot be minimized/eliminated.

Therefore, the degradation half-lives of acrylate and urethane SCFPs in the environment and biota will remain to some extent uncertain, in part reflecting real-world variability associated with the factors described above. Still, more of this uncertainty is because the characterization of many of these parameters are not available in the public domain (e.g., molecular size and specific surface areas of SCFP particles in commercial formulations) and may change over time (e.g., molecular size decreases when the degradation mechanism B occurs). Nevertheless, it can be concluded that these SCFPs generally will degrade under environmental conditions, with half-lives often falling roughly at a century or less, and thus serve as a long-term source of non-polymeric PFASs in the environment and biota.

In contrast to abiotic and biotic degradation, little is known about the fate of acrylate and urethane SCFPs during municipal waste incineration of SCFP-treated articles.[33] Yamada et al. (2005) investigated the thermal degradation of a polyester/cellulose fabric substrate treated with a fluorotelomer acrylate SCFP (that was described in the US Patents 4742140 and 5344903) under laboratory conditions with an average temperature of 1000 ºC or greater[34] over approximately 2 seconds of residence time. The results observed thermal degradation of the SCFP started at ca. 600 ºC and increased with increasing temperature (90% sample destruction at ca. 850 ºC, and 99.9% sample destruction at 1000 ºC), with no formation of PFOA. Fluorinated radicals such as $\bullet CF_3$ and $\bullet CF_2CH{=}CH_2$ were major extracted species at 600 ºC, and their levels decreased with increasing temperature (they still existed at 1000 ºC, but the relative amount remaining was ≤0.1%). It is currently unknown whether other non-polymeric PFASs would be generated during incineration, as they were not monitored in the study.

[33] More is known about incineration of other PFASs including fluoropolymers. For more details, see, e.g., Olsavsky et al., 2020 (https://doi.org/10.3390/app10196921) and Winchell et al., 2020 (https://doi.org/10.1002/wer.1483).

[34] Note that in Europe, the flue gases from municipal waste incinerators are meant to run at a temperature of 850 °C for at least two seconds, see https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=LEGISSUM:l28072&from=EN.

*Table 3.2. Reported experimental degradation half-lives of commercial acrylate and urethane polymers.**

Reference	SCFP type (characterization)	Degradation half-life [years]	Notes
Russell et al. 2008	A commercial n:2 fluorotelomer acrylate SCFP (number-average molecular weight of 40000 Dalton and 10.095 weight% fluorine)	Alfisol soil: 217 (SAS calculations) / 1140 (Excel calculations) Inceptisol soil: 95 (SAS calculations) / 637 (Excel calculations) Mollisol soil: 202 (SAS calculations) / 1270 (Excel calculations) Ultisol soil: >2000 (SAS calculations & Excel calculations)	These degradation half-lives may be an overestimate, as the study did not follow the recommendation by Larsen et al. (2006) to capture all non-polymeric residues remained in the polymer – an issue that was detailed in Washington et al. (2009).
Washington et al. 2009	A commercial n:2 fluorotelomer acrylate SCFP that is pre-treated by the manufacturer to minimize non-polymeric residue level (unknown)	870–1400 for coarse-grained test polymer in soil 10–17 for more-finely grained polymers in soil (based on modelling, assuming degradation is surface-mediated)	The specific area of the test SCFP was about 0.05 m^2/g, lower than the specific area of a typical commercial acrylate SCFP at about 14 m^2/g.
Russell et al. 2010	A commercial n:2 fluorotelomer urethane SCFP (number/weight-average molecular weight of 3500 Dalton and 10 weight% fluorine)	Alfisol soil: 241 Inceptisol soil: 72 Molisol soil: 219 Ultisol soil: 28 (use data through day 273) to 79 (use all data)	These degradation half-lives may be an overestimate, as the study did not follow the recommendation by Larsen et al. (2006) to capture all non-polymeric residues remained in the polymer – an issue that was detailed in Washington et al. (2009).
Washington et al. 2015A	Two commercial n:2 fluorotelomer acrylate SCFPs – FTP3 and FTP4 (unknown)	Quantitative rate-constant treatment: Appling (ultisol) soil (FTP4, drying at 127 °C, soil moisture saturated, endogenous microbial community, 7 sampling rounds, 5 microcosms per sample rounds) = 65 (use C_8 data and 80% recovery)–112 (first-order sum of all analytes and 100% recovery); Semi-quantitative range-finding treatments: 5 sample media (2 ultisol soils, 1 alfisol soil, 1 commercial soil, and 1 water); 2 moisture states (moist and saturated); FTP3 and FTP4; 2 FTP dispersion drying temperatures (22 ? and 127 ?); 2 assumed recoveries (80% and 100%) = 30–77; Best composite estimate: 33–112	Abiotic hydrolysis control unexpectedly degraded to form FTOHs roughly at the same rate as soil treatments.
Washington et al. 2015B	A commercial n:2 fluorotelomer acrylate SCFP – FTP3 (unknown)	Abiotic hydrolysis at 25 °C ca. 55 (based on C_8 data) / 89 (based on C_{10} data) at pH = 5–8 34 (based on C_8 data) / 34 (based on C_{10} data) at pH = 9 15 (based on C_8 data) / 18 (based on C_{10} data) at pH = 10 4.9 (based on C_8 data) / 5.1 (based on C_{10} data) at pH = 11 0.7 (based on C_8 data) / 0.66 (based on C_{10} data) at pH = 12	Half-lives for pH>8 not expected to represent common environmental conditions, but these data aid elucidation of hydrolysis mechanism.

* Note that the degradation half-lives here refer to the initial degradation step(s) of cleaving PFAS moieties from the polymer backbone. Additionally, Rankin et al. (2014) studied two non-commercial, custom-synthesized homopolymeric n:2 fluorotelomer acrylate SCFPs and observed degradation half-lives of 8–111 years. It should be noted that the number-average molecular weight in this study were 3000–3800, roughly an order of magnitude less than common commercial acrylate SCFPs.

3.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

As stated above, significant amounts of acrylate and urethane SCFPs, and other PFAS impurities present in the commercial formulations, have been and are released via air, waste water and solid waste along the life cycle of SCFPs: during the application of commercial formulations (e.g., Heydebreck et al., 2016), during the processing of treated materials into articles (e.g., 3M, 1999; Liu et al., 2009, 2014), and during the use and disposal of treated articles (e.g., Freriksson et al., 2020; Schellenberger et al., 2022; van der Veen et al., 2022).

3M estimated that total PFAS losses during surface treatment of uncut fibre, textile or leather raw materials using POSF-based SCFPs and downstream industrial operations (e.g., drying, cutting, shearing, packaging and shipping) could range between 10 and 25 percent (3M, 1999);[35] it is unclear how the reported levels are relevant for the SCFPs and processes being used today.

Further, three studies have investigated the presence of target urethane SCFP compositions in two pre- and post-2002 Scotchgard fabric protection formulations in lake sediment, soil samples, sludge from wastewater treatment plants and landfill leachates (see Table S5) (for more analytical details, see, e.g., Chu and Letcher, 2017). Interestingly, the SCFP compositions could be detected in most of the samples tested, showing that the SCFPs may be directly released and act as a long-term source of perfluoroalkyl acids in the environment. Also, the three studies indicate that sludge can be a main source of at least some SCFPs in the environment, particularly when they are subsequently used as biosolids to treat agricultural land. This is in line with another study investigating releases of SCFP-treated textile fibres during washing, where considerable releases of SCFP-containing fibres were detected in washing and rinsing water (Schellenberger et al., 2022), many of which may then be retained in sewage sludge at wastewater treatment plants (Wu et al. 2021). It was also shown that landfill leachate might not be a significant source of some SCFPs themselves (Fredriksson et al. 2020). Nevertheless, landfill leachates can be a significant source of other non-polymeric PFASs (e.g., Lang et al., 2017; Masoner et al. 2020), which may partially originate from SCFP-related sources.

3.5. Summary of critical knowledge and data gaps

It can be qualitatively concluded that production, use and disposal of acrylate and urethane SCFPs are significant sources of non-polymeric PFASs in the environment, particularly in the long term, as also demonstrated in several simplified modelling simulation studies (Wang et al., 2014B; Wang et al., 2017; Li et al. 2017). This is because of historical and ongoing high production volumes, possible presence of high levels of non-polymeric PFASs in the formulations, ability to degrade and form non-polymeric PFASs in the environment and biota, and multiple release pathways along the life cycle.

However, due to presence of the following critical knowledge and data gaps, it is currently not possible to more precisely estimate the contribution of acrylate and urethane SCFPs to non-polymeric PFASs in the environment: (i) a lack of detailed information on the production and use volumes of individual acrylate and

[35] The levels were calculated using material flow analyses, based on 3M's internal sales data, knowledge of product handling and use practices from field sales and technical personnel, best estimates of end-use applications from known customer activities, and knowledge of worldwide activities (where applicable) by St. Paul-based personnel. Calculation details are provided in the original document submitted to the US EPA, but are to a large extent redacted in the publicly accessible version of the document.

urethane SCFP (with many not reported in the public domain due to confidentiality or no reporting requirements), (ii) a lack of a comprehensive overview of acrylate and urethane SCFPs on the market, particularly in terms of their structural details and thus degradation potential, (iii) a lack of understanding of their fate in municipal waste incinerators.

3.6. Options for a way forward

A better understanding of the production, use and releases of acrylate and urethane SCFPs can inform a better understanding of the sources, human and environmental exposure routes, true environmental and human body burden of PFASs. Thus, it can assist in the identification of possible overlooked hotspots/blindspots, particularly as the current analytical and monitoring capability and capacity of PFASs are limited due to various reasons. Future action may include addressing both existing information and current information gaps. Addressing existing information may include: (i) more in-depth research and analysis of additional information sources such as companies' individual technical handbooks and brochures, SDS and patents, and harmonizing reported structural and use information (in terms of, e.g., the level of details, terminologies, and data format), and (ii) exploring ways to make publicly available the structural and use information that has been reported to regulators, but has not been claimed as confidential business information. Addressing current information gaps may include further research on their fate in municipal waste incinerators.

4 The Life Cycle of Oxetane SCFPs

Chapter summary:

- Limited information is available on the historical and current production of oxetane SCFPs.
- They have been primarily used as wetting, flow and levelling agents in different use areas such as coatings, electronic applications, floor finish, and inks, and some may also be used as reactive intermediates for solvent-based coatings, adhesives, electronics and lubricants.
- Little is known about other PFASs present in commercial oxetane SCFPs, but likely include at least two types of other PFASs: unreacted raw materials and intermediates, and reaction by-products (e.g., cyclic oligomers of the oxetane monomers).
- Also, little is known about the degradability of oxetane SCFPs. On one side, in comparison to the ester bonds in acrylate and urethane SCFPs, the ether bonds (–O–) in oxetane SCFPs are more stable. On the other side, many commercial oxetane SCFPs appear to have lower average molecular weight (e.g., about 1500 Dalton for PolyFox PF-136A, PF-656 and PF-2003), which may indicate higher bioavailability than many commercial acrylate and urethane SCFPs.
- No studies on the releases of oxetane SCFPs and other PFASs present in the formulations were identified. However, it is likely that oxetane SCFPs and other PFASs present in the formulations are released during use (given their use patterns as wetting, flow and levelling agents in open applications such as coatings, floor finish, and inks) and end-of-life treatment.
- Overall, little is known about oxetane SCFPs. Future action may first make the current production and use volumes of oxetane SCFPs publicly available and accessible, and then the priority level of investigating oxetane SCFPs in comparison to other SCFPs can be determined by relevant stakeholders.

4.1. Historical and ongoing production and uses

In comparison to acrylate and urethane SCFPs, limited public information is identified on the production of oxetane SCFPs. A range of PACF-based oxetane SCFPs with varied fluorinated carbon chain lengths have been marketed under the brand name "PolyFox" (see Table S1). At least four of them are registered in the EU under REACH; however, the production/import volumes of three have been claimed as confidential, whereas the production/import volume of one monomer is reported to be ≥1 to <10 tonnes/year (see Table 4.1). The oxetane SCFP monomer[36] has also been registered for production in or import into Japan, Vietnam and the US with unknown amounts (see Table S1).

According to the manufacturer, oxetane SCFPs have been primarily used as wetting, flow and levelling agents in different use areas such as coatings, electronic applications, floor finish, and inks, and some may also be used as reactive intermediates for solvent-based coatings, adhesives, electronics and lubricants (see Table S2).

Table 4.1. Production/import volumes of oxetane SCFPs and monomers in the EU reported in the REACH dossiers. n.d. = no date

CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import volume reported
oxetane SCFPs			
449204-80-2	PACF-derivatives	1	**EU:** confidential (n.d.)
1182261-26-2	PACF-derivatives	1	**EU:** confidential (n.d.)
449204-81-3	PACF-derivatives	2	**EU:** confidential (n.d.)
Oxetane SCFP monomer			
449177-94-0	PACF-derivatives	2	**EU:** =1 to <10 tonnes/year (n.d.)

4.2. Presence of other PFASs in the commercial formulations

From the limited public information identified, at least two types of other PFASs can be present in the commercial formulations: unreacted raw materials and intermediates, and reaction by-products. The former is deduced from Dinglasan-Panlilio and Mabury (2006): the authors detected several FTOHs ($C_nF_{2n+1}CH_2CH_2OH$) – the likely starting materials – in a non-commercialized fluorotelomer-based oxetane SCFP that was specially prepared by the oxetane SCFP manufacturer (who produces commercial oxetane SCFPs from $C_nF_{2n+1}CH_2OH$; Buck et al., 2011).

Reaction by-products have been reported by Wesdemiotis et al. (2006); the authors observed that during the polymerization of an oxetane monomer and other co-monomers/reactants (like other commercial oxetane SCFPs; Kausch et al., 2002), cyclic oligomers of the oxetane monomers were formed in small yields (about 5%), with the tetramer being predominant (at least one order of magnitude more abundant than other oligomers).

Commercial oxetane SCFPs are available both in the form of aqueous dispersion (e.g., PolyFox PF-2003; Synthomer, 2020A) and in pure form (e.g., PolyFox PF-656; Synthomer, 2020B). It is unknown whether

[36] Oxetane (or 1,3-propylene oxide) is a heterocyclic organic compound with the molecular formula C_3H_6O, and has a four-membered ring. Oxetanes are highly reactive as they are strained cyclic ethers, and frequently used as reactive intermediates for further organic molecular synthesis.

the impurities mentioned above would be removed from the commercial products before being put on the market.

4.3. Degradation of oxetane SCFPs during use and after end-of-life

No studies on the degradation of oxetane SCFPs during use and after end-of-life are identified.[37] It is also challenging to theoretically project the degradation behaviour of oxetane SCFPs from the chemical structures. On one side, in comparison to the ester bonds in acrylate and urethane SCFPs (see point A in Figure 3.2), the ether bonds (–O–) in oxetane SCFPs are more stable. On the other side, many commercial oxetane SCFPs appear to have lower average molecular weight (e.g., about 1500 Dalton for PolyFox PF-136A, PF-656 and PF-2003; Synthomer, 2020A,B,C), which may indicate higher bioavailability than many commercial acrylate and urethane SCFPs. Future studies investigating the degradation of oxetane SCFPs during use and after end-of-life are needed.

4.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

No studies on the environmental releases of oxetane SCFPs and other PFASs present in the commercial formulations are identified.[38] However, it is likely oxetane SCFPs and other PFASs present in the commercial formulations are released during use (given their use patterns as wetting, flow and levelling agents in open applications such as coatings, floor finish, and inks) and end-of-life treatment. Future studies investigating their releases during use and after end-of-life and environmental presence are needed.

4.5. Summary and options for a way forward

Overall, little is known about oxetane SCFPs. Future action may first make the current production and use volumes of oxetane SCFPs publicly available and accessible, and then the priority level of investigating oxetane SCFPs in comparison to other SCFPs can be determined by relevant stakeholders.

[37] Google Scholar searches using the combination of keywords “fluoro”, “oxetane”, “polyfox”, “stability”, “degradation”, “thermolysis” and/or “pyrolysis” did not return relevant results.

[38] Google Scholar searches using the combination of keywords “fluoro”, “oxetane”, “polyfox”, “environmental”, “presence”, “occurrence” and/or “release” did not return relevant results.

5 The Life Cycle of Silicone SCFPs

Chapter summary:

- Various silicone SCFPs and monomers, belonging to different categories of PFAS moiety types with varied fluorinated chain lengths, have been and are being produced and used. Ultrashort-chain silicone SCFPs (where fluorinated carbon chain length = 1) have been produced at the scale of tens of thousands tonnes per annum, whereas less is known about longer-chain silicone SCFPs (due to confidentiality, no reporting requirements, etc.).
- Commercial silicone SCFPs are available in a wide range of different forms, including different polymers that are manufactured at the industrial scale, and commercial formulations (e.g., spray) containing monomers of silicone SCFP which can then form silicone SCFPs on the material surface upon application.
- Silicone SCFPs have been used in a wide range of applications, including as surface protectors to treat different materials, in medical applications, in personal care products, as antiformers, as lubricants, and in rubber applications.
- Similar to acrylate, oxetane and urethane SCFPs, at least two types of other PFAS impurities can be found in the silicone SCFPs, at likely significant levels: unreacted raw materials and intermediates, and reaction byproducts. For PFAS silane-based commercial formulations, presence of non-polymeric PFASs on the final treated products depends not only on the compositions in commercial formulations, but also the reactions that take place on the material surface upon application.
- Similar to acrylate and urethane SCFPs, degradation of silicone SCFPs may occur at the side chains and/or at the silicone polymer backbone, thus releasing various PFAS degradation products including cyclic PFAS siloxanes and PFCAs during use and after end-of-life. The dominant degradation half-lives, mechanisms and products depend on the PFAS moieties and conditions. Once released, cyclic PFAS siloxanes can further degrade under different mechanisms, and possibly form highly stable PFCAs as the end products.
- Significant amounts of SCFPs and other PFASs present in the commercial formulations may be and are released from the production, use and disposal, via air, wastewater and solid waste, with elevated levels of ultrashort-chain monomers detected close to the manufacturing sites in China, and in sewage sludge and sediments in several parts of the world.
- Similar to acrylate and urethane SCFPs, given the high production volumes and wide use of silicone SCFPs, possible presence of high levels of other PFASs in the commercial formulations, and their ability to degrade to non-polymeric PFASs including PFCAs, silicone SCFPs are very likely significant sources of non-polymeric PFASs in the environment. Future efforts may collect further information and reduce the uncertainties to reach more precise estimates.

5.1. Historical and ongoing production and uses

Various silicone SCFPs[39] and monomers, belonging to different categories of PFAS moiety types with varied fluorinated chain lengths, have been registered for production/import in many jurisdictions (see Table S1). Table 5.1 summarizes the production/import volumes of various silicone SCFPs and monomers reported in the EU, in the US, and in the Nordic Countries (Denmark, Finland, Norway and/or Sweden). Many are available in large tonnage ranges (e.g., >454 to <4540 tonnes/year), and many others have been claimed as confidential business information and not made public.

Nevertheless, it can be concluded that significant amounts of silicone SCFPs have been and are being produced, from the numbers reported in Table 5.1. Furthermore, in 2016, the total global production of trifluoropropyl-based silicone SCFPs (i.e., fluorinated carbon chain length = 1) was reported to be about 43600 tonnes, with the demand from China being about 3000 tonnes (Xiang et al., 2021).

[39] They are often called “polysiloxanes” in the technical literature.

Table 5.1. Production/import volumes of silicone SCFPs and monomers in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; and in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting); and in the EU reported in the REACH dossiers. t = tonnes; yr = year; n.d. = no date.

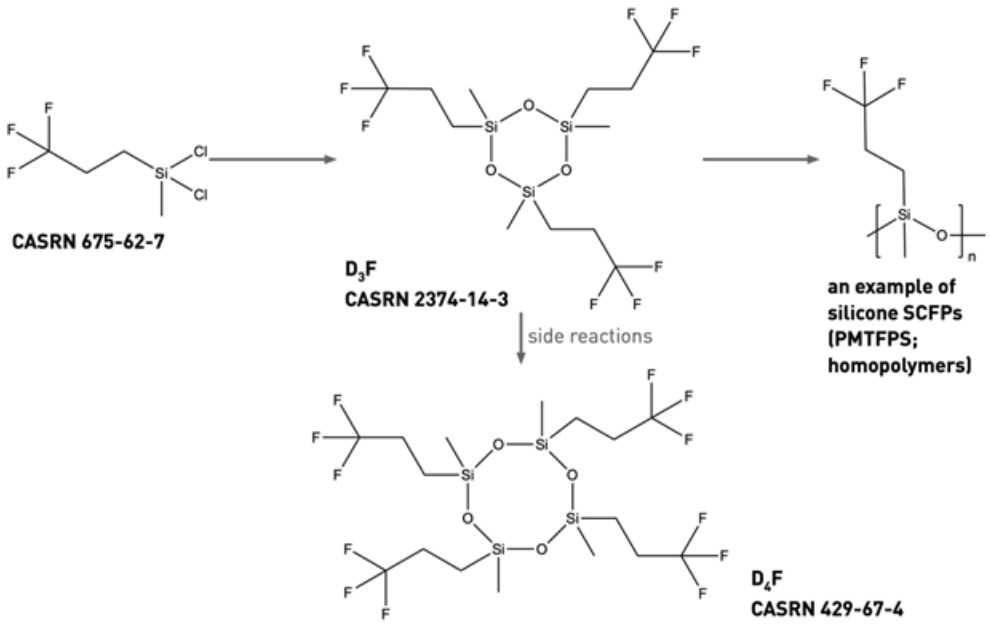
CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import volume reported [tonne; t]
silicone SCFPs			
104780-70-3	n:2 fluorotelomers	6	**SPIN:** confidential (2000–2019)
115340-95-9	n:2 fluorotelomers	6	**SPIN:** confidential (2000–2019)
262292-17-1	n:2 fluorotelomers	6	**SPIN:** confidential (2001–2019)
273737-91-0	n:2 fluorotelomers	6	**SPIN:** 0.3 t + confidential (2007–2019)
125476-71-3	n:2 fluorotelomers	8	**US:** confidential in 2011, <454 t/yr in 2012–2015 **SPIN:** confidential (2013–2019)
143372-54-7	n:2 fluorotelomers	8	**SPIN:** confidential (2000–2019)
146632-08-8	PASF-derivatives	8	**SPIN:** confidential (2001–2017)
162567-79-5	Perfluoroalcohol	8;9;10;11;12;13;14	**SPIN:** confidential (2000–2019)
silicone SCFP monomers			
429-60-7	n:2 fluorotelomers*	1	**SPIN:** confidential (2018–2019)
675-62-7	n:2 fluorotelomers*	1	**EU:** =100 to <1000 t/yr (n.d.) **US:** >454to <4540 t/yr in 1985 and 1989, >227 to <454 t/yr in 1993, >454to <4540 t/yr in 1997, 2001, 2005 and 2011, >454 to <908 t/yr in 2012–2015
2374-14-3	n:2 fluorotelomers*	1	**EU:** =100 to <1000 t/yr (n.d.) **US:** >454 to <4540 t in 1985, >227 to <454 t/yr in 1989 and 1993, >454 to <4540 t/yr in 1997 and 2001, <227 t in 2005, confidential in 2011, >454 to <4540 t/yr in 2012–2015 **SPIN:** confidential (2001–2019)
85877-79-8	n:2 fluorotelomers	4	**EU:** confidential (n.d.)
85857-16-5	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.) **SPIN:** confidential (2017–2019)
51851-37-7	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.) **SPIN:** confidential (2003–2019)
73609-36-6	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.)
78560-45-9	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.)
96383-55-0	n:2 fluorotelomers	6	**EU:** =10 to <100 t/yr (n.d.)
101947-16-4	n:2 fluorotelomers	8	**EU:** confidential (n.d.)
137606-16-7	n:2 fluorotelomers	8	**EU:** confidential (n.d.)
83048-65-1	n:2 fluorotelomers	8	**SPIN:** confidential (2015–2019)
475644-38-3 358750-76-2	PFPEs	Unclear	**EU:** confidential (n.d.)
EC 458-200-2	Unclear	Unclear	**EU:** confidential (n.d.)
EC 429-350-6	Unclear	Unclear	**EU:** confidential (n.d.)
EC 442-180-7	Unclear	Unclear (likely 1)	**EU:** confidential (n.d.)
EC 442-330-1	Unclear	Unclear	**EU:** confidential (n.d.)

* Strictly speaking, these are not n:2 fluorotelomers, as the synthesis of the starting material, trifluoropropene, does not involve fluorotelomerization. Rather, trifluoropropene has been used in telomerization with other telogens/reagents (Boschet et al., 2012). For the purpose of simplification, they are included here in the category of n:2 fluorotelomers.

Commercial silicone SCFPs are available in a wide range of different forms. Industrially, PFAS silanes are first converted into cyclotrisiloxanes, which are then polymerized alone (into high molecular weight polymers, or so-called fluorosilicone gums with about 5000 monomer units), with end-blocking agents (into lower molecular weight polymers, or so-called fluorosilicone fluids/oils; Gelest, n.d.), or with co-monomers (into co-polymers); for an example, see Figure 5.1. The different forms are for different applications. For example, fluid polymers are used as is, or formulated for specific applications. If a reactive end blocking group is incorporated during polymerization, the fluid polymer is then useful for making a coating, a sealant, or a liquid rubber product. Gums can be further processed to produce various rubber products. More details on industrial polymerization of PFAS silanes and subsequent processing can be found in Kirk-Othmer (2006) and Yang et al. (2022).

In addition, commercial products (e.g., sprays) are also available in the form of formulations containing PFAS silane monomers [e.g., $C_nF_{2n+1}CH_2CH_2Si–(R)_3$, R = Cl, OCH_3 or OC_2H_5]. The active terminal groups R attached to silicon in the molecular structures can be easily hydrolysed to form reactive silanol (Si–OH) groups. Upon application, mono, double or triple functional silanol groups can either react with the hydroxyl groups on the material surface (e.g., SiO_2/Si surface) to form siloxane (Si–O–Si) linkages, or form intermolecular polysiloxane network, i.e., silicone SCFPs directly on the material surface (ECHA 2016; Zhu et al. 2019; Adamopoulos et al. 2021).

Figure 5.1. An example of synthesis routes of silicone SCFPs from PFAS silanes and side reactions



Different forms of silicone SCFPs have been used in a wide range of applications, including the following several major use areas (more uses and additional technical details can be found in Kirk-Othmer, 2006). It should be noted that much of the use information reported to the SPIN database has been claimed as confidential business information (see Table S2).

Surface protection

Solutions of silicone SCFPs can be used to impart oil and water repellent finishes to nylon-cotton fabrics (Kirk-Othmer, 2006). Furthermore, as stated above, PFAS-based silanes have been incorporated into commercial/consumer impregnation spray products for surface treatment of a wide range of materials with

non-absorbing surfaces such as stone, glass and enamels and with absorbing surfaces such as leather and textiles, providing water- and oil-repellency (ECHA, 2016). For instance, Dynasylan F 8261 has been used for treatment of automotive glass, coating of float glass, easy-to-clean coatings on ceramics and other silicate substrates including silica, quartz powder, sand, sandstone, cristobalite, wollastonite, mica, kaolin, and talc (ECHA, 2016). Fluowet ETC 100 and ETC 140 (likely fluorotelomer-based) have been specifically marketed for ceramic tiles in kitchens, glass doors of shower cabins, ceramic sanitary ware, wash basins, bath tubs and enamel (ECHA, 2016). Protectosil® Antigraffiti has been applied to surfaces of concrete, brick, concrete masonry units and natural stone to allow easy removal of a wide variety of graffiti (ECHA, 2016). X-Shield FluroSil 100 (likely based on PFAS-based silanes) has been marketed for protection of reinforced concrete structures, e.g., highways, bridge structures, parking decks, commercial buildings, marine structures and industrial facilities (X-Calibur, n.d.). Previously, a perfluorohexanoic acid (PFHxA)-derivative [CASRN 154380-34-4; $CF_3(CF_2)_4CONH(CH_2)_3Si(OCH_3)_3$] was marketed by the then Miteni as a surface treatment for glasses, natural stones, metals, wood, cellulose, cotton, leather and ceramics (Wang et al. 2013).

Medical applications

Different silicone SCFPs are used in many medical applications (Kirk-Othmer, 2006). For example, medical devices such as gastric feeding tubes use silicone SCFP-based rubber balloons for feeding tube retention while resisting gastric fluids. The low permeability of silicone SCFPs versus dimethylsilicone is utilized to control the rate of release in drug devices and in medical tubing to stop the migration of active ingredients into the tubing. Silicone SCFP fluids are used in the treatment of detached retina and other eye diseases. It is reported that from 1982 to 1993, Dow Corning produced polydimethylsiloxane (PDMS) implants with a total content of 2% PMTFPS (Kählig et al., 2009).

Personal care products

Silicone SCFP fluids and copolymers are used in a variety of personal care products, e.g., cosmetic foundations (where silicone SCFPs can provide durable water- and oil-repellency) (Kirk-Othmer, 2006). In addition, the low permeation of silicone SCFPs provides a degree of protection as a hand lotion.

Antifoams

Silicone SCFP fluids and copolymers are effective antifoams in nonaqueous systems (Kirk-Othmer, 2006). Successful application in the petroleum industry allows the full capacity of gas–oil separators to be used on offshore production platforms. Diesel fuels also require fluorosilicone antiforms due to the profoaming nature of dimethylsilicones in nonaqueous systems.

Lubricants

Silicone SCFP fluids are used as lubricants for pumps and compressors in harsh chemical service, such as those using acids, bases, and halogenated compounds and solvents (Kirk-Othmer, 2006). Silicone SCFP fluids are also found in many automotive and aerospace lubrication applications, since they are not easily leached by fuels from mechanical joints (Gelest, n.d.). In addition, silicone SCFPs, particularly the co-polymers, have been employed as lubricants for electrical contacts and precision timing devices (Gelest, n.d.). Greases formulated from silicone SCFPs and solid fluoropolymer thickeners have been used in sealed transmission and other extreme pressure applications (Gelest, n.d.).

Rubber applications

The majority of silicone SCFPs is used in elastomers/rubber applications (Kirk-Othmer, 2006). Silicone SCFP elastomers can be formulated to provide specific durometer (hardness), tear strength, modulus, and solvent resistance properties. It is used as O-rings for fuel lines containing gasoline and aviation fuels, particularly for low temperature sealing.

5.2. Presence of other PFASs in the commercial formulations

Similar to acrylate, oxetane and urethane SCFPs, at least two types of other PFAS impurities can be found in the silicone SCFPs, at likely significant levels (Fei et al., 2014): unreacted raw materials and intermediates (e.g., D_3F is often present as an impurity in PMTFPS; see Figure 5.1), and reaction by-products (e.g., the synthesis of PMTFPS from D_3F could form its other cyclic homologues such as the tetramer homologue–D_4F; see Figure 5.1). The levels of impurities may vary considerably among commercial silicone SCFP products depending on the actual synthesis conditions (Fei et al., 2014) and whether purification process may take place. A market overview could not be found using Google Scholar searches of keywords "PMTFPS", "fluorosilicones", "poly[methyl(3,3,3-trifluoropropyl)siloxane]", "impurities", and/or "residuals".

For PFAS silane-based commercial formulations, presence of non-polymeric PFASs on the final treated products depends not only on the compositions in commercial formulations, but also the reactions that take place on the material surface upon application. For the former, Zhu et al. (2019) investigated several commercial antifingerprint formulations with a focus on fluorotelomer silanes, and detected, in addition to 6:2, 8:2 and 10:2 fluorotelomer silanes as expected, also 7:2 fluorotelomer silanes and perfluorooctyl vinyl ether ($C_8F_{17}OCH{=}CH_2$)[40] in some formulations. The origin of 7:2 fluorotelomer silanes is unclear, whereas perfluorooctyl vinyl ether was likely intentionally added as a co-monomer for generating a highly ordered copolymer thin film (Zhu et al., 2019). Future work may investigate the mass balance of different compositions on the material surface after application.

5.3. Degradation of silicone SCFPs during use and after end-of-life

Similar to acrylate and urethane SCFPs, degradation of silicone SCFPs may occur at the side chains (similarly to point A in Figure 3.2) and/or at the silicone polymer backbone (similarly to point B in Figure 3.2), thus releasing various PFAS degradation products during use and after end-of-life. The dominant degradation half-lives, mechanisms and products depend on the PFAS moieties and conditions.

- Degradation of anti-sticking layers based on Optool DSX [$R–(CF_2CF_2CF_2O)_n–Si(OCH_3)_3$] and F_{13}-TMS [$C_6F_{13}CH_2CH_2–Si(OCH_3)_3$] in UV nanoimprint lithography was observed during use and at the side chains (Truffier-Boutry et al., 2010).
- PMTFPS products suffer from poor thermal stability and tend to degrade when exposed to temperatures over 200 ℃ for extend periods of time, with cyclic siloxanes such as D_3F and D_4F being the primary products (You et al., 2020). When thermolysis was carried out at a relatively high temperature (600 ℃), an additional decomposition product, trifluoropropene, was observed (You et al., 2020). Such thermolysis mechanisms, i.e., re-arrangement of the silicone backbone (causing

[40] In this case, the unique formula $[C_{10}H_4F_{17}O]^+$ was assigned within the mass error of 5 ppm, which was tentatively identified as perfluorooctyl vinyl ether through database search (e.g., PubChem CID 54096250).

formation of D_3F and D_4F in the example) and removal of the side chains (causing formation of trifluoropropene in the example), might occur for other silicone SCFPs as well, though possibly at different temperatures and with different yields.

- Photodegradation of the self-assembled monolayer derived from a 8:2 fluorotelomer silane [$C_8F_{17}CH_2CH_2Si(OCH_3)_3$], which contained likely 8:2 fluorotelomer silicone SCFP, was observed after UV–visible light exposure. After a 10-day exposure, the authors observed the formation of PFCAs (a mean molar yield of 0.2%), 8:2 fluorotelomer carboxylic acid (8:2 FTCA; a mean molar yield of 0.06%) and 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA; a mean molar yield of 0.009%) (Zhu et al., 2019). However, the study did not investigate the degradation mechanisms.

Once released, PFAS cyclic siloxanes can further degrade under different mechanisms, and possibly form highly stable PFCAs as the end products.

- They may undergo hydrolysis, and yield various transformation products including homologues (e.g., $D_3F \rightarrow D_4F$) and breakdown products [e.g., D_3F and $D_4F \rightarrow CF_3(CH_2)_2MeSi(OH)_2$] (Zhi et al., 2018). Zhi et al. (2018) further reported that under the laboratory conditions, the hydrolysis half-lives of D_3F and D_4F at different pH values (5.2, 6.4, 7.2, 8.3, and 9.2) varied from 80.6−154 h and from 267−533 h, respectively.
- They may also undergo biodegradation, e.g., in sludges. Their biodegradation half-lives are likely longer than their hydrolysis half-lives, with one study reported 41.1 d for D_3F and about 55 days for D_4F (Huang et al., 2020). The same authors also reported, from the degradation of D_3F and D_4F, the formation of $CF_3(CH_2)_2MeSi(OH)_2$ (similarly to hydrolysis) and $MeSi(OH)_3$ (which was not observed in the hydrolysis study by Zhi et al., 2018). The latter means that PFAS moieties were released, which may be further transformed into highly stable of PFCAs; a recent study shows that n:2 fluorotelomer silanes [e.g., $C_8F_{17}CH_2CH_2Si(OCH_3)_3$] can be easily oxidized to corresponding PFCAs using the total oxidizable precursor assay (Zhu et al., 2019).

5.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

Given the high levels of historical and ongoing production as well as the myriad of uses, significant amounts of silicone SCFPs and other PFASs present in the commercial formulations are expected to have been released from production, use and disposal, via air, wastewater and solid waste. For example, Zhi et al. (2018) reported elevated levels of D_3F and D_4F in surface water (up to 291 ng/L for D_3F and up to 168 ng/L for D_4F) and sediment (up to 5478 ng/g for D_3F and up to 6277 ng/g for D_4F) near a fluorinated methylsiloxane manufacturing plant in Weihai, China. In addition, both Truffier-Boutry et al. (2010) and Zhu et al. (2019) provide evidence of significant levels of non-polymeric PFASs present in the silicone SCFP layer after applying PFAS silanes, which can be released during use and disposal. Furthermore, van Bavel et al. (2016) detected D_3F and D_4F in the leachates from the ISI and Lindum landfills in Norway, showing releases from solid waste treatment.

Several other studies have also detected elevated levels of D_3F and/or D_4F in the sewage sludge from Sweden and sediment from some lakes in Sweden and Norway (McLachlan et al., 2014), in the effluents of two WWTPs in Norway (van Bavel et al., 2016), and in about 20% of the sludge samples from 29 WWTPs at 25 cities distributed over seven geographic regions of China (Huang et al., 2020). These studies did not report the likely sources of these observations.

5.5. Summary and options for a way forward

Silicone SCFPs share many similarities to acrylate and urethane SCFPs. They are likely significant sources of non-polymeric PFASs in the environment, particularly in the long term because their high production volumes and wide use, possible presence of high levels of non-polymeric PFASs in the formulations, ability to degrade and form non-polymeric PFASs in the environment and biota, and multiple release pathways along the life cycle. Also, due to the presence of many critical knowledge and data gaps such as on the production volumes, use patterns, levels of other non-polymeric PFAS impurities in the formulations, and degradation potential, it is currently not possible to more precisely estimate the contribution of silicone SCFPs to non-polymeric PFASs in the environment.

A better understanding of the production, use and releases of silicone SCFPs can better inform the sources, human and environmental exposure routes, true environmental and human body burden of PFASs. Thus, it can assist in the identification of possible overlooked hotspots/blindspots. Future action may include addressing both existing information and current information gaps. Addressing existing information may include the following activities: (i) more in-depth research and analysis of additional information sources such as companies' individual technical handbooks and brochures, SDS and patents, (ii) harmonizing reported structural and use information to the same level, and (iii) exploring ways to make public available the structural and use information that has been reported to regulators but has not been claimed as confidential business information. Addressing current information gaps may include further research on their material flows and degradation behaviour.

6 The Life Cycle of Ethoxylate SCFPs

Chapter summary:

- Limited information is available on the production of ethoxylate SCFPs, with several that may have been produced up to hundreds of tonnes per annum.
- Ethoxylate SCFPs have mainly been used as surfactants/surface active agents in industrial processing, commercial applications and consumer uses. Some ethoxylate SCFPs may also be used to treat certain material surfaces (e.g., glasses) to impart water- and oil-repellency.
- Significant presence of unreacted residuals (up to 4%) has been reported in fluorotelomer- and PASF-based ethoxylate SCFPs.
- The ethoxy part in ethoxylate SCFPs can likely undergo biotic degradation and release the PFAS moieties over time.
- The use pattern of ethoxylate SCFPs will likely result in (uncontrolled) releases of the ethoxylate SCFPs themselves, other PFASs present in the commercial formulations, and their degradation products into the environment during use and after disposal, via air, wastewater, landfill leachates, etc.
- Future action may look into the current production and use volumes of ethoxylate SCFPs, as well as longer-term degradation behaviour, and thus provide a better understanding of PFASs releases from the production, use and disposal of ethoxylate SCFPs.

6.1. Historical and ongoing production and uses

Limited information on the historical and ongoing production of ethoxylate SCFPs was identified in the national/regional chemical inventories. Reporting to the US EPA by manufacturers/importers via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act is summarized in Table 6.1. In addition, at least 12 ethoxylate SCFPs were identified on the SPIN database, but their production or import volumes (and uses) have been mostly claimed as confidential business information and thus sealed from the public. For more details, see Table S1, Table S2, and the corresponding entries in the national/regional chemical inventories.

Table 6.1. Production/import volumes of ethoxylate SCFPs in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; and in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting). t = tonnes; yr = year.

CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import volume reported
68298-79-3	PASF-derivatives	4	**SPIN:** confidential (2000–2011)
68298-80-6	PASF-derivatives	5	**SPIN:** confidential (2000–2011)
56372-23-7	PASF-derivatives	6	**SPIN:** confidential (2000–2011)
68298-81-7	PASF-derivatives	7	**SPIN:** confidential (2000–2011)
68958-60-1	PASF-derivatives	7	**SPIN:** confidential (2000–2006)
68958-61-2	PASF-derivatives	8	**US:** >4.54 to <227 t in 2001* **SPIN:** confidential (2000–2006)
29117-08-6	PASF-derivatives	8	**US:** >4.54 to <227 t in 2001* **SPIN:** confidential (2000–2011)
52550-44-4	n:2 fluorotelomers	6	**SPIN:** confidential (2013–2019)
65545-80-4	n:2 fluorotelomers	6;8;10;12;14;16**	**US:** >4.54 to <227 t in 2001, >11.3 to <45.4 t/yr in 2012–2015 **SPIN:** confidential (2000–2019)
200013-65-6	PFPEs	unclear	**US:** <454 t/yr in 2012–2015 **SPIN:** confidential (2015–2017)
162492-15-1 1000390-73-7	PFPEs	Unclear	**SPIN:** confidential (2008–2019)
56467-05-1	Perfluoroalcohol	6	**SPIN:** confidential (2000–2006, 2017)

* According to another reporting by 3M to the US EPA, it produced >10.6 tonnes of CASRN 68958-60-1 and about 10–30 tonnes of CASRN 29117-08-6 in the US in 1997 (US EPA Administrative Record 226, #580, #582, and #600).
** The fluorinated carbon chain length of CASRN 65545-80-4 is retrieved from the SDS of DuPont's Zonyl FSN fluorosurfactant (e.g., https://www.yumpu.com/en/document/view/10055541/zonyl-fsn-fluorosurfactant-msds-dupont) and the patent US 8367756 B2 (https://patentimages.storage.googleapis.com/88/07/2a/6fc07e409a037c/US8367756.pdf).

On the use side, more information is available, showing a wide range of use areas for ethoxylate SCFPs, particularly as surfactants/surface active agents in industrial processing, commercial applications and consumer uses. For example, Zonyl FSO-100 (CASRN 122525-99-9) is described as a non-ionic surfactant able to impart low aqueous surface tensions at low concentrations, and thus has been incorporated into applications such as caulks, paints, coatings and adhesives (Dinglasan-Panlilio and Mabury, 2006). Similar surfactant use has also been reported for other PASF-, fluorotelomer- and PFPE-base ethoxylate SCFPs, though in some cases incorporated into formulations for broader application areas including ink, oil and gas drilling, soap and cleaning products, automotive care products, lubricants, food packaging (e.g., CASRN 200013-65-6) and fire-fighting foam agents (e.g., CASRN 65545-80-4). For more details, see Table S2.

In a recent study, fluorotelomer-based ethoxylate SCFPs have also been detected as the major fluorinated components in several anti-fog sprays and cloths purchased from Amazon.com (Herkert et al. 2022). This is in line with 3M's reporting that PASF-based ethoxylate SCFPs were "used as received or diluted with water or butyl acetate to impart soil or water repellency to surfaces (including printed circuit boards or photographic film)" (3M, 1999). 3M also reported that some formulators used PASF-based ethoxylate SCFPs as a thickener to aqueous coatings used to protect tile, marble and concrete.

6.2. Presence of other PFASs in the commercial formulations

Significant presence of unreacted residuals (i.e., n:2 FTOHs) in two commercial fluorotelomer-based ethoxylate SCFPs has been reported (see Table S3): Zonyl FSO 100 contained 6:2, 8:2 and 10:2 FTOHs (1.03% of dry weight; Dinglasan and Mabury, 2006), and Zonyl FSH contained 6:2 FTOH (0.54%) and 8:2 FTOH (0.29%) (Frömel and Knepper, 2010).[41] These levels are also in line with recent measurements of 6:2 FTOH in two anti-fog sprays primarily based on 6:2 fluorotelomer-based ethoxylate SCFP formulations (Herkert et al. 2022).[42] Further, 3M reported that PASF-based ethoxylate SCFPs typically contained 4% or less PFAS residuals (3M, 1999). Due to the high volatility of FTOHs, they may be released during the production, use and disposal of commercial ethoxylate SCFPs. Similar levels of unreacted residuals might be expected to be present in other commercial ethoxylate SCFPs unless they were purified.

6.3. Degradation of SCFPs during use and after end-of-life

The ethoxy part in ethoxylate SCFPs can likely undergo biotic degradation and release the PFAS moieties over time, as concluded by an assessment of Capstone FS-30–a n:2 fluorotelomer-based ethoxylate SCFP–by NICNAS that "over time, the notified polymer is expected to ultimately degrade into perfluorohexanoic acid (PFHxA)" (NICNAS, 2018). However, such degradation may take a long time and thus ethoxylate SCFPs themselves may be persistent in the environment. For example, Frömel and Knepper (2010) studied biodegradation of a n:2 fluorotelomer-based ethoxylate SCFP. The authors observed that the alcohol group at one end of the polymer chain can be oxidized and form a carboxylic group, i.e., $C_nF_{2n+1}CH_2CH_2(OCH_2CH_2)_mOH \rightarrow C_nF_{2n+1}CH_2CH_2(OCH_2CH_2)_{m-1}OCH_2COOH$. The authors further hypothesized that the ether bond can be cleaved, as observed for non-fluorinated ethoxylate polymers, and such chain-shortening continues until the ethoxylate SCFP is transformed to the corresponding n:2 FTOHs, which are precursors to PFCAs. The authors noticed that the ethoxylates did not further degrade once the chain length was shortened to a certain degree (where $m < 9$), but the authors noted the limited testing time period (48 days) might be too short to observe full transformation. In another biodegradation study of $C_9F_{19}CH_2CH_2O(CH_2CH_2O)_nH$ following the OECD guideline 301C, the ethoxy unit profile hardly changed during the 28-day test (Yamamoto et al., 2014).

6.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

The use pattern of ethoxylate SCFPs (see Section 5.1 above) will likely result in (uncontrolled) releases of the ethoxylate SCFPs themselves, other PFASs present in the commercial formulations, and their degradation products into the environment during use and after disposal, via air, wastewater, landfill

[41] The results from the two studies cannot be directly compared due to the use of different methods.

[42] The authors also screened for 4:2, 8:2, 10:2, 12:2, 14:2 and 16:2 FTOHs in all sampled anti-fog spray and cloth products, but did not detect them in any of the products except one (this specific product is likely based on an old formulation, with 8:2 and 10:2 fluorotelomers being the dominant species).

Furthermore, the authors also tested another two anti-fog sprays and reported higher levels of 6:2 FTOH, up to ca. 40%; however, in these two products, 6:2 FTOH and 6:2 fluorotelomer ethoxylates could explain only ca. 60% of the total organic fluorine. It is likely that other 6:2 fluorotelomer-based substances were added in the two anti-fog sprays, interfering the data interpretation. Therefore, the levels of 6:2 FTOH in these two anti-fog sprays are not considered in the comparison here.

leachates, etc. For example, the presence of a fluorotelomer-based ethoxylate SCFP [$C_9F_{19}CH_2CH_2O(CH_2CH_2O)_nH$] in the leachates from a disposal facility located in the Kansai area in 2010 was reported by Yamamoto et al. (2014).

6.5. Summary and options for a way forward

Their historical and current production and use volumes, as well as degradation half-lives, are key parameters that need to be improved in order to better understand the contribution of ethoxylate SCFPs to PFASs in the environment.

7 Conclusions

Compared to many non-polymeric PFAS, SCFPs and their known and unknown degradation products have received comparatively little attention from scientists and regulators, despite their manifold industrial uses and high volumes, their propensity to release non-polymeric PFAS, and their potential environmental and health impacts.

Overall, a wide range of information on the chemical identities of SCFPs, other PFASs present therein, historical and ongoing production and use, degradation of SCFPs, and release of SCFPs and associated non-polymeric PFASs is identified in the public domain and has been synthesized in this report.

Despite the many knowledge and data gaps identified in the respective chapters above, the following can be concluded from the information synthesized here: A wide range of SCFPs have been produced and used in many different applications, with at least some SCFPs at high volumes (up to tens of thousands of tonnes/year); as a comparison, 3M reported that its estimated global production of POSF-derivatives for fire-fighting foams was about 150 tonnes in 2000 (3M, 2000). Many non-polymeric PFASs may be present in the commercial SCFP formulations, sometimes at percentage levels. During the production, use and disposal of SCFPs and SCFP-treated products, substantial amounts of SCFPs and associated non-polymeric PFASs may have been released. It is well expected that SCFPs can degrade and form non-polymeric PFASs, including PFCAs and/or PFSAs, in the environment and biota. Thus, many SCFPs are acting as long-term significant sources to the global burden of non-polymeric PFASs including PFCAs and PFSAs.

Therefore, concerted action by all stakeholders is needed to address SCFPs in an efficient and effective manner. This includes identifying, making funding available and conducting research on those critical knowledge and data gaps that are most relevant for soundly regulating/managing SCFPs in different jurisdictions, building on the gaps identified in the respective chapters above. When addressing critical knowledge and data gaps, to increase efficiency, the following concerted action may be taken: (i) investigating additional information that is available in SDSs and patents (but was not actively searched and considered in this analysis due to time and resource constraints[43]); (ii) working with manufacturers to enable open access to information that has been generated by them (and made available to specific regulators), but has not been made publicly available; and (iii) regularly gathering newly available public information and synthesizing them to further increase the knowledge base on SCFPs.

In parallel to action on critical knowledge and data gaps, concerted action may be taken to develop, facilitate and promote national and international stewardship programmes and regulatory approaches to reduce emissions of SCFPs and related PFASs and to work toward global elimination, where appropriate and technically feasible.

[43] It should also be noted that SDS often contain inaccurate or missing information; and the listed chemical(s) could be found at higher concentrations than what the SDS listed. Thus, the information would need to be evaluated during review.

References

3M (1999). *Fluorochemical Use, Distribution and Release Overview*. US EPA Administrative Record (AR)226-0550.

3M (2000). *Re: Phase-out Plan for POSF-Based Products.* US EPA Administrative Record (AR)226-0600.

3M (2018). *Safety Data Sheet: Scotchgard™ Fabric Protector (Cat. No. 4101, 4106).* https://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSuUn_zu8l00xMx_14x2GOv70k17zHvu9lxtD7SSSSSS-- (last accessed on 25 April 2022)

Adamopoulos, F. G., Vouvoudi, E. C., Achilias, D. S. & Karapanagiotis, I. Fluorosilane Water-Repellent Coating for the Protection of Marble, Wood and Other Materials. *Heritage* **4,** 2668–2675 (2021).

Banks, R. E., Smart, B. E., Tatlow, J. C. (1994). *Organofluorine Chemistry: Principles and Commercial Applications*. Springer New York, NY. http://doi.org/10.1007/978-1-4899-1202-2

Blumenthal, J., Diamond, M. L., Hoffmann, M. & Wang, Z. Time to Break the “Lock-In” Impediments to Chemicals Management. *Environ Sci Technol* **56,** 3863–3870 (2022).

Boschet, F., Kostov, G., Ameduri, B., Jackson, A. & Boutevin, B. Synthesis of 3,3,3-trifluoropropene telomers and their modification into fluorosurfactants. *Polym Chem-uk* **3,** 217–223 (2011).

Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., Voogt, P. de, Jensen, A. A., Kannan, K., Mabury, S. A. & Leeuwen, S. P. van. Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integr Environ Asses* **7,** 513–541 (2011).

Chu, S. & Letcher, R. J. In Vitro Metabolic Formation of Perfluoroalkyl Sulfonamides from Copolymer Surfactants of Pre- and Post-2002 Scotchgard Fabric Protector Products. *Environ Sci Technol* **48,** 6184–6191 (2014).

Chu, S. & Letcher, R. J. Side-chain fluorinated polymer surfactants in aquatic sediment and biosolid-augmented agricultural soil from the Great Lakes basin of North America. *Sci Total Environ* **607,** 262–270 (2017).

Dinglasan-Panlilio, M. J. A. & Mabury, S. A. Significant Residual Fluorinated Alcohols Present in Various Fluorinated Materials. *Environ Sci Technol* **40,** 1447–1453 (2006).

ECHA (2016). *Annex XV Report. Proposal for a Restriction. Substance Names: (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyle)silanetriol and any of its mono-, di- or tri-O-(alkyl)*

derivatives. https://echa.europa.eu/documents/10162/113d1f03-c74b-96c1-0a41-76805decf289 (last accessed on 25 April 2022)

Evich, M. G., Davis, M. J. B., McCord, J. P., Acrey, B., Awkerman, J. A., Knappe, D. R. U., Lindstrom, A. B., Speth, T. F., Tebes-Stevens, C., Strynar, M. J., Wang, Z., Weber, E. J., Henderson, W. M. & Washington, J. W. Per- and polyfluoroalkyl substances in the environment. *Science* **375,** eabg9065 (2022).

Fei, H.-F., Xie, W., Wang, Q., Gao, X., Hu, T., Zhang, Z. & Xie, Z. Controlled synthesis and characterization of poly[methyl(3,3,3-trifluoropropyl)siloxane] with selective end groups. *Rsc Adv* **4,** 56279–56287 (2014).

Fiedler, H., Kennedy, T. & Henry, B. J. A Critical Review of a Recommended Analytical and Classification Approach for Organic Fluorinated Compounds with an Emphasis on Per- and Polyfluoroalkyl Substances. *Integr Environ Asses* **17,** 331–351 (2021).

Fredriksson, F., Eriksson, U., Kärrman, A. & Yeung, L. (2020). *A Pilot Study oft he Fluorinated Ingredient of Scotchgard Products and Their Levels in WWTP Sludge and Landfill Leachate from Sweden.* http://www.diva-portal.org/smash/get/diva2:1432762/FULLTEXT01.pdf (last accessed on 25 April 2022)

Freilich, J. & Ouellette, L. L. Science fiction: Fictitious experiments in patents. *Science* **364,** 1036–1037 (2019).

Frömel, T. & Knepper, T. P. Fluorotelomer ethoxylates: Sources of highly fluorinated environmental contaminants part I: Biotransformation. *Chemosphere* **80,** 1387–1392 (2010).

Gelest (n.d.) *Technical Library - Fluorosilicone Fluids.* https://technical.gelest.com/brochures/silicone-fluids/fluorosilicone-fluids/ (last accessed on 25 April 2022)

Herkert, N. J., Kassotis, C. D., Zhang, S., Han, Y., Pulikkal, V. F., Sun, M., Ferguson, P. L. & Stapleton, H. M. Characterization of Per- and Polyfluorinated Alkyl Substances Present in Commercial Anti-fog Products and Their In Vitro Adipogenic Activity. *Environ Sci Technol* **56,** 1162–1173 (2022).

Heydebreck, F., Tang, J., Xie, Z. & Ebinghaus, R. Emissions of Per- and Polyfluoroalkyl Substances in a Textile Manufacturing Plant in China and Their Relevance for Workers' Exposure. *Environ Sci Technol* **50,** 10386–10396 (2016).

Huang, Z., Xiang, X., Xu, L. & Cai, Y. Phenylmethylsiloxanes and trifluoropropylmethylsiloxanes in municipal sludges from wastewater treatment plants in China: Their distribution, degradation and risk assessment. *Water Res* **185,** 116224 (2020).

Kabadi, S. V., Fisher, J. W., Doerge, D. R., Mehta, D., Aungst, J. & Rice P. Characterizing biopersistence potential of the metabolite 5:3 fluorotelomer carboxylic acid after repeated oral exposure to the 6:2 fluorotelomer alcohol. *Toxicol Appl Pharmacol* **388,** 114878 (2020).

Kählig, H., Zöllner, P. & Mayer-Helm, B. X. Characterization of degradation products of poly[(3,3,3-trifluoropropyl)methylsiloxane] by nuclear magnetic resonance spectroscopy, mass spectrometry and gas chromatography. *Polym Degrad Stabil* **94,** 1254–1260 (2009).

Kausch, C. M., Leising, J. E., Medsker, R. E., Russell, V. M., Thomas, R. R. & Malik, A. A. Synthesis, Characterization, and Unusual Surface Activity of a Series of Novel Architecture, Water-Dispersible Poly(fluorooxetane)s. *Langmuir* **18,** 5933–5938 (2002).

Kirk-Othmer (2006). *Kirk-Othmer Encyclopedia of Chemical Technology, Volumen 20, 5th Edition*. Published by Wiley. ISBN: 978-0-471-48503-2

Lang, J. R., Allred, B. M., Field, J. A., Levis, J. M. & Barlaz M. A. National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Lanfill Leachate. *Environ Sci Technol* **51,** 2197–2205 (2017).

Larsen, B. S., Stchur, P., Szostek, B., Bachmura, S. F., Rowand, R. C., Prickett, K. B., Korzeniowski, S. H. & Buck, R. C. Method development for the determination of residual fluorotelomer raw materials and perflurooctanoate in fluorotelomer-based products by gas chromatography and liquid chromatography mass spectrometry. *Journal of chromatography A* **1110,** 117–124 (2006).

Letcher, R. J., Chu, S. & Smyth, S.-A. Side-chain fluorinated polymer surfactants in biosolids from wastewater treatment plants. *J Hazard Mater* **388,** 122044 (2020).

Li, L., Liu, J., Hu, J. & Wania, F. Degradation of Fluorotelomer-Based Polymers Contributes to the Global Occurrence of Fluorotelomer Alcohol and Perfluoroalkyl Carboxylates: A Combined Dynamic Substance Flow and Environmental Fate Modeling Analysis. *Environ Sci Technol* **51,** 4461–4470 (2017).

Liu, J. & Avendaño, S. M. Microbial degradation of polyfluoroalkyl chemicals in the environment: A review. *Environ Int* **61,** 98–114 (2013).

Liu, X., Krebs, K., Guo, Z. & Roache, N. Method development for liquid chromatographic/triple quadrupole mass spectrometric analysis of trace level perfluorocarboxylic acids in articles of commerce. *Journal of chromatography A* **1216,** 3910–3918 (2009).

Liu, X., Guo, Z., Krebs, K. A., Pope, R. H. & Roache, N. F. Concentrations and trends of perfluorinated chemicals in potential indoor sources from 2007 through 2011 in the US. *Chemosphere* **98,** 51–57 (2014).

Masoner, J. R., Kolpin, D. W., Cozzarelli, I. M., Smalling, K. L., Bolyard, S. C., Field, J. A., Furlong, E. T., Gray, J. L., Lozinski, D., Reinhart, D., Rodowa, A. & Bradley, P. M. Landfill Leachate Contributes Per-/Poly-Fluoroalkyl Substances (PFAS) and Pharmaceuticals to Municipal Wastewater. *Environ Sci Water Res Technol* **6,** 1300–1311 (2020).

McLachlan, M. S., Kierkegaard, A., Radke, M., Sobek, A., Malmvärn, A., Alsberg, T., Arnot, J. A., Brown, T. N., Wania, F., Breivik, K. & Xu, S. Using Model-Based Screening to Help Discover Unknown Environmental Contaminants. *Environ Sci Technol* **48,** 7264–7271 (2014).

Ng, C., Cousins, I. T., DeWitt, J. C., Glüge, J., Goldenman, G., Herzke, D., Lohmann, R., Miller, M., Patton, S., Scheringer, M., Trier, X. & Wang, Z. Addressing Urgent Questions for PFAS in the 21st Century. *Environ Sci Technol* **55,** 12755–12765 (2021).

NICNAS (2018). *Public Report – Polyfluorinated Polymer in Capstone® FS-30.* File No: EX/211 (STD/1409). https://www.industrialchemicals.gov.au/sites/default/files/EX211%20Public%20Report%20PDF.pdf (last accessed on 25 April 2022)

Nørgaard, A. W., Larsen, S. T., Hammer, M., Poulsen, S. S., Jensen, K. A., Nielsen, G. D. & Wolkoff, P. Lung Damage in Mice after Inhalation of Nanofilm Spray Products: The Role of Perfluorination and Free Hydroxyl Groups. *Toxicol Sci* **116,** 216–224 (2010).

Nørgaard, A. W., Hansen, J. S., Sørli, J. B., Levin, M., Wolkoff, P., Nielsen, G. D. & Larsen, S. T. Pulmonary Toxicity of Perfluorinated Silane-Based Nanofilm Spray Products: Solvent Dependency. *Toxicol Sci* **137,** 179–188 (2014).

OECD (2020). *PFASs and Alternatives in Food Packaging (Paper and Paperboard): Report on the Commercial Availability and Current Uses*. Series on Risk Management No. 58 https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/PFASs-and-alternatives-in-food-packaging-paper-and-paperboard.pdf (last accessed on 25 April 2022)

OECD (2021). *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance.* Series on Risk Management No. 61 (ENV/CBC/MONO(2021)25). https://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV/CBC/MONO(2021)25&docLanguage=En (last accessed on 25 April 2022)

POPRC (2022). *Updated indicative list of substances covered by the listings of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds (UNEP/POPS/POPRC.17/INF/14/Rev.1).* http://www.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC17/Overview/tabid/8900 (last accessed on 25 April 2022)

Rankin, K., Lee, H., Tseng, P. J. & Mabury, S. A. Investigating the Biodegradability of a Fluorotelomer-Based Acrylate Polymer in a Soil–Plant Microcosm by Indirect and Direct Analysis. *Environ Sci Technol* **48,** 12783–12790 (2014).

Rice, P. A., Aungst, J., Cooper, J., Bandele, O. & Kabadi, S. V. Comparative Analysis of the Toxicological Databases for 6:2 Fluorotelomer Alcohol (6:2 FTOH) and Perfluorohexanoic Acid (PFHxA). *Food Chem Toxicol.* **138,** 111210 (2020).

Russell, M. H., Berti, W. R., Szostek, B. & Buck, R. C. Investigation of the Biodegradation Potential of a Fluoroacrylate Polymer Product in Aerobic Soils. *Environ Sci Technol* **42,** 800–807 (2008).

Russell, M. H., Berti, W. R., Szostek, B., Wang, N. & Buck, R. C. Evaluation of PFO formation from the biodegradation of a fluorotelomer-based urethane polymer product in aerobic soils. *Polymer Degradation and Stability* **95,** 79–85 (2010).

Schellenberger, S., Liagkouridis, I., Awad, R., Khan, S., Plassmann, M., Peters, G., Benskin, J. P. & Cousins, I. T. An Outdoor Aging Study to Investigate the Release of Per- And Polyfluoroalkyl Substances (PFAS) from Functional Textiles. *Environ Sci Technol* **56,** 3471–3479 (2022).

Shirai, T., Fukumoto, H., Kanno, Y., Kubota, T. & Agou, T. Synthesis, structure, and surface properties of Poly(meth)acrylates bearing a vinylene-bridged fluoroalkyl side chain. *Polymer* **217,** 123478 (2021).

Sigma (n.d.). *SIGMA AFFF.* https://www.quimicasigma.com/pdf/MSDS_SIGMA_AFFF.pdf (last accessed on 25 April 2022)

Solberg (n.d.). *Sicherheitsdatenblatt Solberg 1X3 ATC 1%-3%.* https://www.solbergfoam.com/getattachment/978a72c6-2a5a-4bc4-92c1-ca004de055af/SDS_1X3_ATC_Safety-Data_DE.aspx (last accessed on 25 April 2022)

Solvay, n.d. *Fluorolink® for Low Surface Energy Coatings.* https://www.acota.co.uk/wp-content/uploads/2018/11/Solvay-SpP-Fluorolink-Presentation.pdf (last accessed on 25 April 2022)

SPIN, (n.d.). *SPIN: Substances in Preparations in Nordic Countries*. http://www.spin2000.net/spinmyphp/ (last accessed on 25 April 2022)

Stockholm Convention (2019). *The new POPs under the Stockholm Convention*. http://www.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511 (last accessed on 25 April 2022)

Synthomer. (2020A). *Technical Data Sheet: Polyfox™ PF-2003.* https://www.synthomer.com/fileadmin/files/tds/POLYFOX%20PF-2003.pdf (last accessed on 25 April 2022)

Synthomer. (2020B). *Technical Data Sheet: Polyfox™ PF-656.* https://www.synthomer.com/fileadmin/files/tds/POLYFOX%20PF-656.pdf (last accessed on 25 April 2022)

Synthomer. (2020C). *Technical Data Sheet: Polyfox™ PF-136A.* https://www.synthomer.com/fileadmin/files/tds/POLYFOX%20PF-136A.pdf (last accessed on 25 April 2022)

Truffier-Boutry, D., Beaurain, A., Galand, R., Pelissier, B., Boussey, J. & Zelsmann, M. XPS study of the degradation mechanism of fluorinated anti-sticking treatments used in UV nanoimprint lithography. *Microelectron Eng* **87,** 122–124 (2010).

Uehara, T., Matsuda, M., Enomoto, T. (2021). *Pulp Molded Product and Method for Manufacturing Same.* United States Patent Application Publication US 2021/0054569 A1. https://patentimages.storage.googleapis.com/6a/55/a6/576d5de4c33551/US20210054569A1.pdf (last accessed on 25 April 2022)

US EPA (2016). *Access CDR Data – 2016 CDR Data.* https://www.epa.gov/chemical-data-reporting/access-cdr-data (last accessed on 25 April 2022)

US EPA (n.d.). *Fact Sheet: 2010/2015 PFOA Stewardship Program.* https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program#how (last accessed on 25 April 2022)

US FDA (n.d.) *Authorized Uses of PFAS in Food Contact Applications.* https://www.fda.gov/food/chemical-contaminants-food/authorized-uses-pfas-food-contact-applications (last accessed on 25 April 2022)

van Bavel, B., Thomas, K. V., Langford, K., Reid, M., Vogelsang, C., Øxnevad, S., Bæk, K., Fjeld, E., Brooks, S., Schlabach, M., Rostkowski, P., Warner, N., Borgen, A., Halse, A. K., Davanger, K. & Gundersen, H. (2016). *Screening Programme 2015: Benzothiazoles, Siloxanes, Pigments & PBT Compounds.* https://www.miljodirektoratet.no/globalassets/publikasjoner/m596/m596.pdf (last accessed on 25 April 2022)

van der Veen, I., Schellenberger, S., Hanning, A.-C., Stare, A., Boer, J. de, Weiss, J. M. & Leonards, P. E. G. Fate of Per- and Polyfluoroalkyl Substances from Durable Water-Repellent Clothing during Use. *Environ Sci Technol* (2022). doi:10.1021/acs.est.1c07876

Wang, Z., Cousins, I. T., Scheringer, M. & Hungerbühler, K. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. *Environ Int* **60,** 242–248 (2013).

Wang, Z., Cousins, I. T., Scheringer, M., Buck, R. C. & Hungerbühler, K. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ Int* **70,** 62–75 (2014A).

Wang, Z., Cousins, I. T., Scheringer, M., Buck, R. C. & Hungerbühler, K. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, part II: The remaining pieces of the puzzle. *Environ Int* **69,** 166–176 (2014B).

Wang, Z., Boucher, J. M., Scheringer, M., Cousins, I. T. & Hungerbühler, K. Toward a Comprehensive Global Emission Inventory of C4–C10 Perfluoroalkanesulfonic Acids (PFSAs) and Related Precursors: Focus on the Life Cycle of C8-Based Products and Ongoing Industrial Transition. *Environ Sci Technol* **51,** 4482–4493 (2017).

Wang, Z., Wiesinger, H. & Groh, K. Time to Reveal Chemical Identities of Polymers and UVCBs. *Environ Sci Technol* **55,** 14473–14476 (2021).

Washington, J. W., Ellington, J. J., Jenkins, T. M., Evans, J. J., Yoo, H. & Hafner, S. C. Degradability of an Acrylate-Linked, Fluorotelomer Polymer in Soil. *Environ Sci Technol* **43,** 6617–6623 (2009).

Washington, J. W., Naile, J. E., Jenkins, T. M. & Lynch, D. G. Characterizing Fluorotelomer and Polyfluoroalkyl Substances in New and Aged Fluorotelomer-Based Polymers for Degradation Studies with GC/MS and LC/MS/MS. *Environ Sci Technol* **48,** 5762–5769 (2014).

Washington, J. W., Jenkins, T. M., Rankin, K. & Naile, J. E. Decades-Scale Degradation of Commercial, Side-Chain, Fluorotelomer-Based Polymers in Soils and Water. *Environ Sci Technol* **49,** 915–923 (2015A).

Washington, J. W. & Jenkins, T. M. Abiotic Hydrolysis of Fluorotelomer-Based Polymers as a Source of Perfluorocarboxylates at the Global Scale. *Environ Sci Technol* **49,** 14129–14135 (2015B).

Wesdemiotis, C., Pingitore, F., Polce, M. J., Russell, V. M., Kim, Y., Kausch, C. M., Connors, T. H., Medsker, R. E. & Thomas, R. R. Characterization of a Poly(fluorooxetane) and Poly(fluorooxetane-c o-THF) by MALDI Mass Spectrometry, Size Exclusion Chromatography, and NMR Spectroscopy. *Macromolecules* **39,** 8369–8378 (2006).

Wu, M., Tang, W., Wu, S., Liu, H. & Yang, C. Fate and effects of microplastics in wastewater treatment processes. *Sci Total Environ* **757,** 143902 (2020).

X-Calibur (n.d.). *Technical Data Sheet – X-shield FluroSil 100*. https://www.x-calibur.us/datasheets/coating-systems/chloride_ingress_and_carbonation_protection/X-Shield_FluroSil_100.html (last accessed on 25 April 2022)

Xiang, X., Liu, N., Xu, L. & Cai, Y. Review of recent findings on occurrence and fates of siloxanes in environmental compartments. *Ecotox Environ Safe* **224,** 112631 (2021).

Yamada, T., Taylor, P. H., Buck, R. C., Kaiser, M. A. & Giraud, R. J. Thermal degradation of fluorotelomer treated articles and related materials. *Chemosphere* **61,** 974–984 (2005).

Yamamoto, A., Hisatomi, H., Ando, T., Takemine, S., Terao, T., Tojo, T., Yagi, M., Ono, D., Kawasaki, H. & Arakawa, R. Use of high-resolution mass spectrometry to identify precursors and biodegradation products of perfluorinated and polyfluorinated compounds in end-user products. *Anal Bioanal Chem* **406,** 4745–4755 (2014).

Yang, Z., Bai, Y., Meng, L., Wang, Y., Pang, A., Guo, X., Xiao, J. & Li, W. A Review of Poly[(3,3,3-trifluoropropyl)methylsiloxane]: Synthesis, Properties and Applications. *Eur Polym J* **163,** 110903 (2021).

You, Y., Chen, J., Zheng, A., Wei, D., Xu, X. & Guan, Y. Effect of silanol on the thermal stability of poly[methyl(trifluoropropyl)siloxane]. *J Appl Polym Sci* **137,** 49347 (2020).

Young, C. J. & Mabury, S. A. Atmospheric Perfluorinated Acid Precursors: Chemistry, Occurrence, and Impacts. *Review of Environmental Contamination and Toxicology* **208,** 1–109 (2010).

Zhi, L., Xu, L., Qu, Y., Zhang, C., Cao, D. & Cai, Y. Identification and Elimination of Fluorinated Methylsiloxanes in Environmental Matrices near a Manufacturing Plant in Eastern China. *Environ Sci Technol* **52,** 12235–12243 (2018).

Zhu, B., Jiang, W., Wang, W., Lin, Y., Ruan, T. & Jiang, G. Occurrence and Degradation Potential of Fluoroalkylsilane Substances as Precursors of Perfluoroalkyl Carboxylic Acids. *Environ Sci Technol* **53,** 4823–4831 (2019).

This report provides an overview of existing scientific and technical information on side-chain fluorinated polymers (SCFPs), focusing on their identities and life cycle, and with a particular goal to map the existing landscape and highlight critical knowledge and data gaps.

It focuses on the life cycle of SCFPs, including production and use, presence of other PFASs in the commercial formulations, degradation of SCFPs during use and end-of-life treatment, and environmental releases of SCFPs and other PFASs present in the commercial formulations.

The report comes with a separate Annex comprising five spreadsheets providing information on: substances identities, use information, PFAS-impurity studies, degradation studies and SCFP release.

oe.cd/pfass



SUMMARY OF THE PTFE STUDIES PERFORMED WITH INDEPENDENT LABORATORIES TO INVESTIGATE PERSISTENCE, DEGRADATION, TRANSFORMATION TO OR RELEASE OF SUBSTANCES OF CONCERN

Background

Polytetrafluoroethylene, PTFE (CAS no. 9002-84-0) is a polymer of tetrafluoroethylene. PTFE comes in three forms: granular (the highest volume used globally; made without polymerization aids), aqueous dispersion (made with polymerization aids), fine powder (per ASTM D4895; made with polymerization aids). There are many textbooks and peer-reviewed publications on the properties of PTFE and how to manufacture and process it.

The form of PTFE used in W. L. Gore & Associates products is fine powder PTFE meeting the ASTM D4895-18 standard and the OECD criteria for Polymer of Low Concern. The ASTM standard covers dry-powder resins of PTFE produced from aqueous dispersion. The specification states that the resin shall be uniform and shall contain no additives or foreign material and that the color shall be natural white. The specification does not include mixtures of PTFE with additives such as colors, fillers, or plasticizers, reprocessed or reground resin or any fabricated articles because the properties or such materials have been irreversibly changed when they were fibrillated or sintered. 100% of the PTFE used by Gore meets this ASTM 4895 standard. This is critical to point out because it limits the substances that may leach from the polymer into the environment or living organisms.

Given the extreme durability/persistence of PTFE and interest in what, if anything leaches from the fluoropolymer into biota or the environment, this body of work was undertaken with independent contract laboratories to investigate degradation, release or transformation and leachability of substances of concern into media that may be potential routes of exposure: air, water, and soil. The following studies were performed at the Charles River Labs in Den Bosch, the Netherlands. Standard OECD (and US EPA) efate protocols were used. Studies were performed under Good Laboratory Practices. They were performed to investigate if persistence implies future degradation, release, or transformation into a continuous source of substances of concern. The plan to conduct these studies as well as the results have been shared at scientific meetings including SETAC (NA and EU), FLUOROS Global 2021, and Emerging Contaminants.

Studies to Address Potential Partitioning to Water

OED 105 Water Solubility

Soluble substances may contaminate drinking, surface and ground water and move with the water. Results of this study were that PTFE was insoluble in water.

Ready Biodegradation OECD 301B

This is a biotic stability test which looks for biodegradability within 28 days. PTFE was determined not to be biodegradable.

Inherent Biodegradation OECD 302C

This is a biotic stability test for biodegradability. PTFE was determined not to be biodegradable in this test.

These data confirm the low probability of water exposure to PTFE, degradants or leachables.

Studies to Address Potential Partitioning to Soil

Molecular Weight OECD 118

This test was performed to determine if low molecular weight fractions are available for migration out of the polymer, and, if the polymer is bioavailable. Molecular weights above 1,000 Da do not pass through the cell membrane and are considered not to be bioavailable or, therefore, bioaccumulative. PTFE was determined not to be sufficiently soluble for gel permeation chromatography even after sonication and stirring for 19 hours in tetrahydrofuran, dichloromethane, dimethylformamide, or dimethyacetamide. Using alternative methods of standard specific gravity and melt flow rheology, the molecular weight was determined to be above 500,000 Da.

Soil Adsorption OECD 106
This study was performed to determine the likelihood of the substance partitioning to soil and/or to the sediment. Results of this study are still pending.

Phototransformation on Soil Surfaces OECD draft document
This is an abiotic stability test for degradation in sunlight on soil surfaces. Results of this study are still pending.

Based on the high molecular weight, no partitioning to soil is anticipated.

Studies to Address Potential Partitioning to Air

Molecular Weight OECD 118
See above.

Vapor Pressure OECD 104
This study was performed because volatility helps predict the likelihood of partitioning to air and long-range transport potential. The vapor pressure was determined to be very low less than 1 x 10-10 mm Hg @ 20°C.

Melting Temperature OECD 102
Performance of the melting temperature supports thermal stability at environmentally relevant temperatures. The melt transition was around 350°C. No further melting or decomposition occurred at less than 400°C.

Thermal Stability OECD 113
This test is for degradation from heat at environmentally relevant temperatures. No decomposition or chemical reaction was observed at less than 150°C.

Thermal Gravimetric Analysis
This is a method of thermal analysis where mass is measured over time as the temperature changes and mass is lost to the air. No observable weight loss below 549°C, however at 549°C a 5% weight loss was observed.

This data supports the lack of inhalation exposure potential at environmentally relevant temperatures.

Leaching Potential

Because there were no OECD guidelines specifically addressing the potential of a polymer to leach substances under environmental conditions, a first tier leaching potential test, Toxicity Characteristic Leaching Potential (US EPA SW-846 Test Method 1311), was performed by ALS Laboratories in Kelso, Washington (USA). This test has historically been used by EPA to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. This TCLP test generate a leachate in a lab setting designed to simulate landfill conditions to evaluate potential environmental impact from uncontrolled land disposal.

Tier 1: Toxicity Characteristic Leaching Potential EPA SW-846 Test Method 1311
100 grams of each of two PTFE fine powder samples were tumbled, in 5.7 ml of glacial acetic acid per 1 liter of reagent water, at room temperature for 18-20 hours at 30 rpm, before being filtered using a borosilicate glass fiber filter with a 0.6 to 0.8 µm pore size. 100 ml of the extraction fluid was then extracted in 60 ml of dichloromethane for approximately 3 hours at room temperature. The extracts were analyzed by GC/MS for this list of EPA analytes. The TCLP test was passed.

Conclusions from the Charles River Laboratory and ALS studies

These results support the stability of PTFE and lack of transformation to other PFAS, such as perfluoroalkyl acids. PTFE will not partition to air, water, or soil. Potential inhalation, oral or dermal exposure to PTFE for biota or the environment is unlikely based on this data.

Dr. Barbara Henry
January 2022

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FIGURE 1 100-foot diameter shop fabricated PTFE secondary containment liner ready for final QC and packaging.



Contamination from a leaking geomembrane—A necessary and imminent evil?

Using an inert geomembrane solution with 100% PTFE material is one possibility.

By John Tippett, P.E., and Michael Goard, P.Eng.

One major purpose of a geomembrane in many lining applications around the world is to prevent the contamination of groundwater (water below the ground that can affect rivers, lakes, oceans and drinking water sources) by the chemicals contained above the geomembrane. Geomembranes have other purposes, but maintaining clean and healthy drinking water is likely the most important one.

For many geomembrane materials, a 10- or 20-year warranty is typical. With the concept of long-term sustainability being ever-present in every facet of life and industry, can owners and operators realistically afford to think in terms of geomembrane barriers that will degrade and leak due to corrosion? Should a geomembrane be considered "successful" if contamination of groundwater occurs after the warranty period?

Recent evolution within the last decade of material science allows us to consider inert geomembrane materials. An inert geomembrane material is a barrier that is unaffected by any chemical, regardless of time. By using an inert geomembrane material, "lifetime" containment and indefinite protection of groundwater can be considered a realistic target. Certainly, if the bar is set higher and the overall target to prevent contamination is "lifetime" containment rather than "warranty-life" containment, the higher expectation will ultimately result in a cleaner world.

The corrosion variable

In any containment application using a polymeric geomembrane liner, numerous variables present design challenges. The recent paper "Protecting the Environment from Contamination with Barrier Systems: Advances and Challenges" (Rowe, Jefferis, et al. 2022) highlights the complexities involved in the design of containment systems and the selection of a liner material. Tensile/tear/puncture/burst strength, temperature

PROJECT HIGHLIGHTS

400 DEGREES "HOT TANK" ABOVE GROUND STORAGE TANK SECONDARY CONTAINMENT

OWNER
Refinery in Canada

LOCATION
Alberta, Canada

CONTRACTOR
Terrafix Geosynthetics Inc.

CONSTRUCTION COMPANY
Cyntech Construction

ENGINEERS
Cyntech Construction

GEO PRODUCT
Everliner 2130

GEO MANUFACTURER
Textiles Coated International (TCI)

John Tippett, P.E. holds a degree in chemical engineering from Dartmouth College and is CEO of Textiles Coated International (TCI), a world leading manufacturer of fluoropolymer films and related products based in Manchester, N.H.

Michael Goard, P.Eng. holds a degree in civil engineering from McGill University and is a product manager who has worked in the manufacturing of industrial products and materials for over 25 years. He is based near Montreal, Quebec, Canada.

resistance, thermal stability characteristics, chemical resistance, UV resistance, seam strength, permeability, coefficient of friction and many other properties may need to be taken into consideration. This article explores how this task can be simplified by removing one of the most important and potentially less predictable variables: corrosion.

John Scheirs' 2020 webinar and document on the "Periodic Table of Geomembranes" illustrates the wide range of available materials to select from. Each has its advantages and disadvantages, but each also has some susceptibility to corrosion—except one category.

Many geomembrane materials contain additives that help provide or enhance needed properties like UV protection and crack resistance. While the base material may be suitable for the foreseen conditions, these antioxidants/plasticizers/stabilizers can be subject to chemical attack or degradation.

Inert liners eliminate the corrosion variable

Different geomembrane materials can be selected to guard against corrosion, depending on the expected chemical exposure. During the early design phase, it is critical to know what chemicals the liner will be expected to be exposed to and therefore to resist. A material selection can then be made, and clear instructions/directives for its use can be established and provided to the user. During the entire life of the liner, it is then critical to ensure that only the chemicals the liner was designed to contain are what the liner ends up being exposed to. While every attempt can be made to predict what will be put into a landfill or containment area, there is always a risk that something unforeseen may be introduced.

There are situations when exposure to certain amounts of a particular chemical is expected. One such challenging industrial process, the Bayer Process for manufacturing alumina (and ultimately aluminum metal), results in bauxite residue with an average pH of 11 (pH range of 9–13). With such severe alkaline exposure, an inert liner is a necessity to avoid long-term contamination. Clearly, this is an industrial case where a typical high-density polyethylene (HDPE) liner will not be a long-term barrier to leakage due to corrosion.

There are also unexpected results that can lead to entirely unpredicted concentrations of chemicals. Most, if not all, geomembrane applications are susceptible to combinations of chemistry, temperature and/or moisture. Chemistry can change over time as the contained materials decompose and mix with each other. As the biodegradation takes place, heat may result, thus hastening the degradation of a geomembrane. As moisture gets introduced, new chemicals may result from the new molecules that have formed as the result of biodegradation. Geomembrane materials with an inability to handle the full pH range of 0–14 are ill-equipped to survive a witch's brew scenario in a challenging landfill with many variables.

There are many items considered household hazardous waste (HHW) that are not permitted in landfills. These include paints, solvents, bleach, batteries, household cleaners, glue and adhesives, electronics, oil mixtures, etc. Many of the HHW items are extreme pH products that are incompatible with geomembrane materials. Given the extensive list of HHW products used in the typical household, it is not hard to conceive that even households with the best intentions put extreme pH products into their garbage.

Should the world rely upon perfect behavior of household and business disposal practices or is it safer to assume bad behavior and noncompliance? From a long-term safety perspective, assuming good behavior over bad behavior results in failure. Systems must be designed around bad behavior to provide an indefinite safety sustainability. The same is true for geomembrane systems. The geomembrane material should be

compatible to the full pH range of 0–14 in case bad behavior persists, and extreme pH products enter landfills.

Inert liners are made from materials that will not corrode regardless of the chemical exposure. PTFE is an example of an inert material. PTFE will not corrode when exposed to virtually any known chemical, and it is compatible to the full pH range of 0–14. Selecting such an inert material simply removes one of the most critical variables, corrosion, from the equation. The consideration of compatibility to chemicals for PTFE is an easy one, as the table below reflects.

Reduce the number of different materials—additives and reinforcements

Many geomembrane materials contain additives that help provide or enhance needed properties like UV protection and crack resistance. While the base material may be suitable for the foreseen conditions, these antioxidants/plasticizers/stabilizers can be subject to chemical attack or degradation, thereby leading to losses in the desired properties over time. In some cases, these additives may migrate to the surface of the material and become a contaminant.

This is another aspect that introduces a variable into the effective life span of a liner. How long will the additive remain functional? If both the geomembrane base material and the additives sustaining the life of the geomembrane are not fully inert materials, two corrosion variables must be considered instead of one.

One plus one does not equal two when combining an inert material with a chemically susceptible material.



FIGURE 2 Shop fabricated PTFE liner accordion folded and ready for shipment and rapid deployment at site.

CHEMICAL	PVC-EIA	HDPE	PVDF	PTFE
Acetic acid (50%)	Chemically attacked	Chemically resistant	Chemically resistant	Chemically resistant
Acetone	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Ammonium hydroxide	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Benzene	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant
Diesel	Chemically resistant	Chemically attacked	Chemically resistant	Chemically resistant
Ethyl acetate	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Furfural	Chemically attacked	Chemically resistant	Chemically resistant	Chemically resistant
Gasoline	Chemically resistant	Chemically attacked	Chemically resistant	Chemically resistant
Methyl ethyl ketone	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Methyl isoamyl ketone	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Nitric acid (50%)	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant
Perchloroethylene	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant
Phenol	Chemically attacked	Chemically resistant	Chemically resistant	Chemically resistant
Sulphuric acid	Chemically attacked	Chemically resistant	Chemically attacked	Chemically resistant
Toluene	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant
Xylene	Chemically attacked	Chemically attacked	Chemically resistant	Chemically resistant

TABLE 1

Consistent with ordinary geomembrane installation, the geosynthetic instal… established … target seam… temperature, …peed and pressure appropriate for the geomembrane material and ambient weather conditions.

NEW PQ

Until recently, the only way to realistically employ a fluoropolymer like PTFE, with its extreme corrosion resistance and high temperature capability, was by using it in combination with other materials that compensate for certain properties, like strength.

Supported geomembrane materials may have improved tensile strength, owing to a reinforcement (scrim) that is incorporated into the material. In applications where high strength is paramount, this reinforcement can give the material the necessary property. A weakness of scrim-reinforced material can occur if the scrim becomes subject to degradation due to corrosion. While the scrim is intact, it gives the material the strength it is intended to provide. However, the scrim can be chemically attacked at discontinuities such as seams. At every seam, there is a likely interruption in the protection of the scrim by the base material. Exposure to corrosive chemicals at the exposed edges will lead to corrosion of the reinforcement and loss of the property it is there to provide—strength.

A general way of thinking about it is that if all the strength of a material comes from a component that can be chemically degraded in time, then the geomembrane will have a regression of strength over the years that eventually leads to failure/leakage. The strength of the liner must come from inert material that will not weaken over time due to chemical exposure. Using a material that never weakens from chemical exposure eliminates the corrosion variable and prevents the strength of the geomembrane from regressing toward zero, which may result in leakage.

By combining an inert material with a chemically susceptible material, chemical attack can still occur. The corrosion variable must still be considered. But by simply using an inert material, chemical attack cannot happen. The corrosion variable no longer needs to be considered. Further, by joining or seaming one inert material with another, the concern for edge exposure at a seam is eliminated. This is also true for repairs or patches that may be required on-site if damage occurs.

100% PTFE—Nothing else

One possibility for an inert geomembrane solution is a 100% PTFE material. PTFE is one of the family of fluoropolymers, well known in many industrial applications for their amazing chemical resistance and high temperature properties. Because the geomembrane is inert across the pH scale of 0–14, the corrosion variable is eliminated with PTFE. Even with long-term severe chemical exposure, the properties of PTFEs will not change.

In addition, the temperature range of PTFE of -400°F to 600°F (-240°C to 316°C) eliminates concern for geomembrane failure due to significant excursion temperature situations. Even the biodegradation temperature of 149°F (65°C), which can often be found in a landfill, does not get anywhere near the maximum temperature capability of an all-PTFE material.

Ultraviolet exposure is also a major cause of destruction of geomembranes. An inert liner will be one that is unaffected by severe and continuous exposure to sunlight.

Equal or better in terms of other properties

Testing done by ExcelPlas Polymer Testing demonstrates that multilayer, laminated PTFE has:

- Better/comparable tear strength to that of HDPE
- Significantly better puncture resistance than HDPE

- Significantly better flex fatigue resistance than HDPE and linear low-density polyethylene (LLDPE)

For any application where the tear, puncture and flex fatigue characteristics of HDPE meet the requirements, one can be confident that PTFE will meet them as well. See **Table 2**.

Fatigue Resistance per AS 4878.9–2001 Results Summary	
SAMPLE ID	**CYCLES UNTIL FAILURE**
Cross-laminated PTFE 1.5mm	5,390,648 (No Failure Observed)
HDPE 1.5mm	105,366

Excelplas Polymer Analysis

TABLE 2

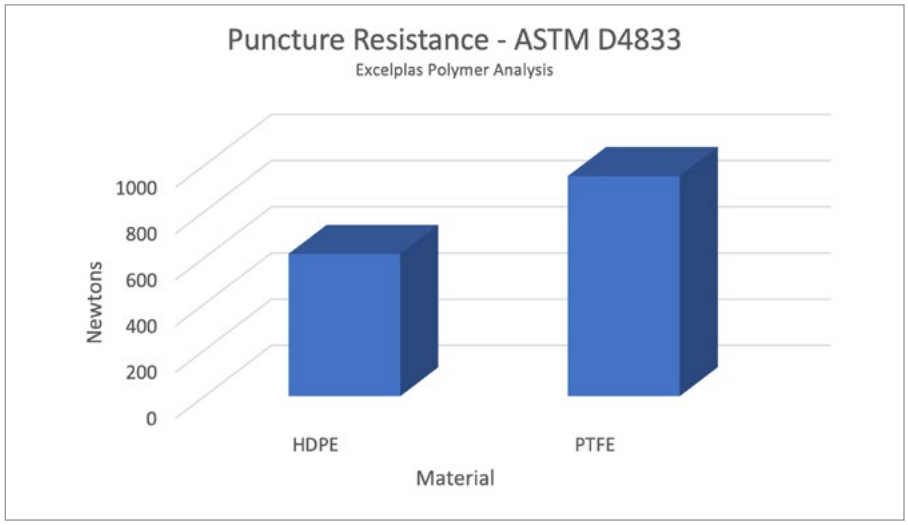


FIGURE 3

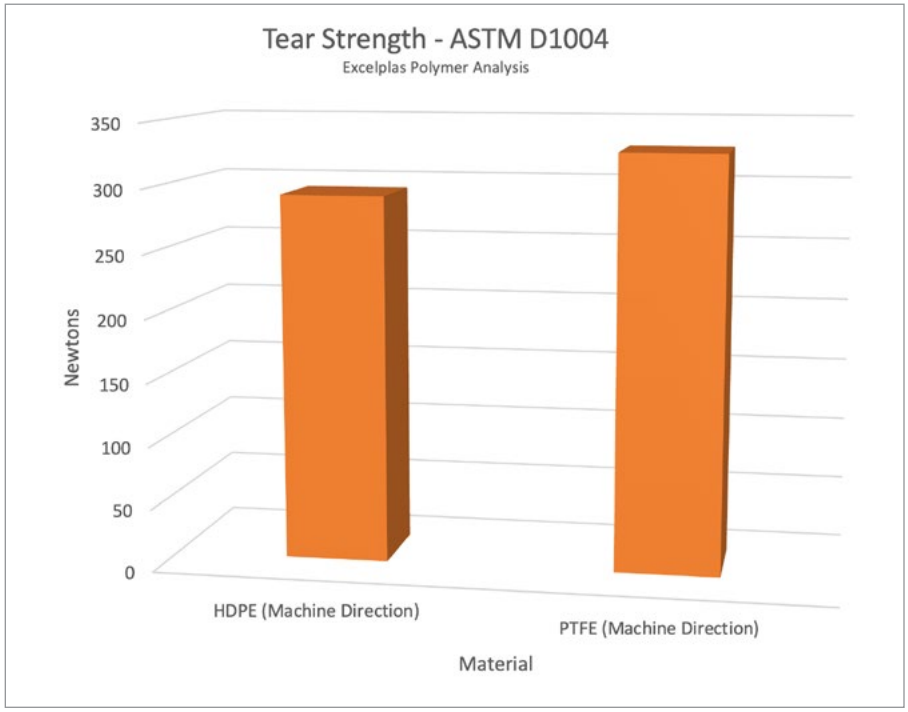


FIGURE 4

Conclusion

Contamination of rivers, lakes, oceans and drinking water sources should not occur in the future due to corrosion of geomembranes. The job of installing a geomembrane system without leaks is a challenging one with many design considerations.

Furthermore, the absence of the corrosion variable sets the bar much higher for the geomembrane industry. Instead of discussing a potential life for a geomembrane in terms of years or decades, the industry can start focusing on design consideration to achieve "forever" containment using inert materials. In the past, "forever" could not be a realistic target when using materials susceptible to corrosion. But the use of inert materials eliminates corrosion and makes "forever" a realistic target; certainly, rivers, lakes, oceans, drinking water sources and future generations deserve this inspirational target.

References

Rowe, R. K., Jefferis, S., et al. (2022). "Protecting the environment from contamination with barrier systems: Advances and challenges." Proc., 20th International Conf. on Soil Mechanics and Geotechnical Engineering, Australian Geomechanics Society, Sydney, Australia.

Scheirs, J. (2020). "Periodic table of geomembranes." Webinar, May 26, ExcelPlas Materials Testing.

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UPDATE

Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers under Representative European Municipal Waste Combustor Conditions

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Significance and Motivation

A recent study by Conversio, a consultancy based in Germany, has shown that at its end-of-life approximately 85% of all fluoropolymers end up in waste-to-energy recovery incinerators. A subsequent question of regulators was: Do fluoropolymers get fully incinerated without any formation of short chain or long chain PFAS? A recent project executed by the Karlsruhe Institute of Technology (KIT) in cooperation with Société Générale de Surveillance (SGS) was conducted to assess the same.

Experimental Parameters

Main applications of the four highest volume fluoropolymers (PTFE, PVDF, PFA and FKM) representing more than 80% of commercial fluoropolymer production based on data from Pro-K (German association of polymers processors) were considered. Post-use samples from these applications were incinerated as a mixture under standard operating conditions for municipal and industrial waste incineration. Figure 1 presents the experimental conditions. Experiments were conducted under two sets of conditions over a period of 9 days. The first experiments were conducted at a process setting of 860°C and 2.0 s residence time. These experiments were conducted in three stages. Initially, background tests were performed using natural gas and 100 kg/h wood chips. This was followed by the same fuel conditions with the addition of 320 g/h of fluoropolymer. The final test involved switching back to background conditions. The duration of each of these tests ranged from 9 – 13 hrs. A second set of experiments was conducted at a process setting of 1100°C and 2.0 s residence time. These tests were conducted in the same sequence as the first set of tests. The feed rates for the wood chips and the fluoropolymer mixture were identical to the tests at 860°C and 2.0 s residence time. The test duration for this second set of tests also ranged from 9 – 13 hrs.

test	parameters	number of HF and PFAS sampling	locations	duration [hrs]	RUN	date / remarks		day
start-up with natural gas and oil				24		25.2.23; 10 a.m.	day 1 and 2	
starting solid feeding (wood chips)				24		26.2.23; 10 a.m.		
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips	T_{PCC}: 860 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	1	27.2.2023; 9 am	day 3	Monday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	2	28.2.2023; 9 am	day 4	Tuesday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouropolymers in the evening		
		3		11	3	01.03.2023; 9 am	day 5	Wednesday
Change of temperature post combustion chamber				12		over night		
background of rotary kiln / combustion chamber with oil, natural gas and wood chips	T_{PCC}: 1100 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	4	02.03.2023; 9 am	day 6	Thursday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	5	03.03.2023; 9 am	day 7	Friday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouropolymers in the evening		
		3		11	6	04.03.2023; 9 am	day 8	Saturday
shut down				24			day 9	

Material	Mass fraction [wt.-%]
PTFE tubes	63,00
PTFE tape	7,00
PVDF	18,00
PFA	6,00
FKM rubber	6,00

mass flow = 320 g/h

Figure 1: Experimental setup

The fluoropolymers were fed as a mixture at relative proportions that correspond to the mass fractions sold in the European marketplace. These data are also shown in Figure 1. Suspension and emulsion polymerized PTFE application samples represented about 70 mass percent of the fluoropolymer feed rate.

The main operational parameters for the two sets of tests are summarized in Figure 2. The temperature of the flue gas outlet exiting the rotary kiln was in the range of 800-900°C. The temperature of the flue gas post-combustion chamber outlet was very close to the targets for these tests (860°and 1100°C in the combustion chamber for setting 1 and 2, respectively). The O_2 and CO measurements for setting 1 and 2 varied somewhat. For setting 1, the values were 11.2 vol % dry and 0.2 mg/m^3, respectively, while for setting 2 the O_2 measurements were somewhat lower (7.0 % with an increase in the CO concentration (1.2 mg/m^3). The water vapor concentration as measured in the boiler exit ranged from 6.2% in setting 1 to 8.49% in setting 2.

			setting S1	setting S2
		unit	RUN 1, 2, 3	RUN 4, 5, 6
Rotary kiln	mass flow wood chips	kg/h	98	98
	main air	m_N^3/h	418	423
	mass flow heating oil	kg/h	61	46
	volume flow natural gas	m_N^3/h	4	4
	volume flow combustion air	m_N^3/h	872	753
	inclination	°	2	
	rotation speed	rev p.m.	0.2	0.4
	temperature flue gas outlet	°C	800 - 900	
	thermal power	MW	1.1	0.9
combustion chamber	volume flow natural gas to burner D4.1	m_N^3/h	22	35
	sum of volume flow combustion air to burner D4.1	m_N^3/h	671	429
	volume flow natural gas to burner D4.2	m_N^3/h	22	35
	sum of volume flow combustion air to burner D4.2	m_N^3/h	671	428
	residence time	s	2	
	temperature flue gas post-combustion chamber outlet (with control)	°C	860	1095
	CO (level E2)	mg/m^3	0.2	1.2
	O_2 (level E2)	Vol.-% dry	11.2	7.0
	thermal power	MW	0.46	0.72
	total thermal power rotary kiln and post combustion chamber	MW	1.59	1.67
boiler / fluegas	volume flow	m_N^3/h	3958	3238
	O_2	Vol.-% dry	11.9	9.0
	CO	mg/m^3	1.35	1.64
	water vapour	Vol.-% wet	6.20	8.49

Figure 2: Main operational parameters at two experiments

There were multiple sampling locations for this study. Flue gas was sampled near the exit of the combustion chamber (location 1), at the exit of the boiler (location 2), and at the entrance to the stack (location 3), while liquids and residues were also sampled and analyzed after each RUN (see Figure 3, Test facility sampling locations).

The test facility BRENDA comprises a rotary kiln with a post-combustion chamber, a boiler for heat recovery and a flue gas cleaning system, which complies with German emission regulations (17 BImschV). The thermal power of the rotary kiln is of maximum 1.5 MW, while that of the post-combustion chamber is about 1 MW, which results in a total thermal output of BRENDA of maximum 2.5 MW.

The fluoropolymers mixture after blending with wood chips and consequent weighing was delivered to the rotary kiln. To secure optimal combustion conditions, natural gas and heating oil were supplied additionally to the rotary kiln, while the post combustion chamber was supplied with natural gas only.

The mass flow of the fluoropolymers mixture was set at 320 g/h, which corresponds to a pure Fluorine mass flow of 230 g/h. This level increases the fluoropolymer ratio to fuel, while at the same time keeps the Fluor-concentration below the total halogen limit of 1%, as set by the legislature.

The combustion gases of the rotary kiln enter the post combustion chamber (PCC). It contains two natural gas burners staggered in an antiparallel manner, with a slight shift to each other. The temperature and the residence time in PCC were adjusted mainly with the help of the above mentioned burners, supported by a slight shift of about 200 kW into the post combustion chamber.

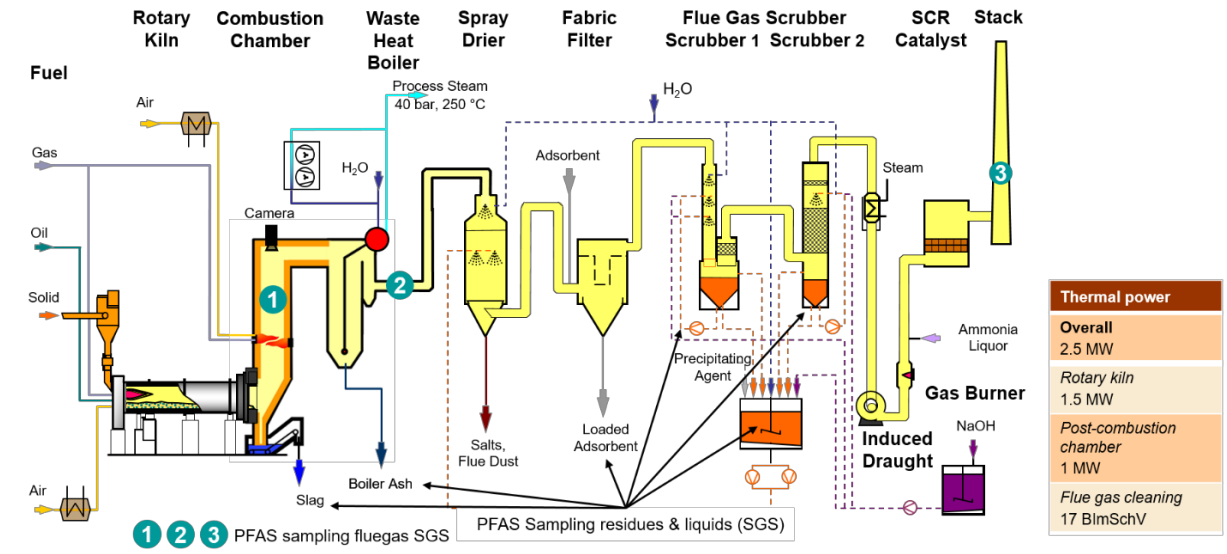


Figure 3: Test facility-BRENDA at KIT

The minimum residence time is calculated according the methodology of the German Technical Supervision Agency ("TÜV") from 2007. The data which were published in the report were re-calculated and then adapted to the operational conditions in this study (Setting 1 and Setting 2). Figure 4 presents the layout of the post combustion chamber with the geometry relevant for the determination of the residence time.

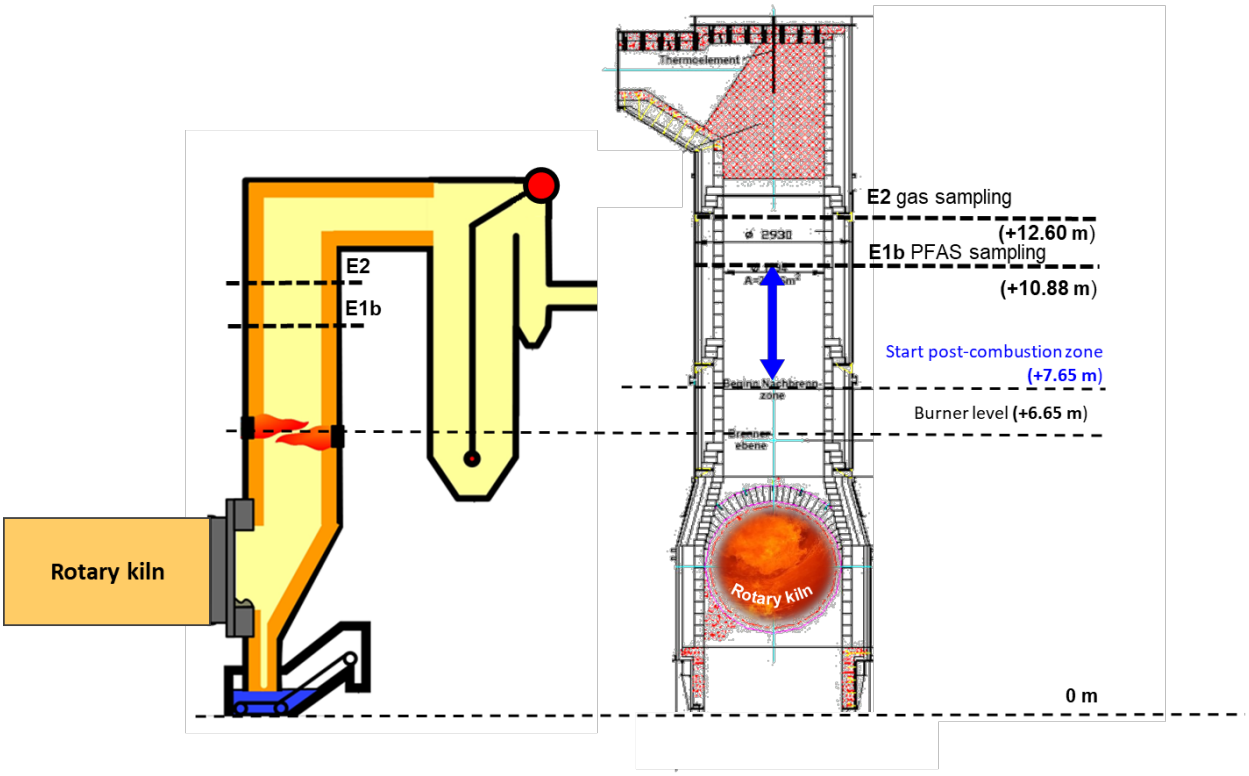


Fig. 4: BRENDA layout with details relevant for the residence time

Table 1 shows the detailed values for the design of the settings.

The volume flow of the required flue gas amount to reach the two seconds was calculated with a target value search.

Table 1. Parameters calculated for the residence time in the PCC

PFAS Project, Level E1b		
	setting 1	**setting 2**
Start post combustion zone [m] 1 meter above the burners	7.65	7.65
Temperature in the post combustion chamber (PCC) [°C]	860	1100
Volume flow V_{PCC} [m_N^3/h wet] after boiler	3947	3257
Cross section PCC [m^2]	2.82	2.82
Volume flow V_{PCC} [m^3/h]	16,382	16,382
Height h [m] level E1b	10.88	10.88
Residence time from start PCC zone to level E1b [s]	**2.00**	**2.00**

The two seconds are the residence time of flue gas from start of post-combustion zone until PFAS sampling point E1b, calculated with calibrated temperature measurements on the top of post combustion chamber (PCC).

The flue gas was sampled for both short-chain and long-chain PFAS in addition to organic and inorganic fluoride. Volatile organic C_1-C_4 fluorocarbons were also sampled using a tedlar bag at all three sampling locations. At location 2, gas-phase HF was measured in near real-time using a tunable diode laser (TDL). The purpose of the three gas-phase sampling locations was to assess the potential emissions of PFAS at different locations in the system and to use this data to assess potential sources of PFAS in this system. PFAS sampling of residues and liquids is also shown in Figure 3. In addition to these three sampling points, flue gas scrubber water upstream of the SCR catalyst was collected and analyzed for PFAS.

Table 2 provides a list of analytes measured in this study and the Limit of Quantification (LOQ). In addition to PFAS and fluoride ion, volatile C_1-C_4 fluorocarbons and trifluoroacetic acid (TFA) were also measured. The C_1-C_4 fluorocarbons were measured by gas chromatography coupled to mass spectrometry (GC-MS). Adsorbable organic fluoride (AOF) was measured using Combustion Ion Chromatography (CIC) and inorganic fluorine in impinger samples were measured by Ion Selective Electrode. TFA was measured using Ion chromatography (IC) and long chain PFAS from impinger samples were measured using Ultrahigh-Performance Liquid Chromatography coupled to tandem Mass Spectrometry (UPLC-MS/MS). HF was also measured at the post-combustion zone location using TDL spectroscopy.

Appendix 1 presents a list of long-chain PFAS measured in this study.

Table 2. Analytes and reporting limits

Analyte	LOQ
Volatile C1-C4 Compounds	5-30 ug/m^3
(CF4, CHF3, C2F6, C2HF5, CF2=CF-CF3, cy-C4F8)	
Adsorbable Organic Fluorine	2 ug/L
Inorganic Fluorine	0.1 ug/L
Trifluoroacetic Acid	0.02 ug/L
PFAS (see Appendix for list of compounds measured)	0.02 ug/L

Note: LOQ for AOF, Inorganic fluorine, TFA, and PFAS are for aqueous samples.

Experimental Results

Fluorine Recoveries

Fluorine recoveries ranged from 69 to 84% using the TDL (at sample location 2). The variability in these data from run to run was low. In contrast, the impinger data analyzed at the same sample location showed about 10 to 20% lower fluorine recoveries. The data are summarized in Table 3. The TDL data provide strong evidence for complete mineralization of fluoropolymer feed mixture.

Table 3: Fluorine Recovery (TDL Measurement)

Run	Settings	HF (TDL)	volume flow @standard wet conditions	volume flow @270 °C	Fluorine	Fluorine Recovery
		mg/m_B^3 wet Gas	[m_N^3/h]	[m_B^3/h]	g/h	%
2	860°C, > 2s, oil + nat. gas + wood chips + 230 g/h F	23.50	3,956	7,866	175.64	76%
		23.93	3,952	7,859	178.62	78%
		25.80	3,943	7,841	192.16	84%
5	1100°C, > 2s, oil + nat. gas + wood chips + 230 g/h F	25.44	3,299	6,560	158.53	69%
		26.58	3,231	6,424	162.23	71%
		26.93	3,217	6,397	163.64	71%

Long-chain PFAS

A large majority of the PFAS measured in impinger samples were near or below reporting limits (>98% of data collected at 860°C and >96% of data collected at 1100°C). Table 3 presents PFAS data for 4 compounds where measurements exceeded reporting limits in several cases. Of particular note is a HFPO-DA measurement which exceeded reporting limits by a factor of 47. Maximum PFBA, PFBS, and 6:2 FTS measurements exceeded reporting limits by much lower factors, ranging from 9 – 12.

These data was re-analyzed to assess the veracity of data. The results are also presented in Table 4. The results indicate that the high measurement values for HPFO-DA could not be reproduced. The results for PFBA and PFBS were also lower when re-analyzed. The lack of reproducibility of data and the lower

measurement values upon re-analysis suggests that cross-contamination is a possible reason for high measurement values for HPDO-DA, PFBA, and PFBS in the initial analysis.

PFAS analyses of wastewater and ash residue samples indicated a large majority of the samples were below reporting limits. One notable exception was a deslagger water bath sample where HFPO-DA was a factor of 16 above the report limit.

Table 4. PFAS Analysis of Impinger Samples

Initial Analysis

PFAS Compound	RL (ng/m^3)	# > RL	ng/m^3 (max)
PFBA	2.8	5	35.8
PFBS	1.4	22	19.5
6:2 FTS	1.4	17	12.5
HFPO-DA	1.4	31	66.3

Re-Analysis

PFAS Compound	RL (ng/m^3)	# > RL	ng/m^3 (max)
PFBA	2.8	0	2.8
PFBS	1.4	7	10.7
6:2 FTS	1.4	11	16.2
HFPO-DA	1.4	16	25.2

Note: For each data set, the total number of measurements equal 54: 27 for each combustion condition.

Short-chain PFAS

TFA was non-detect for all 76 impinger samples analyzed, at a reporting limit of 14 $\mu g/m^3$ (ppb).

Volatile Fluorocarbons (FC)

Tetrafluoromethane (CF_4) was the only volatile FC detected in the GC-MS analysis. Values of CF_4 at stack were near detection limits (20-27 $\mu g/m^3$) and detected in 2 of 14 samples. The results are considered questionable because CF_4 was only detected in one post-combustion sample. There is no plausible reason for larger CF_4 values downstream of the combustion unit unless a non-combustion source is considered.

Discussions

There is one prior published pilot-scale study of the combustion of PTFE (Aleksandrov et al. 2019). Combustion tests were performed at two conditions: 870°C and 4 s residence time and 1020°C and 2.7 s residence time and wood chips were used as the supplemental fuel. The prior study burned 0.3 wt % PTFE. Sampling was performed at a single location, downstream of the waste heat boiler. Thirty-one PFAS compounds were sampled and analyzed (see Table 1 of Aleksandrov et al. for a list of PFAS measured).

Fluorine recoveries were determined indirectly via IR water vapor measurements. The fluorine recoveries ranged from 56 to 78%, with three of the four tests yielding recoveries less than 70%. Eleven PFAS compounds were detected from the combustion and/or control samples and each at a level above 100 ng/m^3 in at least one sample. PFOA was detected in all but one sample and at values as high as 2.7 $\mu g/m^3$ (see Table 3 of Aleksandrov et al.).

The current study differs from the prior test in two important ways. The fluorine recoveries in this study were determined from direct spectroscopic measurements and were above 70% in five of the six tests. Secondly, PFAS reporting limits were on the order of 1 ng/m^3 or less and a large majority of samples (>98%) were at or below reporting limits. The current study provides strong evidence that incinerating a mixture of fluoropolymers under representative municipal waste combustion conditions leads to complete mineralization of the C-F bonds, no significant emissions of long-chain PFAS, and no significant emissions of TFA or light fluorocarbons such as CF_4 or C_2F_6. The prior study did not provide evidence that the PFAS detected were from sources other than the combustion of PTFE.

Conclusions

The study clearly demonstrated that fluoropolymers are converted to inorganic fluorides and carbon dioxide. The inorganic fluorides detected were hydrogen fluoride. A large majority of samples indicated that long-chain PFAS were below levels of 1 ng/m^3 (> 99% of samples associated with 860°C condition and > 98% of samples associated with 1100°C condition). There were no short chain PFAS detected post incineration. TFA was non-detectable in all samples with a reporting limit of 14 $\mu g/m^3$. **The results confirm that fluoropolymers at their end of life when incinerated under representative European municipal incinerators conditions do not generate any measurable levels of PFAS emissions and therefore pose no risk to human health and the environment.**

The main reason to include fluoropolymers in the EU PFAS restriction proposal was persistence (resistance to degradation in the environment) in the environment. The absence of organic fluorides and more specifically PFAS in tests representative of municipal waste incineration confirms complete mineralization of fluoropolymers and provides critical data in support for exempting Fluoropolymers from the EU REACH PFAS restriction proposal.

References

TÜV report from 19th of January 2007: Expert opinion on compliance with and monitoring of the combustion conditions (residence time, temperature) in the afterburning zone of the THERESA test facility at the Forschungszentrum Karlsruhe GmbH

Aleksandrow, K, Gehrmann, H-J, Hauser, M., Matzing, H., Pigeon, D., Stapf, D., and Wexler, M., Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas, Chemosphere, 2019, 226, 898-906.

Appendices

1. List of long-chain PFAS analytes analyzed in this study

Common Name[a]	Abbreviated Name	CAS[b] Registry Number	Isotopic Pre-Extraction Pair
Perfluoroalkylcarboxylic acids (PFCAs)			
Perfluorobutanoic acid[1,3,4]	PFBA	375-22-4	$^{13}C_4$-PFBA
Perfluoropentanoic acid[1,3,4]	PFPeA	2706-90-3	$^{13}C_5$-PFPeA
Perfluorohexanoic acid[1,2,3,4]	PFHxA	307-24-4	$^{13}C_2$-PFHxA
Perfluoroheptanoic acid[1,2,3,4]	PFHpA	375-85-9	$^{13}C_4$-PFHpA
Perfluorooctanoic acid[1,2,3,4]	PFOA	335-67-1	$^{13}C_4$-PFOA
Perfluorononanoic acid[1,2,3,4]	PFNA	375-95-1	$^{13}C_5$-PFNA
Perfluorodecanoic acid[1,2,3,4]	PFDA	335-76-2	$^{13}C_2$-PFDA
Perfluoroundecanoic acid[1,2,3,4]	PFUnDA	2058-94-8	$^{13}C_2$-PFUndA
Perfluorododecanoic acid[1,2,3,4]	PFDoA	307-55-1	$^{13}C_2$-PFDoA
Perfluorotridecanoic acid[2,3,4]	PFTrDA	72629-94-8	$^{13}C_2$-PFDoA
Perfluorotetradecanoic acid[2,3,4]	PFTeDA	376-06-7	$^{13}C_2$-PFTeDA
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	$^{13}C_2$-PFHxDA
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	$^{13}C_2$-PFDoA
Perfluorinated sulfonic acids (PFSAs)			
Perfluoro-1-butanesulfonic acid[1,2,3,4]	PFBS	375-73-5	$^{13}C_3$- PFBS
Perfluoro-1-pentanesulfonic acid[1,3]	PFPeS	2706-91-4	$^{13}C_3$-PFHxS Or $^{13}C_3$-PFBS
Perfluoro-1 -hexanesulfonic acid[1,2,3,4]	PFHxS	355-46-4	$^{18}O_2$-PFHxS or $^{13}C_3$-PFHxS
Perfluoro-1-heptanesulfonic acid[1,3]	PFHpS	375-92-8	$^{13}C_4$-PFHpA
Perfluoro-1-octanesulfonic acid[1,2,3,4]	PFOS	1763-23-1	$^{13}C_4$-PFOS
Perfluoro-1-nonanesulfonic acid[3]	PFNS	68259-12-1	$^{13}C_4$-PFOS
Perfluoro-1-decanesulfonic acid[3]	PFDS	335-77-3	$^{13}C_4$-PFOS
Perfluorododecane sulfonate	PFDoS	79780-39-5	$^{13}C_4$-PFOS
Perfluorinated sulfonamides (FOSAs)			
Perfluoro-1-octanesulfonamide[3,5]	FOSA	754-91-6	$^{13}C_8$-FOSA
N-Methylperfluorooctanesulfonamide [5]	MeFOSA	31506-32-8	d3-MeFOSA
N-ethylperfluorooctanesulfonamide [5]	EtFOSA	4151-50-2	d5-EtFOSA
Perfluorinated sulfonamidoacetic acids (FOSAAs)			
N-methyl perfluorooctanesulfonamidoacetic acid[2,3]	MeFOSAA	2355-31-9	d3-MeFOSAA
N-ethyl perfluorooctanesulfonamidoacetic acid[2,3]	EtFOSAA	2991-50-6	d5-EtFOSAA
Fluorotelomer sulfonates (FTS)			
1H,1H,2H,2H-Perfluorohexane sulfonic acid[1,3]	4:2 FTS	757124-72-4	M2-4:2 FTS
1H,1H,2H,2H -Perfluorooctane sulfonic acid[1,3]	6:2 FTS	27619-97-2	M2-6:2 FTS
1H,1H,2H,2H -Perfluorodecane sulfonic acid[1,3]	8:2 FTS	39108-34-4	M2-8:2 FTS
1H,1H,2H,2H-perfluorododecane sulfonate (10:2)	10:2 FTS	120226-60-0	M2-10:2 FTS
Fluorinated Replacement Chemicals			
4,8-Dioxa-3H-perfluorononanoic acid	ADONA[1]	919005-14-4	$^{13}C_4$-PFOS
Hexafluoropropylene Oxide Dimer Acid	HFPO-DA (GenX)[1]	13252-13-6	$^{13}C_3$-HFPO-DA
Additional Targets			
Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate)[4]	PFecHS	67584-42-3	$^{18}O_2$-PFHxS

Fluorinated Replacement Chemicals			
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS (F-53B Major)[1]	756426-58-1	$^{13}C_4$-PFOS
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid OR 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate[a]	11Cl-PF3OUdS (F-53B Minor)[1]	763051-92-9 83329-89-9	$^{13}C_4$-PFOS

Perfluorinated sulfonamide ethanols (FOSEs)			
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol[5]	N-MeFOSE	24448-09-7	d7-N-MeFOSE
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol[5]	N-EtFOSE	1691-99-2	d9-N-EtFOSE
Additional Targets			
Nonafluoro-3,6-dioxaheptanoic acid[1,5]	NFDHA	151772-58-6	$^{13}C_5$-PFHxA
Perfluoro(2-ethoxyethane)sulfonic acid[1,5]	PFEESA	113507-82-7	$^{13}C_3$-PFBS
Sodium perfluoro-1-dodecanesulfonate[5]	PFDoS	1260224-54-1	$^{13}C_4$-PFOS
Perfluoro-4-methoxybutanoic acid[1,5]	PFMBA	863090-89-5	$^{13}C_5$-PFPeA
Perfluoro-3-methoxypropanoic acid[1,5]	PFMPA	377-73-1	$^{13}C_4$-PFBA
3:3 Fluorotelomer carboxylic acid[5]	3:3 FTCA	356-02-5	$^{13}C_2$-FHEA
5:3 Fluorotelomer carboxylic acid[5]	5:3 FTCA	914637-49-3	$^{13}C_2$-FHEA
7:3 Fluorotelomer carboxylic acid or 3-perfluoropheptyl propanoic acid[4, 5]	7:3 FTCA or FHpPA	812-70-4	$^{13}C_2$-FOEA
2H-perfluoro-2-decenoic acid[4]	8:2 FTUCA or FOUEA	70887-84-2	$^{13}C_2$-FOUEA
2-perfluorodecyl ethanoic acid[4]	10:2 FDEA	53826-13-4	$^{13}C_2$-FDEA
2-perfluorooctyl ethanoic acid[4]	8:2 FTA or FOEA	27854-31-5	$^{13}C_2$-FOEA
2H-perfluoro-2-octenoic acid[4]	6:2 FHUEA	70887-88-6	$^{13}C_2$-FHUEA
2-perfluorohexyl ethanoic acid[4]	6:2FTCA or 6:2 FHEA	53826-12-3	$^{13}C_2$-FHEA

Developments in Fluoropolymer Manufacturing Technology to Remove Intentional Use of PFAS as Polymerization Aids

Bruno Ameduri, Jaime Sales and Michael Schlipf*

Fluoropolymers are heavily impacted by the restriction proposal on per- and polyfluoroalkyl substances (PFAS) that has been recently published under the EU REACH Regulation.[1] While matching the definition of PFAS due to their chemical composition and structure, fluoropolymers are significantly different from other substances in the PFAS family. The only substantial reason for concern associated to fluoropolymers is the use of non-polymeric PFAS as polymerization aids during the manufacturing process. In the past, environmental pollution caused by PFOA and PFOS, which are prominent non-polymer substances in the PFAS family, has attracted regulatory attention. PFOS has been restricted and PFOA has been banned under the EU Regulation on Persistent Organic Pollutants. This article highlights the progress that industry has made over the last years in relation to control of PFAS emissions due to their use in fluoropolymer production. Such a progress is based on the improvement of abatement techniques, but more importantly, on the removal of PFAS polymerization aids, introducing alternative technologies that do not require using such chemicals. It is expected that most of the fluoropolymer production will be developed completely free from PFAS polymerization aids in a relatively short time frame. Thus, it appears reasonable to claim that fluoropolymers that are manufactured without the use of PFAS polymerization aids should be exempted from any regulatory initiative, and that their uses should be allowed without any unjustified restriction.

I. Introduction

The PFAS family of chemicals is currently under strong regulatory scrutiny globally. Some of the substances covered by this group are known for being highly harmful to the environment and human health, due to their persistency, bioaccumulation/mobility and other toxic effects. However, the broad definition that is frequently used to describe PFAS, which was not originally introduced to be used for regulatory purposes[2], results in a very large number of substances covered jointly in this family of chemicals, more than 4,700 according to the OECD[3] as being present on the global market. There have been significant efforts to group and classify the different substances that can be regarded as meeting the definition of PFAS (Figure 1). One such group is that of fluoropolymers.[4]

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1 ECHA, 'Registry of restriction intentions until outcome - Per- and polyfluoroalkyl substances (PFAS)' (2023).

2 J K Anderson, R W Brecher, I T Cousins, J DeWitt, H Fiedler, K Kannan, C R Kirman, J Lipscomb, B Priestly, R Schoeny, J Seed, M Verner, S M Hays, 'Grouping of PFAS for human health risk assessment: Findings from an independent panel of experts' (2022) Regulatory Toxicology and Phamacology, 134.

3 OECD, 'Toward a new comprehensive global database of per- and polyfluoroalkyl substances (PFASs)' (2018) Series on Risk Management No. 39. Organisation for Economic Co-operation and Development.

4 Bruno Ameduri, 'Fluoropolymers: A special class of per- and polfluoroyalkyl substances (PFASs) essential for our daily life' (2023) Journal of Fluorine Chemistry 267, 110117.

One of the key features of fluoropolymers is that they fulfil the conditions set out by the OECD to meet the definition of Polymers of Low Concern (PLC). This has been demonstrated for the vast majority of these substances, accounting for >96% of global production.[5] This means that fluoropolymers are not toxic, mobile or bioaccumulative. While they are persistent, the lack of degradability during normal conditions of use and at end of life makes fluoropolymers completely inert and not hazardous to human health and the environment.

Due to their intrinsic nature based on the carbon-fluorine bond, fluoropolymers offer a combination of various properties of interest that render them highly valuable products in different industrial sectors such as renewable energy, in applications such as back sheets for photovoltaic panels and lubricants in wind turbines, binders and separators for lithium-ion batteries and proton exchange membranes and frame gaskets for hydrogen production and fuel cells. Fluoropolymers are also valuable in industries such as semiconductors, food and water processing, automotive, aerospace, chemical processing, electrical, electronics, and construction. It is to be noted that the broad applications of fluoropolymers, which are virtually irreplaceable in critical industrial sectors needed by modern society is not in scope of this paper, and significant information on this can be found in literature.[6]

II. Historical Concerns Related to Manufacture of Fluoropolymers

The manufacture of fluoropolymers has been flagged by researchers as a source of environmental damage in different locations in Europe (Italy, France, the Netherlands), the USA and China.[7] However, it needs to be stressed that this concern is not related to the fluoropolymers as individual substances, but to the use of non-polymeric PFAS that have been frequently used as polymerization aids. These Fluorinated Polymerization Aids (FPAs), also referred to as surfactants, facilitate the development and completion of the polymerization reaction. In the past, this use has led to specific situations of uncontrolled emissions of these surfactants, which are known to pose an environmental hazard.[8]

In terms of global production, fluoropolymers represent a very small share compared to the total amount of plastics, with estimated 320,000 tonnes of fluoropolymers in 2019[9] in front of 460 million tonnes of total plastics.[10] It is estimated that only 50% of fluoropolymer production requires the use of FPAs, based on standard manufacturing practices by industry to this date;[11] while manufacture of fluoropolymers via suspension process normally does not require the use of surfactants, these have traditionally been required to achieve high molecular weight polymer emulsions.[12]

5 Barbara J Henry, Joseph P Carlin, Jon A Hammerschmidt, Robert C Buck, L William Buxton, Heidelore Fiedler, Jennifer Seed and Oscar Hernandez, 'A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers' (2022) 14 Integrated Environmental Assessment and Management 13, 316–334; Stephen H. Korzeniowski, Robert C. Buck, Robin M. Newkold, Ahmed El kassmi, Evan Laganis, Yasuhiko Matsuoka, Bertrand Dinelli, Severine Beauchet, Frank Adamsky, Karl Weilandt, Vijay Kumar Soni, Deepak Kapoor, Priyanga Gunasekar, Marco Malvasi, Giulio Brinati, Stefana Musio, 'A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers' (2022) Integrated Environmental Assessment and Management.

6 Bruno Ameduri and Sergey Fomin, *Fascinating Fluoropolymers and Applications* (Elsevier, 2020); Bruno Ameduri, 'The Promising Future of Fluoropolymers' (2020) Macromol Chem Phys 221, 1900573; Bruno Ameduri, *Issues, Challenges, Regulations and Applications of Perfluoroalkyl Substances* (Oxford University Press, 2022).

7 Wouter A Gebbink, Laura van Asseldonk and Stefan P J van Leeuwen, 'Presence of Emerging Per- and Polyfluoroalkyl Substances (PFASs) in River and Drinking Water near a Fluorochemical Production Plant in the Netherlands' (2017) 51 Environ Sci Technol 19, 11057–11065; Rainer Lohmann, Ian T. Cousins, Jamie C. DeWitt, Juliane Glüge, Gretta Goldenman, Dorte Herzke, Andrew B. Lindstrom, Mark F. Miller, Carla A. Ng, Sharyle Patton, Martin Scheringer, Xenia Trier, and Zhanyun Wang, 'Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?' (2022) Environ Sci Technol 54, 12820–12828; Xuan Jia, Hongyan Guan, Zhongbao Guo, Chengjing Qian, Yali Shi and Yaqi Cai, 'Occurrence of Legacy and Emerging Poly- and Perfluoroalkyl Substances in Fluorocarbon Paint and Their Implications for Emissions in China' (2021) 8 Environ Sci Technol Lett 11, 968-974.

8 Rob Bonta, Superior Court of the State of California, County of Alameda 10 November 2022.

9 ETC/WMGE Consortium Partners, 'Fluorinated polymers in a low carbon, circular and toxic-free economy - Technical report' <https://www.eionet.europa.eu/etcs/etc-wmge/products/etc-wmge-reports/fluorinated-polymers-in-a-low-carbon-circular-and-toxic-free-economy> accessed 1 May 2023.

10 OECD, 2022. Plastic pollution is growing relentlessly as waste management and recycling fall short, says OECD. Available at: https://www.oecd.org/environment/plastic-pollution-is-growing-relentlessly-as-waste-management-and-recycling-fall-short.htm. Last access December 2022.

11 Jaime Sales, Francisco Hernández, Deepak Kapoor, Marcel van den Noort, 'Fluoropolymers: The Safe Science That Society Needs' (2022) 5 International Chemical Regulatory and Law Review 1, 13-23.

12 Ebnesajjad, *Fluoroplastics, Volume 1: Non-Melt Processible Fluoropolymers - The Definitive User's Guide and Data Book* (Elsevier, 2014).

Aqueous emulsions are required to produce high performance grades of some fluoropolymers.[13] Surfactants are highly soluble in water, but the final fluoropolymer substances are not; hence after separation, the residual water contains amounts of dissolved surfactant, which may lead to PFAS emissions when FPAs are used.[14]

Another consequence of the use of these surfactants is that sometimes the final fluoropolymer product may carry residuals of such non-polymeric PFAS, which can be also emitted to the environment during the life cycle of fluoropolymers. Again, in this case there is an indirect pollution associated to fluoropolymers, not related to the intrinsic specific properties of these substances.

As a final step in the life cycle of fluoropolymers, disposal and waste treatment has been frequently flagged as a reason for concern of these products. However, recent studies have demonstrated that the waste generation of fluoropolymers is insignificant compared to that of other plastics,[15] and that the most common waste treatment technique for fluoropolymers - incineration - will not result in any PFAS species of concern.[16] In addition to this, fluoropolymers do not degrade during normal use or environmental conditions[17] and do not pose any significant risk if they are landfilled.[18]

In summary, it can be established that the only real source of concern for human health or the environment related to fluoropolymers is the use of PFAS as polymerization aids in the manufacture of these polymers of low concern. Providing efficient solutions that would completely neutralize such concerns would result in completely safe manufacture, use and disposal of fluoropolymers.

III. How to Avoid PFAS Emissions (Polymerization Aids) from the Fluoropolymer Value Chain?

For many years, industry has placed significant efforts to reduce emissions of PFAS from the manufacturing process of fluoropolymers. In order to achieve this goal, there are basically two options available:

1. To improve the abatement techniques and recovery of PFAS surfactants from the manufacture of fluoropolymers.
2. To develop alternative processes that do not require the use of such PFAS polymerization aids for the production of fluoropolymers.

In the case of item 1 above, significant improvements have occurred over the last years that have allowed for reduction of 99% of emissions of fluorinated surfactants since the 1990s.[19] More recent research brings that value as high as 99.99%.[20] Extensive literature exists in relation to control and treatment of emitted PFAS from industrial processes.[21] The strategies of containment involve the recovery, removal, purification, sorption techniques, microbial degradability and recyclability of the polymerization aids

13 Oleg N. Primachenko, Alexey S. Odinoko, Elena A. Marinenko, Yuri V. Kulvelis, Valerij G. Barabanov and Svetlana V. Kononova, 'Influence of sulfonyl fluoride monomers on the mechanism of emulsion copolymerization with the preparation of proton-conducting membrane precursors' (2021) Journal of Fluorine Chemistry 244, 109736.

14 Ebnesajjad, *Fluoroplastics, Volume 1: Non-Melt Processible Fluoropolymers - The Definitive User's Guide and Data Book* (Elsevier, 2014).

15 Conversio, 'Fluoropolymer waste in Europe 2020 – End-of-life (EOL) analysis of fluoropolymer applications, products and associated waste streams' (2022).

16 Krasimir Aleksandrov, Hans-Joachim Gehrmann, Manuela Hauser, Hartmut Mätzing, Daniel Pigeon, Dieter Stapf and Manuela Wexler, 'Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas' (2019) 226 Chemosphere; RIVM, 'Per- and polyfluorinated substances in waste incinerator flue gases. Rijksinstituut voor Volksgezondheid en Milieu' (2021).

17 Danish EPA, 'Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances. The Danish Environment Protection Agency' (2013) LOUS Review, Environmental Project No. 1475, 2013.

18 Stephen H. Korzeniowski, Robert C. Buck, Robin M. Newkold, Ahmed El kassmi, Evan Laganis, Yasuhiko Matsuoka, Bertrand Dinelli, Severine Beauchet, Frank Adamsky, Karl Weilandt, Vijay Kumar Soni, Deepak Kapoor, Priyanga Gunasekar, Marco Malvasi, Giulio Brinati and Stefana Musio, 'A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers' (2022) Integrated Environmental Assessment and Management.

19 Daikin Chemicals, 'Measures concerning environment emission of PFAS' (2022) <https://www.daikinchemicals.com/company/sustainability/pfas.html> accessed 1 May 2023. Chemours, 'Our Commitment to Responsible Chemistry' <https://www.chemours.com/en/corporate-responsibility/sustainability-safety/our-commitment-to-pfas-stewardship> accessed 1 May 2023.

20 Rebecca DiStefano, Tony Feliciano, Richard A. Mimna, Adam M. Redding and John Matthis, 'Thermal destruction of PFAS during full-scale reactivation of PFAS-laden granular activated carbon' (2022) Remediation 32, 231–238.

21 ITRC, 'PFAS Technical and Regulatory Guidance Document and Fact Sheets: 12. Treatment Technologies' (2022) Interstate Technology and Regulatory Council; Jinxia Liu and Sandra Mejia Avendaño, 'Microbial degradation of polyfluoroalkyl chemicals in the environment: A review' (2013) Environment International 61, 98-114.

from off-gases, waste-water streams, aqueous dispersions, and final products. The recovery/recycling techniques of the polymerization aids depend on the final form of the fluoropolymer product: they can be removed when the aqueous emulsion is dried for sale as a solid (in the case of powder), or they can be thermally destroyed at high temperatures during the curing process (in the case of aqueous dispersion). Such techniques, including ion exchange technology for removal of FPAs from aqueous emulsions, have been applied for more than 20 years, and at present time, they are installed in most of the fluoropolymer manufacturing facilities around the world.

However, it needs to be acknowledged that achieving an absolute zero value of emissions in processes where PFAS are used is technically impossible. Frequently industry operates with the concepts of As Low As Reasonably Practicable/Achievable.[22] From that point, developing improved technologies becomes complex and significantly resource intensive for industry. Furthermore, with the development of ever more sophisticated analytical techniques, the possibility that (low) PFAS concentrations in the vicinity of industrial sites where these chemicals are used will be detected will continue to increase as well. This is certainly a positive development, due to the properties of the most dangerous PFAS as persistent, bio-accumulative, mobile and toxic. However, if the goal is to ensure zero emissions, it is highly unlikely that continued improvement of abatement techniques (which is nevertheless a clear necessity) will achieve this target.

Instead, option 2 appears to be the only realistic possibility to ensure that the emission of PFAS surfactants will be completely removed; if no PFAS surfactants are used in the manufacturing process of fluoropolymers, then no emissions will occur. Thus, the use of Non-Fluorinated Polymerization Aids (NFPA) can be considered as the most direct path forward to respond to the societal concern related to PFAS pollution associated to fluoropolymers.

However, it needs to be noted that both options are not mutually exclusive. The switch to fluoropolymer manufacture with the use of NFPA will also require the implementation of the most efficient abatement techniques, such as, use of ion exchange resin,[23] filtration[24] or foam fractionation.[25] This is because the process may still lead to small amounts of residual fluorinated by-products coming from side reactions between chemicals involved, such as monomers or the NFPA. Still, an adequate selection of surfactant and process conditions should allow for a minimisation of fluorinated residuals, particularly if compared to the situation where fluorinated surfactants are used.

Indeed, when comparing manufacturing processes of fluoropolymers that may use either FPAs or NFPAs, the whole life-cycle of all the chemicals involved in the process needs to be taken into account. The use of FPAs requires its manufacture, transport, storage and maintenance (e.g., cleaning) of the equipment used in those processes. All these activities will result in potential PFAS emission sources that have to be added to the possible emissions of the FPA (and residuals) that will be generated during the manufacture of the fluoropolymer. In the case of NFPA technology, only the contribution of residuals from the manufacture of fluoropolymer may contribute to emissions. Again, the fact that today such emissions can be adequately controlled via efficient abatement, e.g., by keeping values of fluorinated residuals well below the 250 ppb limit established in the restriction proposal[26] clearly results in favour of the transition to manufacturing processes of fluoropolymers involving NFPA technology.

An overview on the current situation about implementation of NFPA technology and expected future developments is provided next.

1. State of the Art Related to NFPA Technology for the Manufacture of Fluoropolymers and Path Forward

Over the past years, the fluoropolymer industry has undertaken significant efforts in continued attempts

22 HSE, 'ALARP at a glance. Health and Safety Executive' (2022) <https://www.hse.gov.uk/managing/theory/alarpglance.htm> accessed 1 May 2023.

23 Fuhar Dixit, Rahul Dutta, Benoit Barbeau, Pierre Berube and Madjid Mohseni, 'PFAS removal by ion exchange resins: A review' (2021) Chemosphere, 129777.

24 EPA, 'Reducing PFAS in drinking water with treatment technologies' <https://www.epa.gov/sciencematters/reducing-pfas-drinking-water-treatment-technologies> accessed 1 May 2023.

25 Sanne J. Smith, Karin Wiberg, Philip McCleaf and Lutz Ahrens, 'Pilot-Scale Continuous Foam Fractionation for the Removal of Per- and Polyfluoroalkyl Substances (PFAS) from Landfill Leachate' (2022) ACS EST Water 5, 841–851.

26 ECHA, 'Registry of restriction intentions until outcome - Per- and polyfluoroalkyl substances (PFAS)' (2023) <https://echa.europa.eu/es/registry-of-restriction-intentions/-/dislist/details/0b0236e18663449b> accessed 1 May 2023.

to introduce NFPA technologies in the manufacture of fluoropolymers. An overview on patents that have been filed on technology based on non-fluorinated surfactants demonstrates that this is an effort that the whole industry has taken in parallel, and not limited to the initiative of one or a reduced group of suppliers. Several manufacturers of fluoropolymers have filed multiple patents on NFPA technology over the past 2 decades. This explains a high focus and investment in this direction by the industry. Table 1 (Appendix) provides a list of identified patents related to the use of NFPA technologies for the manufacture of fluoropolymers as published over the last years. While this is not an exhaustive list of initiatives in this field, it provides a good description of efforts developed by the whole fluoropolymer industry.

It should be noted that, even if Table 1 lists patents filed in the XXI Century, initiatives to introduce NFPA technology in the manufacture of fluoropolymers have been on-going since the 1960s.[27]

2. Commercialization of NFPA Technology and Successful Market Acceptance

As of today, it is assumed that there are technologies available that allow for the manufacture of more than 80% of fluoropolymer global production in volume without the use of FPAs.[28] This includes 100% of the three main fluoropolymers by volume: polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and fluoroelastomers (FKM). While progress on PVDF was achieved around 15 years ago[29], and some grades of PTFE and FKM have been traditionally manufactured without the use of FPAs, success with other PTFE grades (aqueous dispersions and fine powders) and other FKM grades has only been possible in the last months. Progress on smaller volume products such as is poly (TFE-co-perfluoroalkoxyvinylether) copolymers or perfluoro(alkoxyvinylether)s (PFA) have also been recently announced, and it is expected that further developments will be confirmed in the next months that will involve other fluoropolymers.

It needs to be noted that, while such technologies are currently available, it is not expected that all the suppliers will be in a position to integrate them in their manufacturing processes at the same time. This means, for example, that while one supplier may have developed a procedure to manufacture all grades of PTFE without the use of FPAs, this may not yet be feasible today for all the suppliers. While sublicensing of rights to a specific technology is possible, full implementation of these procedures by all the suppliers may take some time.

For many years, the fluoropolymer industry has made efforts to develop alternative technologies that do not require the use of FPAs. However, it is in the recent past when different fluoropolymer manufacturers have increased the announcements of different developments to replace technologies based on FPAs, either by introducing NFPAs, or by turning to completely alternative processes that simply remove the use of surfactants.[30]

In order to be considered as a completely viable option for fluoropolymer manufacture, the alternative processes must lead to the production of grades that are accepted by downstream users in terms of quality and performance. This can be confirmed since thousands of metric tonnes of fluoropolymers manufactured without the use of FPAs have already been introduced on the global market and have been well accepted by customers. In recent years, it was only possible to manufacture those fluoropolymers with FPAs, however this situation has changed following recent developments by industry. Furthermore, these grades have to ensure that any water-soluble fluorinated by-products present in the final product are brought to insignificant levels, which can

27 Hoashi Juzaemon, Stabilized, concentrated polytetrafluoroethylene dispersions containing non-ionic surfactants. U.S. Patent No. 3,301,807. 31 Jan. 1967.

28 Jaime Sales, Francisco Hernández, Deepak Kapoor, Marcel van den Noort, 'Fluoropolymers: The Safe Science That Society Needs' (2022) 5 International Chemical Regulatory and Law Review 1, 13-23.

29 PCI, 'Arkema Eliminates Fluorosurfactants from Kynar 500® PVDF' (2008) <https://www.pcimag.com/articles/88876-arkema-eliminates-fluorosurfactants-from-kynar-500-pvdf> accessed 1 May 2028.

30 Chemours, 'Chemours Announces Process Innovation with New Viton™ Fluoroelastomers Advanced Polymer Architecture (APA) Offering' (2022) <https://www.chemours.com/en/news-media-center/all-news/press-releases/2022/chemours-announces-process-innovation-with-new-viton-fluoroelastomers-advanced-polymer-architecture> accessed 1 May 2022: Solvay, 'Producing new fluoropolymers without fluorosurfactants' (2022) <https://www.solvay.com/en/article/eliminating-pfas> accessed 1 May 2023; Gujarat Fluorochemicals, 'Company Announcements' (9 March, 2022) <https://www.gfl.co.in/upload/pages/ebce5fed9030753d0ee651bf1f48d0a0.pdf> accessed 1 May 2023; Gujarat Fluorochemicals Limited, 'Company Annoucement' (27 August, 2022) <https://www.gfl.co.in/assets/pdf/Announcement-on-NFPA-technology-FKM-27-Aug-2022.pdf> accessed 1 May 2023; Gujarat Fluorochemicals Limited, 'Company Annoucement' (30 November, 2022) <https://gfl.co.in/assets/pdf/GFL%20Announcement%2030.11.22_new.pdf> accessed 1 May 2023.

also be guaranteed by some suppliers using known analytical methods.

In the recent past, and mainly in 2022, various fluoropolymer manufacturers have released statements announcing discontinuation of use of FPAs in the manufacturing of specific fluoropolymers. A summary of latest announcements is given in Table 2 (Appendix).

The fluoropolymer user industry has already witnessed the transition when PFOA was substituted by other PFAS polymerization aids, except in China where PFOA is still in use.[31] They have now become sensitive to the potentially negative aspects of FPAs currently in use replacing PFOA.[32] Hence, the user industry is requesting fluoropolymer manufacturers to switch to NFPAs. There is an urgency to qualify new versions of fluoropolymer products produced without the use of fluorinated polymerization aids. The regulatory developments from various authorities are pushing the industry to swiftly move towards sustainable technologies. As a result, fluoropolymers produced with NFPA technology are a commercial success and that further motivates the industry to work harder in this direction.

IV. A Regulatory Proposal for Fluoropolymers

The EU Chemicals Strategy for Sustainability (CSS) towards a Toxic-Free Environment proposes the development of a horizontal essential use concept to apply across chemicals legislation (European Commission, 2020). The CSS commits to "define criteria for essential uses to ensure that the most harmful chemicals are only allowed if their use is necessary for health, safety or is critical for the functioning of society and if there are no alternatives that are acceptable from the standpoint of environment and health".

Most harmful substances as defined in the CSS are chemicals that cause cancers, gene mutations, affect the reproductive or the endocrine system, or are persistent and bioaccumulative. It also covers chemicals affecting the immune, neurological or respiratory systems and chemicals toxic to specific organs. It is clear that fluoropolymers as independent substances do not fall into the category of Most Harmful Chemicals as defined in the CSS, based on[33]:

- Fluoropolymers are Polymers of Low Concern as per well-established OECD criteria
- Fluoropolymers are insoluble, non-mobile, non-bio accumulative and non- toxic

However, the FPAs that have been traditionally used in the manufacture of fluoropolymers are small non-polymeric PFAS substances of low molecular weight such as perfluorooctanoic acid (PFOA), ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, or GenX), ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA), or perfluorohexanesulfonic acid (PFHxS) might fall into the category of Most Harmful Chemicals and they would therefore require regulatory control. It is important to highlight that, as mentioned above, at present between 50 and 80% of fluoropolymers do not require the use of fluorinated polymerization aids (depending on suppliers and implemented technology).

Any regulatory process on fluoropolymers should start by differentiating if the polymer has been manufactured with the use of FPAs. If this is not the case, then the fluoropolymer substance should be excluded from any legislative action, because there is no justification to regulate a chemical that will not pose any concern to human health or the environment.

If FPAs have been used in the manufacturing process, fluoropolymers should only be used in situations where the use can be considered to be essential. While the concept of essential use is still under development[34], this is expected to include situations in which it can be clearly demonstrated that the application is critical to ensure health, safety, and an adequate functioning of society. It is out of the scope of this article to discuss about the conditions under which essential use could be demonstrated. Yet it is

31 Rainer Lohmann, Ian T. Cousins, Jamie C. DeWitt, Juliane Glüge, Gretta Goldenman, Dorte Herzke, Andrew B. Lindstrom, Mark F. Miller, Carla A. Ng, Sharyle Patton, Martin Scheringer, Xenia Trier, and Zhanyun Wang, 'Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?' (2022) Environ Sci Technol 54, 12820–12828.

32 Bruno Ameduri, *Issues, Challenges, Regulations and Applications of Perfluoroalkyl Substances* (Oxford University Press, 2022).

33 (n 5).

34 Cefic, 2022. Regulating Chemicals Based on the Essential Use Concept. Available at: https://cefic.org/policy-matters/defining-europes-essential-chemical-for-society/. Last access November 2022; Wood 2022, prepared for European Commission, DG Environment. Supporting the Commission in developing an essential use concept. Workshop report. Available at: https://environment.ec.europa.eu/system/files/2022-05/Essential%20Use%20Workshop%20Report%20final.pdf . Last access December 2022.

expected that many applications of fluoropolymers would meet these criteria.[35]

The essential use concept will be linked to the availability of alternatives. In cases where viable alternatives are proven to be available for a specific use of fluoropolymers, the use should be restricted so that it can be covered by the alternatives. Again, detailed discussions will be required to demonstrate viability of alternatives, particularly in situations where health and safety parameters (or even adequate functioning of society, depending on the case) will be critical. In such cases, equivalent performance to that provided by fluoropolymers will be necessary since downgrades in performance could have extremely negative impacts for the environment or the population. Likewise, the typical parameters of overall reduced risk and economic availability of the alternative (and in sufficient amount) will have to be carefully evaluated. So, availability of alternatives would have to be evaluated with a broad perspective covering items such as performance, accessibility, resource efficiency, waste generation, cost, availability, stability and lifetime. Where viable alternatives are not found for essential uses of fluoropolymers manufactured with FPAs, derogations from the impact of upcoming regulatory restrictions should be granted. Such derogations would need to be based on the introduction of all existing abatement techniques based on the most modern developments, plus the guarantee of a maximum PFAS content in the final product. For example, 250 ppb as has been included in the restriction proposal.[36] However, such derogations should be time limited to provide incentives to move suppliers to fully implement manufacturing process involving NFPA technology as soon as possible.

Figure 2 displays a schematic overview of the proposed regulatory path for fluoropolymers. In the absence of a definitive definition of "Essential Use Concept", the term 'Critical Use for Society' is used.

V. Conclusions

The manufacture of certain grades of fluoropolymers had traditionally required the use of FPAs (short-chain PFAS) to ensure an optimal production. This practice has resulted in PFAS emissions and pollution of certain areas around manufacturing and processing sites, which has been a reason of major concern for the society. This has also triggered significant regulatory actions globally against PFAS. Fluoropolymers have been impacted by such actions, due to use of non-polymeric PFAS in the manufacturing process and the fact that they meet the very broad definition of PFAS based on structure.

For many years the fluoropolymer industry has been looking for alternative technologies that would help to remove the use of FPAs while ensuring top quality end-products. For this to be assured, not only commercial acceptance is required, but it also needs to be ensured that the final fluoropolymer will not lead to emissions of undesirable PFAS. The fact that industry has placed substantial efforts in such developments is proven by the relatively large number of patents that have been deposited over the last two decades.

Due to the increased regulatory pressure, and also to a better understanding by industry of the increasing constraints in terms of societal acceptance of chemical risk, significant progress has been achieved over the past years on the development of NFPA technology. In fact, only in the year 2022, up to 5 announcements from 3 different fluoropolymer suppliers have been released describing upcoming implementation of different manufacturing methods that will remove the need to continue using FPAs. Such announcements are not only based on achieved technical progress, but also on successful introduction of new fluoropolymer grades on the market, including customer acceptance. This demonstrates that such NFPA technology is not a vague concept or an aspiration, but a reality that should be developed by industry in a relatively short timeframe.

It is possible that not all suppliers will be ready to introduce such changes at the same pace, for every single fluoropolymer grade. Due to the well-established high value of fluoropolymers to many critical applications for society, it is expected that those uses should be allowed to continue, while likely on a time-limited basis. Nevertheless, efforts should be made by industry to ensure that all feasible abatement techniques are in place to guarantee that PFAS emissions from the manufacture of fluoropolymer is kept as low as possible.

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35 Bruno Ameduri, 'The Promising Future of Fluoropolymers' (2020) Macromol Chem Phys, 1900573.

36 ECHA, 'Registry of restriction intentions until outcome - Per- and polyfluoroalkyl substances (PFAS)' (2023).

This article also suggests a regulatory frame for fluoropolymers which is based on the need to exclude fluoropolymers that are manufactured with NFPA technology from any future restriction on their use. This is based on the fact that fluoropolymers are substances that pose no hazard to human health or the environment. Removing FPAs from their manufacture takes away the only real concern associated to fluoropolymers. The lack of degradability and the possibility to effectively destroy them during end-of-life without generating further PFAS emissions supports this principle. The proposal considers the need of other considerations such as uses that are critical for society (pending a final definition of the essential use concept) or the availability of alternatives to provide derogations to continue using fluoropolymers manufactured with FPAs, which should in any case be granted under specific time limits and with the obligation to introduce highly efficient abatement techniques to minimize emissions.

Appendix

Table 1: Summary of identified patents on fluoropolymers and NFPA (in no particular order)

Name of the patent	Company	Application	Reference
Fluoropolymer dispersions containing no or little low molecular weight fluorinated surfactant	3M	United States	Dadalas et al., 2005
Polymerization of Halogen-Containing Monomers Using Siloxane Surfactant and Aqueous Composition	ARKEMA	United States	Wille et al., 2005a
Polymerization of fluoromonomers using 3-ally-loxy-2hydroxy-1propanesulfonic acid salt as surfactant	ARKEMA	United States	Wille et al., 2005b
Emulsifier free aqueous emulsion polymerization to produce copolymers of a fluorinated olefin and hydro-carbon olefin	3M	United States	Kaspar et al., 2006
Process for preparing fluoropolymer dispersions	SOLVAY SPECIALTY POLYMERS ITALY	United States	Kapeliouchko et al., 2007
Process for preparing fluoropolymer	DAIKIN	United States	Otsuka et al., 2009
Preparation and Stabilization of Fluoropolymer Dis-persions by Aqueous Emulsion Polymerization with Carbosilane Surfactants	3M	United States	Bissinger et al., 2010
Aqueous process for making fluoropolymers	ARKEMA	United States	Amin-Sanayei et al., 2011
Polymerization of Fluoropolymers Using Alkyl Phos-phonate Surfactants	ARKEMA	United States	Durali et al., 2012
Aqueous Process for Making a Stable Fluoropolymer Dispersion	ARKEMA	United States	Amin-Sanayei et al., 2012a
Aqueous Process for Making Polyvinylidene Fluoride Dispersion	ARKEMA	United States	Amin-Sanayei et al., 2012b
Polymerization of fluoropolymers using polycaprolac-tone	ARKEMA	European patent specification	Hedhi, 2013
Polymerization of fluoropolymers using non-fluorinat-ed surfactants	ARKEMA	United States	Durali et al., 2014
Synthesis of making 2,3,3,3-tetrafluoropropene con-taining fluoropolymers	ARKEMA	United States	Amin-Sanayei et al., 2014
Method for producing aqueous fluorinated polymer dispersion, aqueous fluorinated polymer dispersion and fluorinated polymer	AGC	United States	Toyoda et al., 2015

Fluoropolymer Compositions Containing a Polyol Compound as Emulsifier and Methods of Making Them	3M	United States	Zipplies et al., 2015
Method of producing fluoropolymers using alkyl sulfate surfactants	ARKEMA	United States	Amin-Sanayei et al., 2016
Method of Producing Fluoropolymers Using Acid-Functionalized Monomers	ARKEMA	United States	Durali et al., 2016
Aqueous polymerization of fluoromonomer using hydrocarbon surfactant	CHEMOURS	European patent specification	Brothers et al., 2016
Employing polyalkylene oxides for nucleation in aqueous polymerization of fluoromonomer	CHEMOURS	United States	Brothers et al., 2019
Fluoropolymer aqueous dispersion production method and fluoropolymer aqueous dispersion	DAIKIN	United States	Hayashi et al., 2020
Method for stabilizing aqueous dispersions of fluorinated polymers	SOLVAY SPECIALTY POLYMERS ITALY	United States	Carella et al., 2020
Peroxide curable fluoropolymers obtainable by polymerization with non-fluorinated emulsifiers	3M	United States	Jochum et al., 2020
Method for producing modified polytetrafluoroethylene, method for producing modified polytetrafluoroethylene powder, and method for producing stretched porous material	AGC	United States	Higuchi et al., 2020
Process for preparing fluoropolymers and fluoroelastomers in presence of a non fluorinated sulfonate type hydrocarbon containing surfactant thereof	GUJARAT FLUOROCHEMICALS	European patent specification	Chauhan et al., 2022

Table 2. Summary of recent announcements by fluoropolymer manufacturers on commercial progress to introduce NFPA technology in the manufacture of fluoropolymers that previously required the use of FPA.

Development of NFPA technology by fluoropolymer manufacturers	
PTFE Aqueous dispersions	Gujarat Fluorochemicals (2022a)
PTFE Fine powders	Gujarat Fluorochemicals (2022c)
PVDF	Arkema (PCI, 2008), Solvay (2022), Gujarat Fluorochemicals (2022c)
FKM	Chemours (2022b), Solvay (2022), Gujarat Fluorochemicals (2022b)
PFA	Gujarat Fluorochemicals (2022c)

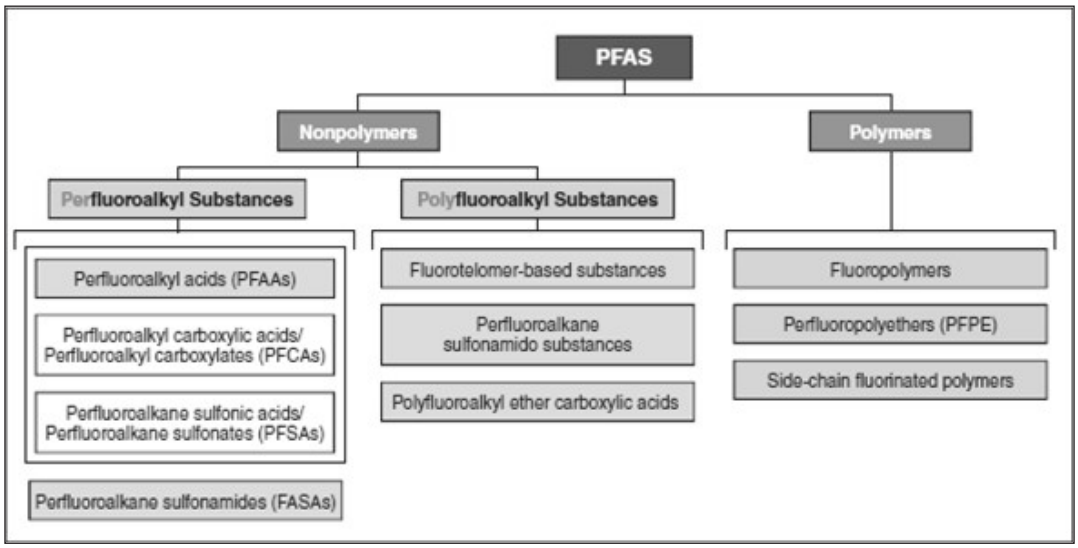


Figure 1: Commonly recognized PFAS groups of substances

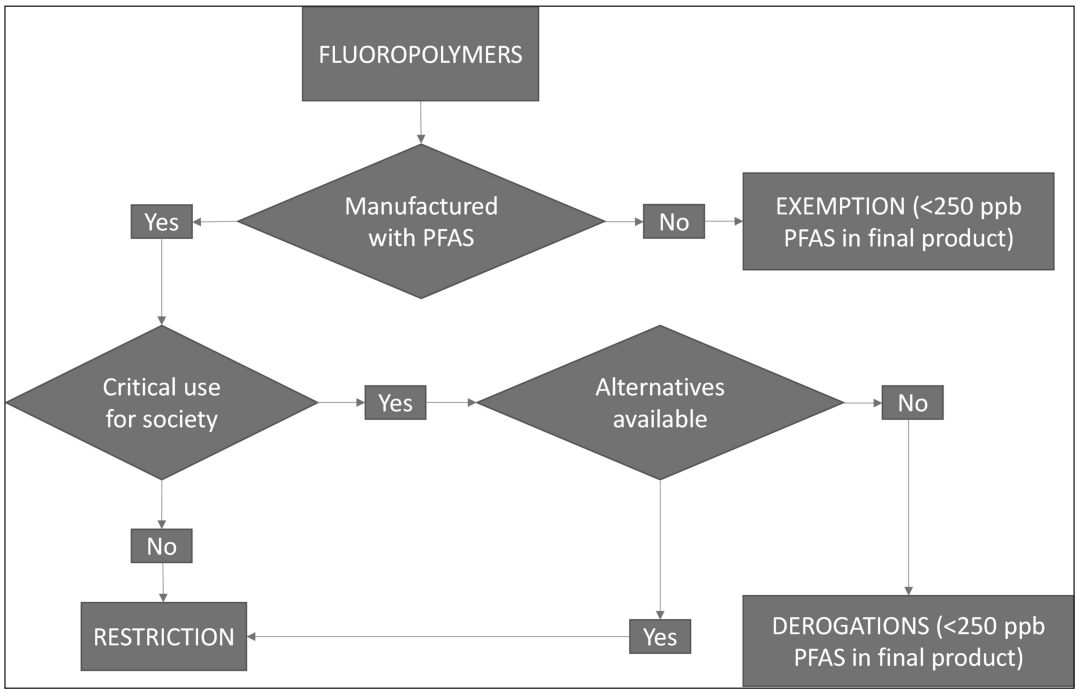


Figure 2: Summary of the regulatory process recommended for fluoropolymers

Responsible manufacturing of fluoropolymers without the use of fluorinated polymerization aids (FPAs)

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Prepared by	**Priyanga Gunasekar**, **Deepak Kapoor**
Checked by	**Christiane Brandt, Ramboll Deutschland GmbH**

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1. Introduction

From the U.S. to Europe and beyond, authorities are developing legislative and regulatory approaches to limit exposure to, and adverse health and environmental effects from, per- and polyfluoroalkyl substances (PFAS). Currently, many of the proposals include fluoropolymers in their definition of PFAS, likely because some manufacturers use and emit fluorinated polymerization aids[1] (FPAs) in the polymerization of their fluoropolymers. Regulators and scientists believe that the use of fluorinated polymerization aids in the manufacture of fluoropolymers is a considerable source of PFAS pollution in the environment (Prevedouros, Cousins, Buck, & & Korzeniowski, 2006).

Several manufacturers like Arkema, Gujarat Fluorochemicals, Honeywell & Solvay can already produce most of their fluoropolymers without the use of fluorinated polymerization aids and are voluntarily committed to completely stop their use in their manufacturing processes.

Fluoropolymers produced without fluorinated polymerization aids pose no risk to the environment and therefore should be exempted from the coming PFAS restrictions.

Fluoropolymers are crucial to, and irreplaceable in semiconductors, lithium-ion batteries and hydrogen fuel cells for electric vehicles, renewable energy, transportation, medical equipment, chemical process industry, food processing, water filtration systems, data transmission and electronics, and so on. It is therefore crucial to develop environmentally sustainable technologies to produce fluoropolymers, as several manufacturers made it possible, and comply with the regulatory requirements.

PFOA (per fluoro octanoic acid) was historically used as a surfactant, e.g., in the emulsion polymerisation of Polytetrafluoroethylene (PTFE), which use, however, has been restricted globally due to its negative impact on the environment and human health. Unfortunately, producers have shifted to C6 PFAS chemistry like HFPO-DA (Gen-X) or ADONA or PFHxS. This shift from C8 PFOA to C6 PFAS can be considered a regrettable substitution of one PFAS of concern by another. Therefore, regulators and environmentalists are demanding to stop the use of any PFAS as polymerization aid in fluoropolymer manufacturing (see Figure 1).

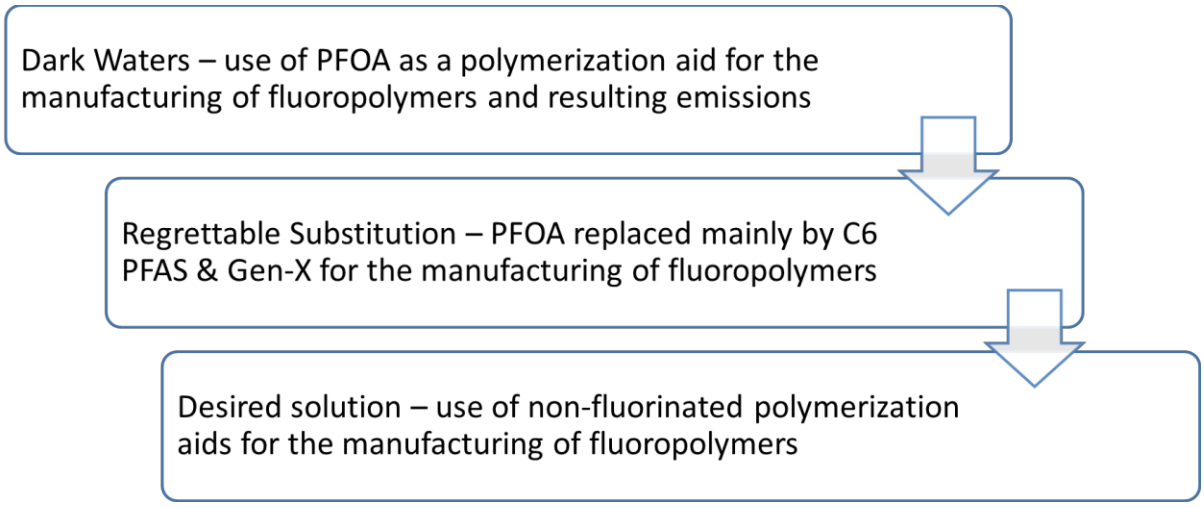


Figure 1: Transition in fluoropolymer manufacturing to the use of non-fluorinated polymerization aids.

[1] Fluorinated polymerization aids (FPAs) are also known as Fluorosurfactants and fluorinated emulsifiers

2. Use of (fluorinated) polymerization aids in fluoropolymer manufacturing

Fluoropolymers can be polymerized using two methods – Suspension polymerization and Emulsion polymerization. Suspension polymerization does not require the use of polymerization aids and therefore more than 50% of fluoropolymers made using suspension processes do not require the use of polymerization aids during manufacturing. However, emulsion polymerization processes require the use of polymerization aids (PFAS or non-PFAS). In emulsion polymerization, the monomer is dispersed in an aqueous medium with the help of an emulsifier. This process involves the formation of micelles, which act as reaction sites for the polymerization reaction to occur. The process offers advantages such as high polymerization rates, control over particle size, and the ability to incorporate hydrophobic monomers.

The manufacture of fluoropolymers has been flagged as a major source of environmental pollution in different parts of Europe (Italy, France, the Netherlands), the USA and China (Gebbink & Leeuwen, 2020); (Lohmann, et al., 2020); (Jia, et al., 2021). It is important to note that, this concern is not related to fluoropolymers as individual substances, but to the use of non-polymeric, low molecular weight, water soluble PFAS that are used as polymerization aids.

Historically, PFOA (per fluoro octanoic acid) was used as a surfactant in the emulsion polymerization of fluoropolymers. After realising its toxic nature and impact to the human health, its manufacturing and use has been restricted globally. At present, except for some producers in China, no one really uses PFOA in the manufacturing of Fluoropolymers. Since then, the producers outside China have shifted to C6 PFAS chemistry like HFPO-DA (Gen-X) or ADONA or PFHxS. Regulators and environmentalists consider this replacement of C8 PFOA by C6 PFAS as a regrettable substitution of one PFAS of concern by another. As a result, and also as evident from the PFAS Restriction Proposal, regulators and environmentalists are demanding to stop the use of PFAS as polymerization aids by fluoropolymer manufacturers (ECHA, 2023).

2.1 Function of polymerization aids/surfactants during emulsion polymerization

Polymerization aids have a strong effect in reducing the surface tension between the water and the air, as well as the interfacial tension between the water and otherwise immiscible liquids such as monomers. These surfactants are made up of long hydrophobic tail (carbon chain) and hydrophilic head which helps in dispersion of colloidal particles (e.g., polymers) in immiscible liquids by forming micelles to make latex (see Figure 2).

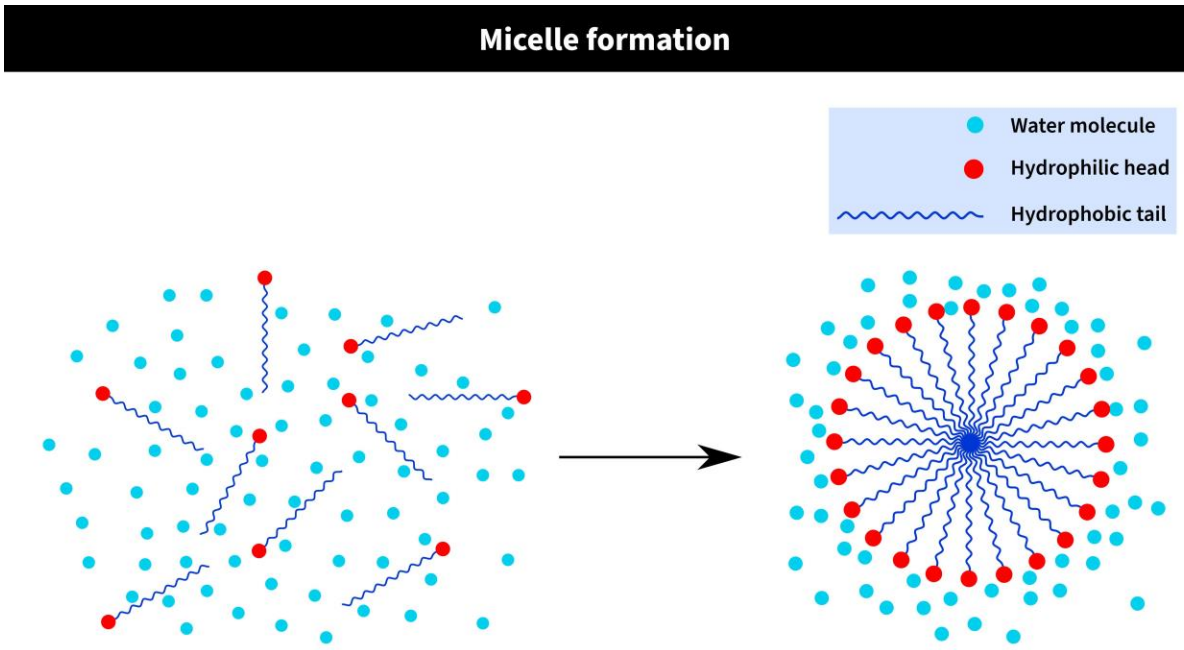


Figure 2: Micelle formation

The amount and chemical structure of the polymerization aid(s)/surfactant(s) used in emulsion polymerization have a strong influence on conversion, particle size and distribution, viscosity, overall latex stability, and purity. Halogenated surfactants and hydrocarbon surfactants are two types of surfactants commonly used in emulsion polymerization. The main difference between them lies in their chemical composition, specifically the presence of halogen atoms.

2.2 PFAS emissions during the lifecycle of fluorinated polymerization aids (FPAs)

When fluorinated polymerization aids are used for fluoropolymer production, PFAS emissions result from various lifecycle stages of FPAs as mentioned below:

a. manufacture of raw materials of FPAs (also PFAS)
b. manufacture of FPAs
c. storage, packaging and transportation of FPAs
d. during the use (and emissions thereof) of FPAs in manufacture of fluoropolymers
e. release of FPAs during processing of fluoropolymers

FPAs are highly water soluble, volatile substances that may breakdown to other unknown, persistent and low temperature volatile PFAS in the environment which are very difficult to identify, and to capture. Furthermore, the packaging of FPAs causes additional environmental burden as the packaging units cannot be completely cleaned from the FPAs. Any surface coming in contact with FPAs would eventually require high temperature resulting in additional PFAS emissions to the environment from the packaging waste stage.

The manufacture, use and disposal of FPAs has been the main source of PFAS emissions linked to manufacturing of fluoropolymers (Prevedouros, Cousins, Buck, & & Korzeniowski, 2006). These FPAs are not intermediates as they are not supposed to get consumed during polymerization. Practically, FPAs entering the reaction vessel(s) must therefore be recovered fully, which is difficult to achieve. The non-recoverable FPAs are partially captured by various abatement techniques such as ultrafiltration,

reverse osmosis, foam fractionation, drying, scrubbing followed by adsorption by ion exchange resin or by granular activated carbon bed (GAC) and destroyed subsequently by thermal oxidation. Not only the FPAs need to be fully recovered and/or abated, their degradation products that could also be low temperature highly volatile PFAS substances also need to be fully captured and destroyed.

2.3 Quantification of FPA use in fluoropolymer production

The projected annual global amount of FPAs used in the production of fluoropolymers in 2025 is estimated on the following data:

FPA used per ton fluoropolymer production:	2-10 kgs
Expected global fluoropolymer consumption in 2025:	400,000 tons
Expected FPA consumption (if unregulated):	400 - 2000 tons

(based on 50% FP production using emulsion polymerization requiring polymerization aids)[2]

2.4 Ways to reduce PFAS emissions from fluoropolymer manufacturing process

The fluoropolymer manufacturing industry has made significant efforts in improving the abatement technologies to recover, reuse and recycle FPAs in order to reduce emissions of PFAS from the manufacturing process of fluoropolymers. The strategies of containment of PFAS emissions involve the recovery, removal and purification, of the polymerization aids from off-gases, waste-water streams, aqueous dispersions, and final products by means of sorption techniques, microbial degradability and recyclability of FPAs.

However, it needs to be acknowledged that achieving an absolute zero value of emissions in manufacturing processes using only best available abatement techniques where PFAS are used is technically impossible because due to the highly adsorptive properties of FPAs every surface that comes in contact with fluorinated polymerization aid would require incineration at high temperatures and FPAs may break down to low temperature volatiles which are difficult to capture. Cleaning of these surfaces would result in environmental emissions of PFAS to water and potentially also air. If the goal is to ensure zero or close to zero PFAS emissions, it is highly unlikely that continued improvement of abatement techniques will achieve this target. With abatement, PFAS emissions due to the use of FPA can be reduced to a certain extent but given the persistent nature of these water soluble and bioaccumulative substances any emissions should be completely avoided. Therefore, the practical and applicable solution is substitution of fluorinated polymerization aids by non-fluorinated polymerization aids supported by abatement (wherever required). We cite two cases below to demonstrate that currently used abatement technologies alone can be insufficient to control PFAS emissions.

Case 1: The Indaver case

As an example, the waste management company Indaver processing waste containing PFAS from Chemours & 3M was found to be the major source of PFAS emissions into water and air (information taken from the ZEMBLA website[3]).

[2] For the estimation of annual global tonnages according to Sales et al., 2022, please refer to Table 2.
[3] Zembla - BNNVARA

In the broadcast, 'The PFAS scandal' (8 September 2022)[4], Zembla revealed that the Dutch government has been very worried about the Antwerp waste processor Indaver behind the scenes for at least a year. The company has been discharging PFAS into the water for years and appears to be an important source of PFAS pollution in the Dutch Western Scheldt. In Belgium, there was a big commotion in 2021 when it turned out that the chemical company 3M in Antwerp has discharged enormous amounts of PFAS into the river Scheldt for years. The water turned out to be contaminated with PFAS as far away as Zeeland in the Netherlands. The revelations about 3M led to a parliamentary investigation in Flanders and to the shutdown of the factory at the end of last year. But the concentrations of PFAS did not decrease after the intervention at 3M, says environmental chemist Chiel Jonker of Utrecht University, who analyses water data for Rijkswaterstaat. The scientist therefore investigated other sources and came to the conclusion that the Antwerp waste processor Indaver is an "important source" for PFAS pollution in the Western Scheldt, he says in Zembla. That company processes large quantities of PFAS-containing material from Europe but fails to destroy all PFAS. Some of the PFAS that Indaver discharged and released into the air until recently also turned out not to be a permit.

Case 2: U.S. EPA's Clean Water Act enforcement action to address PFAS discharges at Washington Works facility

As referenced in the EPA newsletter dated April 26, 2023, the U.S. Environmental Protection Agency has ordered the Chemours Company to take corrective measures to address pollution from PFAS in stormwater and effluent discharges from the Washington Works facility near Parkersburg[5]. The order on consent also directs Chemours to characterize the extent of PFAS contamination from discharges.

This is the first EPA Clean Water Act enforcement action ever taken to hold polluters accountable for discharging PFAS into the environment. According to the EPA order, PFAS levels in the discharges from the facility exceed levels that are set in the facility's Clean Water Act permit.

Under the Clean Water Act, it is unlawful to discharge pollutants into U.S. waterways except pursuant to a National Pollution Discharge Elimination System (NPDES) permit, issued by EPA or a state. The permit sets pollution discharge limits, monitoring and reporting requirements, and other conditions designed to protect water quality.

Chemours operates several manufacturing units at the Washington Works facility, which produce fluorinated organic chemical products including fluoropolymers. The facility discharges industrial process water and stormwater to the Ohio River and its tributaries, under the terms of a NPDES permit issued in 2018 by the West Virginia Department of Environmental Protection. E.I. du Pont de Nemours and Company was the NPDES permit holder at Washington Works until 2015. In 2015, the permit was transferred to Chemours. The permit imposes discharge limits and requires monitoring of certain pollutants, including PFAS such as perfluorooctanoic acid (PFOA), which was used in the past as a processing aid for manufacturing, and HFPO Dimer Acid, also known as GenX -- which replaced PFOA as a processing aid.

In an administrative compliance order on consent (AOC) issued on the date, EPA sets forth that this facility exceeded permit effluent limits for PFOA and HFPO Dimer Acid on various dates from

[4] Podcast: The PFAS scandal - Zembla - BNNVARA

[5] EPA takes first-ever federal Clean Water Act enforcement action to address PFAS discharges at Washington Works facility near Parkersburg, W. Va. | US EPA

September 2018 through March 2023, and that Chemours failed to properly operate and maintain all facilities and systems required for permit compliance.

As an initial step in characterizing PFAS in surface water discharges, EPA's order requires Chemours to implement an EPA-approved sampling plan to analyze PFAS and conduct analysis to further understand the presence of PFAS in stormwater and effluent discharged from the facility. Also, Chemours will submit and implement a plan to treat or minimize the discharge of PFAS to ensure compliance with numeric effluent limits of PFOA and HFPO Dimer Acid.

In conclusion, although highly efficient abatement technologies are available, not all companies are using these best available techniques to minimise PFAS emissions which can lead to significant environmental pollution as demonstrated by the two case studies.

3. Industry's R&D efforts to develop the use of Non-Fluorinated Polymerization Aids (NFPA)

Over the past years, the fluoropolymer industry has undertaken significant efforts to introduce NFPA technologies to manufacture fluoropolymers. Several manufacturers of fluoropolymers have filed multiple patents on NFPA technology over the past 2 decades, which explains a high focus and investment in this direction by the industry.

The below table provides a list of identified patents related to the use of NFPA technologies for the manufacture of fluoropolymers as published over the last years (Ameduri, Sales, & Schlipf, 2023).

Table 1: Non-exhaustive list of identified patents on NFPA technology to manufacture fluoropolymers (Ameduri, Sales, & Schlipf, 2023)

Name of the patent	Company	Application	Reference
Fluoropolymer dispersions containing no or little low molecular weight fluorinated surfactant	3M	United States	Dadalas et al., 2005
Polymerization of Halogen-Containing Monomers Using Siloxane Surfactant and Aqueous Composition	ARKEMA	United States	Wille et al., 2005a
Polymerization of fluoromonomers using 3-allyloxy-2hydroxy-1propanesulfonic acid salt as surfactant	ARKEMA	United States	Wille et al., 2005b
Emulsifier free aqueous emulsion polymerization to produce copolymers of a fluorinated olefin and hydrocarbon olefin	3M	United States	Kaspar et al., 2006
Process for preparing fluoropolymer dispersions	SOLVAY SPECIALTY POLYMERS	United States	Kapeliouchko et al., 2007
Process for preparing fluoropolymer	DAIKIN	United States	Otsuka et al., 2009
Preparation and Stabilization of Fluoropolymer Dispersions by Aqueous Emulsion Polymerization with Carbosilane Surfactants	3M	United States	Bissinger et al., 2010
Aqueous process for making fluoropolymers	ARKEMA	United States	Amin-Sanayei et al., 2011

Name of the patent	Company	Application	Reference
Polymerization of Fluoropolymers Using Alkyl Phosphonate Surfactants	ARKEMA	United States	Durali et al., 2012
Aqueous Process for Making a Stable Fluoropolymer Dispersion	ARKEMA	United States	Amin-Sanayei et al., 2012a
Aqueous Process for Making Polyvinylidene Fluoride Dispersion	ARKEMA	United States	Amin-Sanayei et al., 2012b
Polymerization of fluoropolymers using polycaprolactone	ARKEMA	European patent specification	Hedhi, 2013
Polymerization of fluoropolymers using non-fluorinated surfactants	ARKEMA	United States	Durali et al., 2014
Synthesis of making 2,3,3,3-tetrafluoropropene containing fluoropolymers	ARKEMA	United States	Amin-Sanayei et al., 2014
Method for producing aqueous fluorinated polymer dispersion, aqueous fluorinated polymer dispersion and fluorinated polymer	AGC	United States	Toyoda et al., 2015
Fluoropolymer Compositions Containing a Polyol Compound as Emulsifier and Methods of Making Them	3M	United States	Zipplies et al., 2015
Method of producing fluoropolymers using alkyl sulfate surfactants	ARKEMA	United States	Amin-Sanayei et al., 2016
Method of Producing Fluoropolymers Using Acid-Functionalized Monomers	ARKEMA	United States	Durali et al., 2016
Aqueous polymerization of fluoromonomer using hydrocarbon surfactant	CHEMOURS	European patent specification	Brothers et al., 2016
Employing polyalkylene oxides for nucleation in aqueous polymerization of fluoromonomer	CHEMOURS	United States	Brothers et al., 2019
Fluoropolymer aqueous dispersion production method and fluoropolymer aqueous dispersion	DAIKIN	United States	Hayashi et al., 2020
Method for stabilizing aqueous dispersions of fluorinated polymers	SOLVAY SPECIALTY POLYMERS	United States	Carella et al., 2020
Peroxide curable fluoropolymers obtainable by polymerization with non-fluorinated emulsifiers	3M	United States	Jochum et al., 2020
Method for producing modified polytetrafluoroethylene, method for producing modified polytetrafluoroethylene powder, and method for producing stretched porous material	AGC	United States	Higuchi et al., 2020
Process for preparing fluoropolymers and fluoroelastomers in presence of a non-fluorinated sulfonate type hydrocarbon containing surfactant thereof	GUJARAT FLUOROCHEMICALS	European patent specification	Chauhan et al., 2022

3.1 Commercialization of NFPA technology to manufacture fluoropolymers

For many years, industry has placed significant efforts to reduce emissions of PFAS from the manufacturing process of fluoropolymers by developing alternative processes such as the non-fluorinated polymerization aid (NFPA) technology that do not require the use of PFAS polymerization aids.

In the recent past, and mainly in 2022, various fluoropolymer manufacturers as listed below have released statements announcing discontinuation of use of FPAs in the manufacturing of specific fluoropolymers. Today, technologies exist to produce PTFE, polyvinylidene fluoride (PVDF),

fluoroelastomer[6] (FKM) and perfluoroalkoxy alkane (PFA) that no longer require the use of FPAs. Few major players like Arkema, Solvay, GFL and Honeywell have announced commitments to put a total stop on use of FPAs in the near future[7]. Chemours has announced the development of non-FPA technology in the production of FKM. Hence, PFAS emissions from manufacturing of PFAS polymerization aids, its packaging, transportation and its use during polymerization can be eliminated. Thus, by stopping the use of fluorinated polymerization aids for fluoropolymers, significant amount of PFAS emissions can be prevented.

Table 2: Global fluoropolymer portfolio and its use of FPA (from Sales et al., 2022)

Fluoropolymer	Type	Use of surfactant	NFPA availability	Global volume (MT) in 2018	Expected global volume (MT) in 2025	Percentage volume in 2025
PTFE	Suspension	No	-	85,000	85,000	21%
PTFE	Emulsion	Yes	Yes	85,000	85,000	21%
PVDF	Suspension	No	-	25,000	60,000	15%
PVDF	Emulsion	Yes	Yes	25,000	60,000	15%
FKM Copolymer	Emulsion	No	-	30,000	30,000	8 %
FKM Terpolymer	Emulsion	Yes	Yes	5,000	5,000	1 %
PFA	Emulsion	Yes	Yes	3,500	9,500	3%
PCTFE	Emulsion	Yes	Yes	8,500	8,500	2%
FEP	Emulsion	Yes	No	32,000	32,000	8%
Others		Yes	No	21,000	25,000	6%
Total				320,000	400,000	

As of today, there are technologies available to manufacture 84% of fluoropolymers without the use of fluorinated polymerization aids (Sales, Hernández, Kapoor, & Noort, 2022) as given in the above table. This includes 100% of the three main fluoropolymers by volume: polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and fluoroelastomers (FKM).

[6] Class of fluorinated, carbon-based synthetic rubber, known as fluoroelastomer

[7] GFL - https://www.gfl.co.in/upload/pages/10914fb441b77c128b9a0762dee4fc46.pdf
https://www.gfl.co.in/upload/pages/ebce5fed9030753d0ee651bf1f48d0a0.pdf
https://www.gfl.co.in/upload/pages/a6132d2292fc0ad3a9a0751dad818450.pdf

Solvay - https://www.solvay.com/en/innovation/science-solutions/pfas

Arkema - https://www.arkema.com/global/en/media/newslist/news/global/corporate/2023/20230221-arkema-position-on-european-proposal-to-restrict-pfas/

Therefore, the non-fluorinated polymerization aid technology to manufacture fluoropolymers is well researched and commercially established. A mandate from the regulators to completely stop the use of FPAs will expedite the transition from the use of FPA to NFPA to manufacture fluoropolymers.



3.2 Reduction in PFAS emissions due to the use of NFPA

Ramboll, an independent consultancy, in their case study on the PFAS emissions during the PTFE lifecycle with focus on manufacturing, has estimated that the overall PFAS emissions associated to manufacturing of 20,000 tons of PTFE using FPA such as HFPO-DA/Gen-X is between 4,200-140,000 kilograms per year. This estimate is based on information provided by GFL and publicly available data. In comparison, with a complete shift to NFPA technology, environmental emissions can significantly be reduced to a maximum of 2 kilograms PFAS per year as the release of FPA will stop completely (Ramboll, 2023).

Ramboll has also estimated total PFAS footprint during the lifecycle of PTFE (detailed report submitted to public consultation of ECHA) produced without the use of FPA and under consideration on the proposed future limit of 250 ppb for the sum of PFAS in products to a maximum of 9 kilograms per annum for 20000 tons of PTFE.

4. GFL's development and commercialization of NFPA technology

GFL manufactures 4 fluoropolymers – PTFE, PVDF, PFA and FKM. GFL has made a complete switchover from FPA [redacted] to NFPA in the manufacturing of PTFE aqueous dispersions, PVDF and FKM, at the time of preparation of this report. Furthermore, GFL plans to stop the use of FPA in the manufacturing of PTFE Fine powders before the end of 2023. It has also developed the NFPA technology to manufacture PFA - another fluoropolymer important for the semiconductor industry. GFL has submitted a detailed technical dossier explaining key aspects of its NFPA technology to European regulators in 2022.

GFL is committed to completely stop the use of FPAs in the manufacture of its entire portfolio of fluoropolymers during 2024.

4.1 General properties of NFPA (hydrocarbon polymerization aid)

The NFPA used by GFL is:

- [redacted]
- neither Persistent, Mobile, Bioaccumulative or Toxic (PBT/PMT) nor very Persistent, very Bioaccumulative (vPvB);
- EU REACH registered; is neither listed in EU Candidate List of Substances of Very High Concern (SVHC) for Authorisation, nor on the US Toxics Release Inventory (TRI).

Furthermore:

- NFPA based products exhibit equal or even better properties/specifications when compared to grades based on FPA (see section 4.2).
- **NFPA can be used to manufacture high molecular weight fluoropolymers, homopolymers, modified fluoropolymers, copolymers and terpolymers.**

4.2 Comparative technical analysis of products made with and without FPA

GFL performed analytical studies to demonstrate that all the required physiochemical properties of final polymers are met when using NFPA in the polymerization. Properties of final polymers produced using NFPA show comparable results, or even improved ones, in a selection of critical properties when compared to same products based on FPA (see Table 3 to Table 5).

PTFE:

From the results obtained in the below tables, higher values of stability and critical cracking thickness have been achieved with PTFE dispersion products (both homopolymers and modified polymers) made using the NFPA, which suggests an improved performance over PTFE manufactured with FPA. It is also interesting to note that Standard Specific Gravity (SSG) values and melting points measured indicate the formation of high molecular weight PTFE, which is a desired outcome for both PTFE emulsions and fine powders as required for its industrial applications. Values of Thermal instability index are also meeting the critical level of <50 units as per US FDA requirements.

Table 3: Comparison of basic properties of PTFE manufactured with FPA and with NFPA

Property	Standard[8]	Unit	FPA based PTFE	NFPA based PTFE
Specific Gravity	ASTM D792	-	2.14 - 2.18	2.14 - 2.18
Water Absorption (Max.)	ASTM D570	%	0.004	0.004
Average particle size	ASTM D4895	µm	500	500
Bulk density	ASTM D4895	gm / cc	500	500
Thermal Instability Index	ASTM D4895	-	<50	<50

[8] Refer ASTM D543 for chemicals used for chemical resistance. Observed values are change in weight and dimension by chemical action.

Property	Standard[8]	Unit	FPA based PTFE	NFPA based PTFE
Mechanical				
Tensile Modulus (min.)	ASTM D638	MPa	500	500
Tensile Strength	ASTM D638	MPa	>25	>25
Elongation of Break	ASTM D638	%	>250	>250
Hardness				
Durometer Hardness (shore D)	ASTM D2240		58-62	58-62
Thermal				
Melting Temperature	ASTM D4591	°C	327-345	327-345
CLTE – Axial	ASTM D696	cm/cm/°C	150-275	180
Specific heat	ASTM D4591	Kcal/Kg°C	0.23-0.26	0.23-0.26
Electrical				
Surface resistivity		Ωm	$>10^{15}$	$>10^{15}$
Volume resistivity		Ωm	$>10^{18}$	$>10^{18}$
Aqueous dispersion PTFE				
Solid Content	ASTM D4441	%	58-62	58-62
pH Value	ASTM D4441	-	9.0-11.0	9.0-11.0
Surfactant content (PTFE basis)	ASTM D4441	%	3.0-8.0	3.0-8.0
Latex Particle Size	GFL Internal	nm	200-300	200-300
Viscosity	ASTM D2196	cps	15-30	15-30
Shear Stability	GFL Internal	min	>20	>20
Zeta Potential	GFL Internal	mV	<-50	<-50
Critical cracking thickness	GFL Internal	µm	>15	>15

PVDF:

From the results as in Table 4, it is clear that the mechanical, thermal, electrical properties of PVDF (both homopolymer and copolymer) manufactured using NFPA show similar performance to PVDF manufactured using FPA.

Table 4: Comparison of properties of PVDF manufactured with FPA and with NFPA

Properties	Standard	Unit	FPA based PVDF	NFPA based PVDF
Specific Gravity	D792	g/cc	1.77 - 1.79	1.77 - 1.79
Water Absorption	D570 Immersion for 24 Hours	%	<0.04	<0.04
Rheology				
Melt Mass Flow Rate	ASTM D1238	g/min	1.0 - 30	1.0 - 30
Molding Shrinkage - Flow	Internal Method	%	< 3	< 3
Mechanical				
Tensile Modulus	ASTM D638	MPa	1400 – 2300	1400 – 2300
Tensile Strength (yield)	ASTM D638	MPa	40 – 60	40 – 60
Tensile Elongation (yield)	ASTM D638	%	5 – 10	5 – 10
Tensile Strength (break)	ASTM D638	MPa	30 – 50	30 – 50

Tensile Elongation (Break)	ASTM D638	%	>20	>20
Taber Abrasion Resistance	ASTM D4060	mg	5 – 10	5 – 10
Flexural Modulus at 23°C	D790	MPa	1400 - 2300	1400 - 2300
Hardness				
Durometer Hardness (shore D)	ASTM D2240		73 – 80	73 – 80
Thermal				
Melting Temperature	ASTM D3418	°C	156 – 172	156 – 172
Deflection Temperature under load (1.80Mpa)	ASTM D648	°C	110	110
Vicat Softening Temperature	ASTM D1525	°C	140	140
CLTE – Axial	ASTM D696	cm/cm/°C	1.4×10^{-4}	1.4×10^{-4}
Electrical				
Volume Resistivity	ASTM D257	Ohm-m	$> 10^{12}$	$> 10^{12}$
Dielectric Strength	ASTM D149	kV/mm	20 - 25	20 - 25

Fluoroelastomers:

Table 5: Comparison of properties of FKM terpolymer manufactured with FPA and with NFPA

Properties	**Standard**	**Unit**	**FPA based FKM**	**NFPA based FKM**
Specific gravity at 23°C	ASTM D792	gm/cm^3	1.80 - 1.86	1.80 - 1.86
Mooney viscosity at 121 °C	ASTM D1646	MU	40 - 50	40 - 50
Fluorine content	-	%	66 – 68	66 – 68
Glass transition	ASTM D4591	°C	-20	-20

4.3 The (non)issue of colour difference and its insignificance

In some cases, for example PTFE fine powders and PFA, the color of the product, pre- and post-processing, will change when hydrocarbon polymerization aids are used. This is just a cosmetic difference and has no bearing on product processibility and performance. Fluoropolymers are primarily used in industrial setups where there is no white color requirement.

When fluoropolymer emulsions are formed using hydrocarbon polymerization aid, the coagulated fluoropolymer resin is prone to “thermally induced discoloration”, which means that a non-white color (dark grey or brown) is formed in the fluoropolymer resin upon heating. The change in color is attributed to the trace amounts of hydrocarbon polymerization aid remaining in the coagulated resin. When the polymerization is done, the surfactant is washed out of the polymer mixture, but some residual polymerization aid remains but they have minimal impact on the polymer’s final properties. The change in color is the result of residual traces of hydrocarbon remaining in the final product. These trace amounts of surfactant are present in the product irrespective of whether it is made with fluorinated or hydrocarbon polymerization aid. The C-F bond in fluorinated polymerization aid is chemically and thermally more stable than the C-H bond in hydrocarbon polymerization aid. Thus, during drying and processing of fluoropolymer resin, the traces of hydrocarbon polymerization aid remaining in the product are thermally decomposed resulting in the dark color. The change in color

has no impact on the purity, processibility and performance of fluoropolymer resins. Pigments can be added to give specific color to the applications wherever required, for example, in cable applications.

4.4 Broad selection criteria of hydrocarbon polymerization aid

Polymerization aids act to decrease the interfacial tension between monomer and aqueous phase, stabilize the latex and generate micelles in which monomers are emulsified and nucleation reactions proceed.

When considering polymerization of fluoromonomers to produce fluoropolymers using hydrocarbon surfactant in place of halogenated surfactant, in some cases, telogenecity may be an additional factor to consider.

Telogenic effect or telogenecity is referred to the formation of telomers due to reaction of hydrocarbon surfactant with free radicals of initiators in the polymerization system. This telogenic behavior leads to a reduced number of polymer chains and thereby a reduced rate of polymer production. To overcome the telogenic effect (lowered reaction rate) of such hydrocarbon surfactants (Sodium Lauryl Sulphate or Dioctyl Sodium Sulfosuccinate) containing C-H bonds they require passivation using oxidizing agents such as hydrogen peroxide or a polymerization initiator in the presence of a passivating adjuvant, usually a metal ion.

Therefore, it is important to choose a hydrocarbon polymerization aid that reduces the chances of telogenecity and is suitable to achieve high polymer molecular weights, and less amount of low molecular weight fractions. One such comparison in the case of PTFE emulsion polymerization is given below (see Table 6 and Table 7).

Table 6: Comparison of fluoropolymer properties manufactured with different hydrocarbon polymerization aids

Properties	**GFL's selected NFPA**	**Dioctyl Sodium Sulfosuccinate (DOSS)**
Reaction control	Good	Incomplete polymerization
Passivation of surfactant	Not required	Necessary
Melting point (1st) of resultant PTFE	344°C	337°C
SSG (indicative of molecular weight)	~2.16	~2.20
TII (US FDA requirement)	<50	>50
Extrusion behavior	Smooth	Poor
Non-targeted PFAS analysis (LC-QTOF)	< 1ppm	>5ppm

TII: thermal instability index

Table 7: Thermogravimetric Analysis (TGA) results

	Properties	GFL's patented NFPA	Dioctyl Sodium Sulfosuccinate (DOSS)
TGA	Onset point	540.34°C	517.23°C
	Offset point	596.23°C	587.57°C
	Weight loss between 350-450°C	0.047%	0.501%

When PTFE is polymerized using Sodium Lauryl Sulphate (SLS), Dioctyl Sodium Sulfosuccinate (DOSS) as commonly available hydrocarbon surfactants, based on experimental data, it is found to give undesirable results in terms of incomplete polymerization, lower average molecular weight, higher level of lower molecular weight fractions, high thermal instability index (TII), poor processing behavior and formation of higher level of PFAS by-products. In comparison, the hydrocarbon surfactant selected by GFL to produce PTFE emulsions achieve all desired properties including high molecular weight and performance critical for high end applications.

4.5 Analysis of PFAS by-products in fluoropolymers manufactured using NFPA

Fluoropolymers manufactured using NFPA by GFL were analyzed for the presence of PFAS by-products using U.S. EPA recommended (modified) 537.1 method for PFAS analysis. This method analyses the presence of targeted PFAS by solid phase extraction and Ultra-Performance Liquid Chromatography/Tandem Mass Spectrometry (UPLC-MS/MS).

Using the above method, 45 PFAS commonly found in the environment were analyzed in commercial fluoropolymers (PTFE, PVDF and FKM) manufactured with NFPA. The common result of all tested fluoropolymers confirmed the absence of PFAS by-products above the limit of quantification (0.75 – 3.0 µg/L). From the results, we can safely conclude that fluoropolymers manufactured using NFPA technology lead to a significant reduction in PFAS emissions by avoiding the use of FPAs. Also, by selecting the appropriate hydrocarbon polymerization aid, the formation of PFAS by-products can be reduced to insignificant levels. Detailed information on sample preparation and analytical parameters along with the summary of the test results are included in the appendix.

GFL conducted non-targeted PFAS analysis using best available methods on PTFE, PVDF, FKM products produced with non-fluorinated polymerization aids and the results were found to be considerably lower than 250 ppb sum of all PFAS as proposed in the PFAS restriction proposal.

5. Commitment to stop the use of FPA by major fluoropolymer manufacturers

Gujarat Fluorochemicals has voluntarily committed to completely stop the intentional use of PFAS as polymerization aids during 2024 in the manufacture of its entire fluoropolymer portfolio - PTFE, PVDF, FKM, PFA.

Solvay is working towards the objective of manufacturing nearly 100% of fluoropolymers without the use of fluorosurfactants in Spinetta Marengo, Italy by 2026. Their main goal is to phase out the use of fluorosurfactants globally.

Arkema has voluntarily committed to manufacture its fluorinated polymers in Pierre-Bénite without the use of fluorosurfactants by the end of 2024, as well as its other production sites around the world.

Honeywell does not use fluorosurfactants in their fluoropolymer manufacturing process.

5.1 Ease of transition from FPA to NFPA process

It is important to note that the transition from FPA to non-FPA use in fluoropolymer manufacturing does not require any change in the manufacturing equipment or plant setup.

5.2 Not all fluoropolymers require polymerization aids

It is estimated that only 50% of fluoropolymer production requires the use of fluorinated polymerization aids, based on standard manufacturing practices by industry to this date (Sales et al., 2022). For more details, please refer to Table 2.

6. Summary points

- Use of PFAS as polymerization aids is the main cause of PFAS emissions linked to the fluoropolymer lifecycle.
- PFAS polymerization aids can be replaced by safer hydrocarbon polymerization aids (NFPA).
- Major fluoropolymer producers have developed NFPA technologies and hold patents.
- The NFPA technology is well established and commercialized – products are sold globally.
- Many fluoropolymer producers have committed to stop the use of FPAs in the near future.
- At least 80% of current fluoropolymer production can be done without the use of FPA.
- Once mandated by regulators, complete substitution of FPA by NFPA will happen in the near future.

FLUOROPOLYMERS SHOULD BE EXEMPTED AND INSTEAD HARMFUL FLUORINATED POLYMERIZATION AIDS SHOULD BE RESTRICTED.

8. References

Ameduri, B., Sales, J., & Schlipf, M. (2023). Developments in Fluoropolymer Manufacturing Technology to Remove Intentional Use of PFAS as Polymerization Aids. *International Chemical & Law Review (ICRL) 1*, 18-28.

ECHA. (2023). *Annex XV Report - Proposal for a Restriction - Per- and polyfluoroalkyl substances (PFASs).* European Chemicals Agency.

Gebbink, W. A., & Leeuwen, S. P. (2020). Environmental contamination and human exposure to PFASs near a fluorochemical production plant: Review of historic and current PFOA and GenX contamination in the Netherlands. *Environment International (137), 105583*.

Jia, X., Guan, H., Guo, Z., Qian, C., Shi, Y., & Cai, Y. (2021). Occurrence of Legacy and Emerging Poly- and Perfluoroalkyl Substances in Fluorocarbon Paint and Their Implications for Emissions in China. *Environ. Sci. Technol. Lett., 8, 11*, 968-974.

Lohmann, R., Cousins, I. T., DeWitt, J. C., Glüge, J., Goldenman, G., Herzke, D., . . . Wang, Z. (2020). Are fluoropolymers really of low concern for human and environmental health and separate from other PFAS? *Environ Sci Technol., 54 (20)*, 12820–12828.

Prevedouros, K., Cousins, I. T., Buck, R. C., & & Korzeniowski, S. H. (2006). Sources, Fate and Transport of Perfluorocarboxylates. *Environmental Science & Technology, 40 (1)*, 32-44.

Ramboll. (2023). *Assessment of PFAS Esmissions during the Lifecycle pf PTFE: A Case Study.* unpublished report.

Sales, J., Hernández, F., Kapoor, D., & Noort, M. v. (2022). Fluoropolymers: The Safe Science That Society. *Chemical Regultaory & Law Review (ICRL), 1*, 1-11.