CHEMSERVICE

POSITION PAPER

Fluoropolymers: an outlier in the PFAS class of substances

Final report

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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

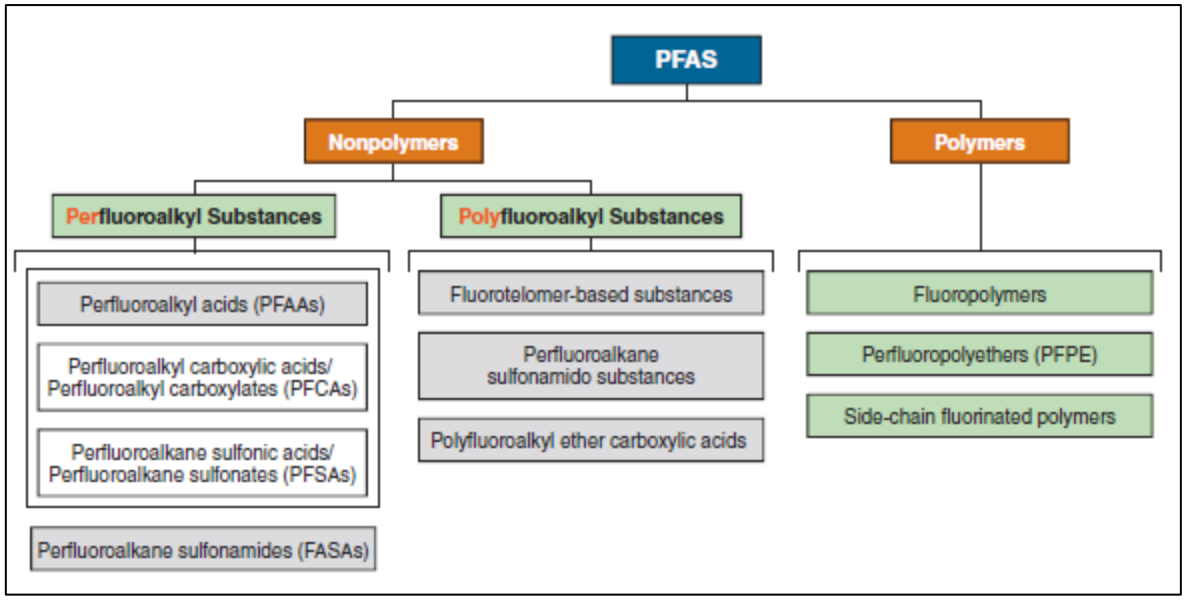
A restriction proposal under the REACH Regulation[1] on per-and polyfluoroalkyl substances (PFAS) is currently under development, in order to limit the risks to human health and the environment from their manufacture and use. Fluoropolymers (FPs), which are high molecular weight polymers with unique 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).

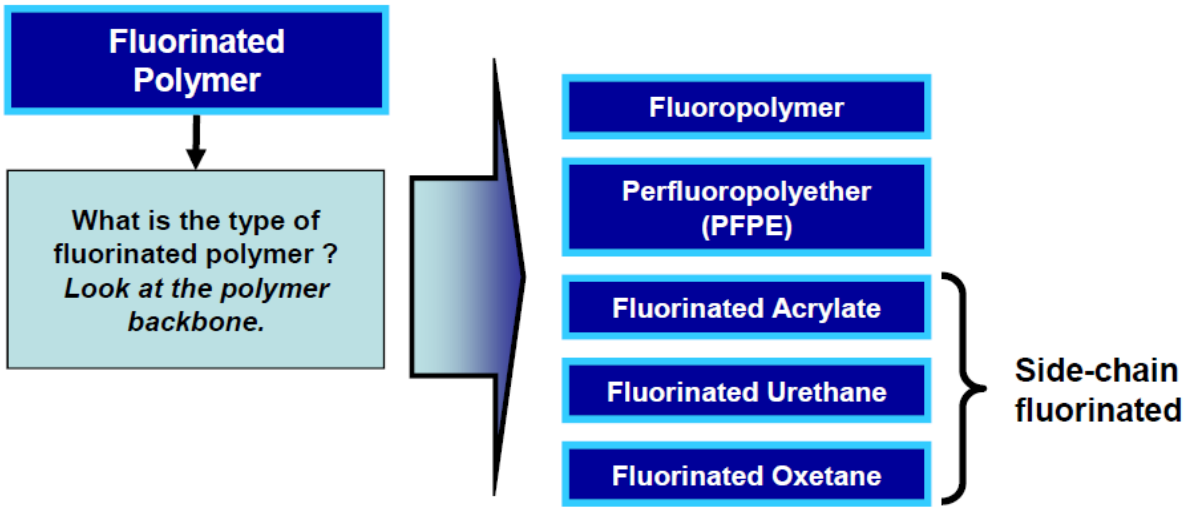
In the case of FPs, this macromolecule is a long chain (backbone) of thousands of connected carbon atoms (C) to which fluorine atoms (F) are bound (FPG, 2022).

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.



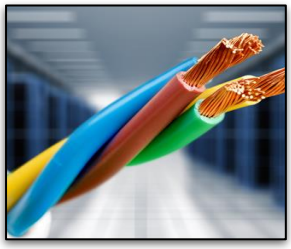
Use and applications.

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).

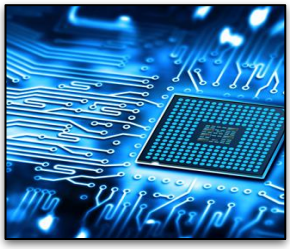
Pharmaceutical

Medical devices

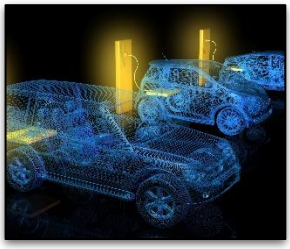
Renewable energy



Telecommunications



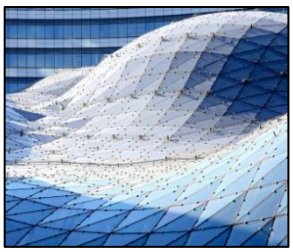
Electronic and semiconductors



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):

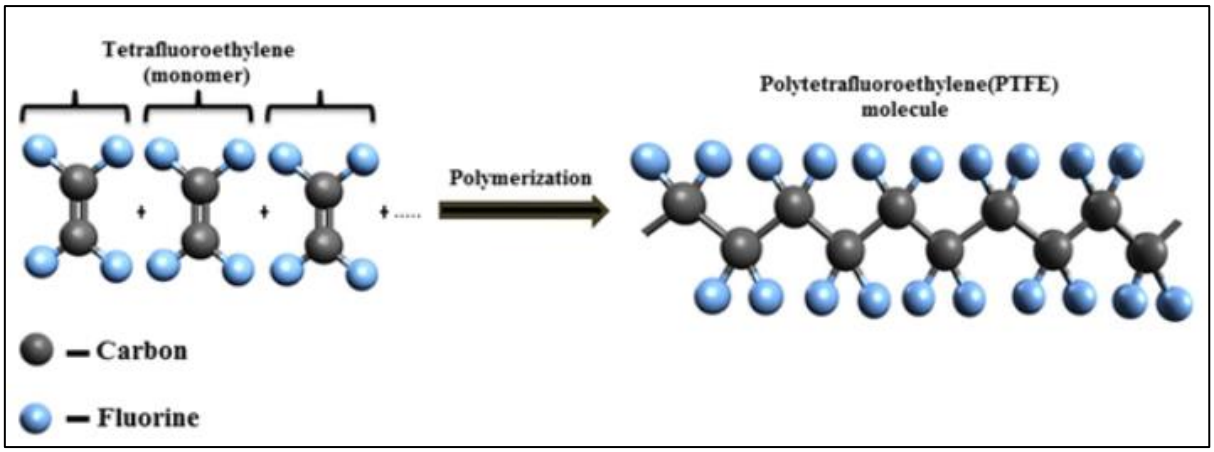
- FPs: have a carbon polymer backbone with F directly attached to C in the backbone.
- PFPEs: have a polyether polymer backbone, in which repeating monomer contains a carbon-oxygen (C-O) bond, with F directly attached to C in the backbone.
- SCFPs: have a carbon polymer backbone with fluorinated side 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.

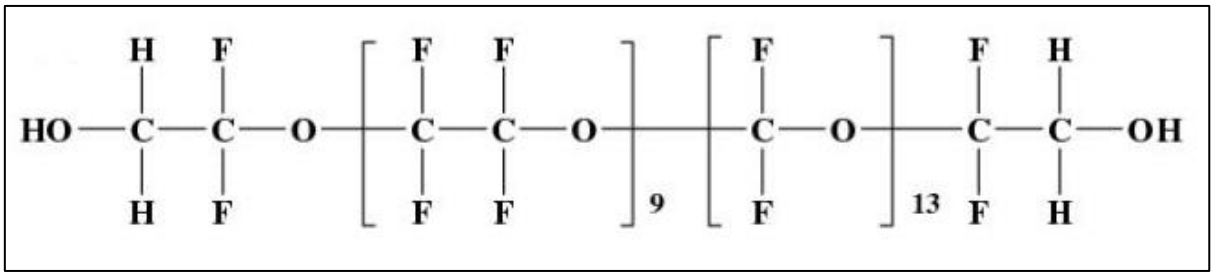
Figure 3. Chemical structure of PTFE.



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.

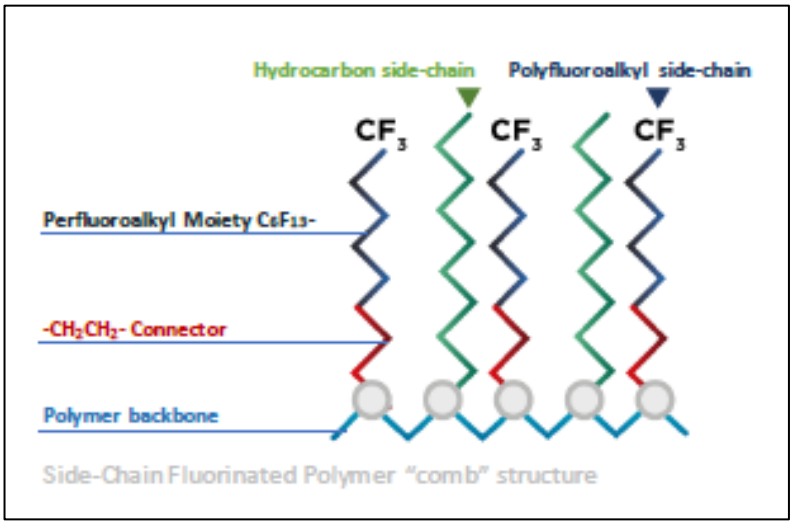


Side-chain fluorinated polymers

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

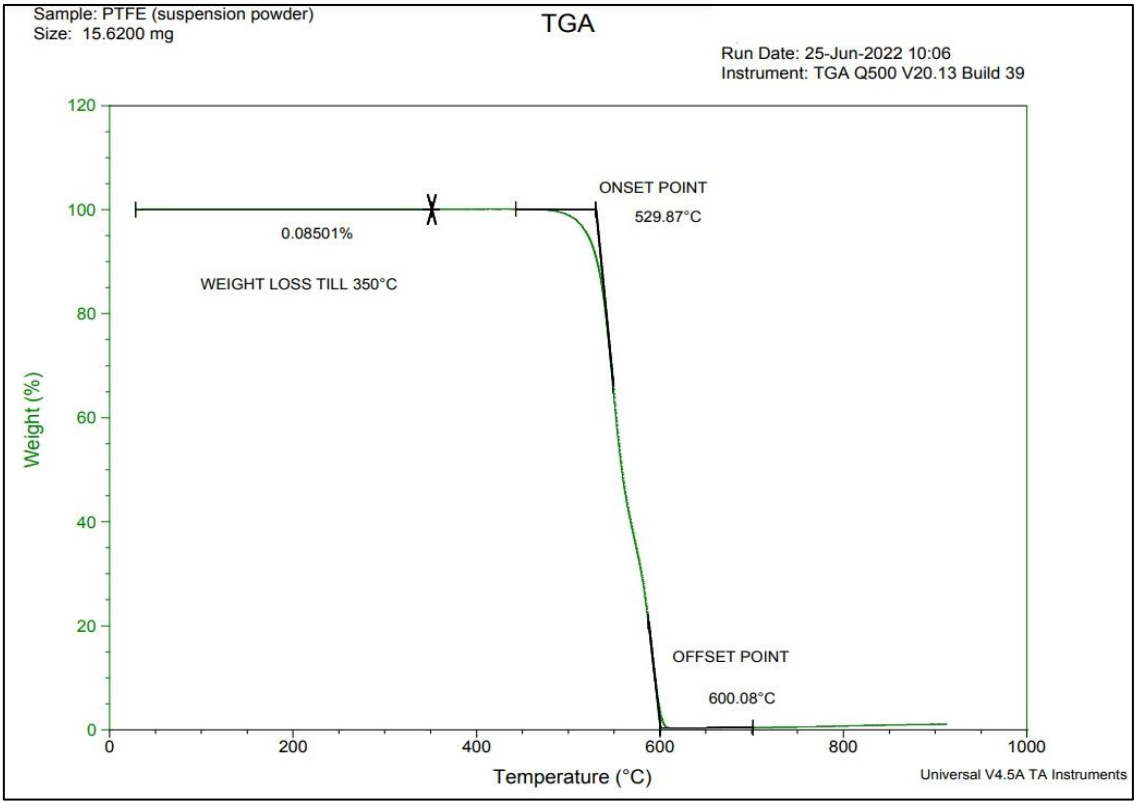


Figure 7. TGA analysis of Polytetrafluoroethylene (PTFE) emulsion powder

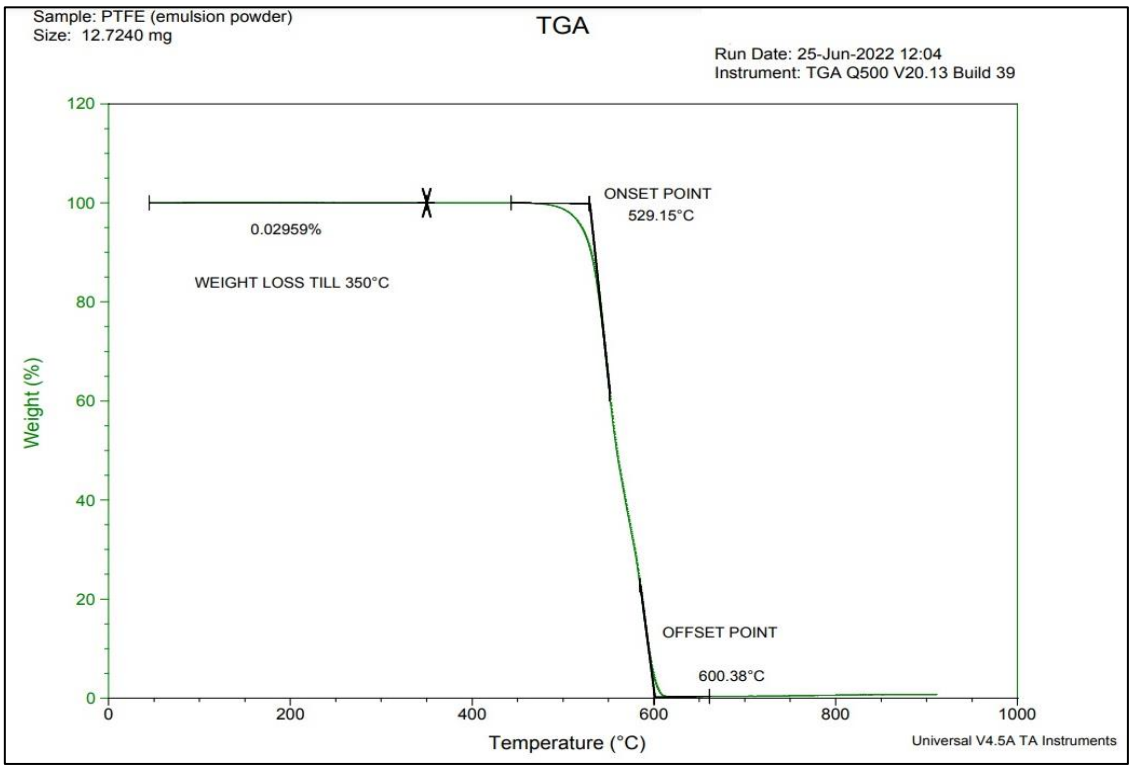


Figure 8. TGA analysis of Perfluoroalkoxy alkane (PFA)

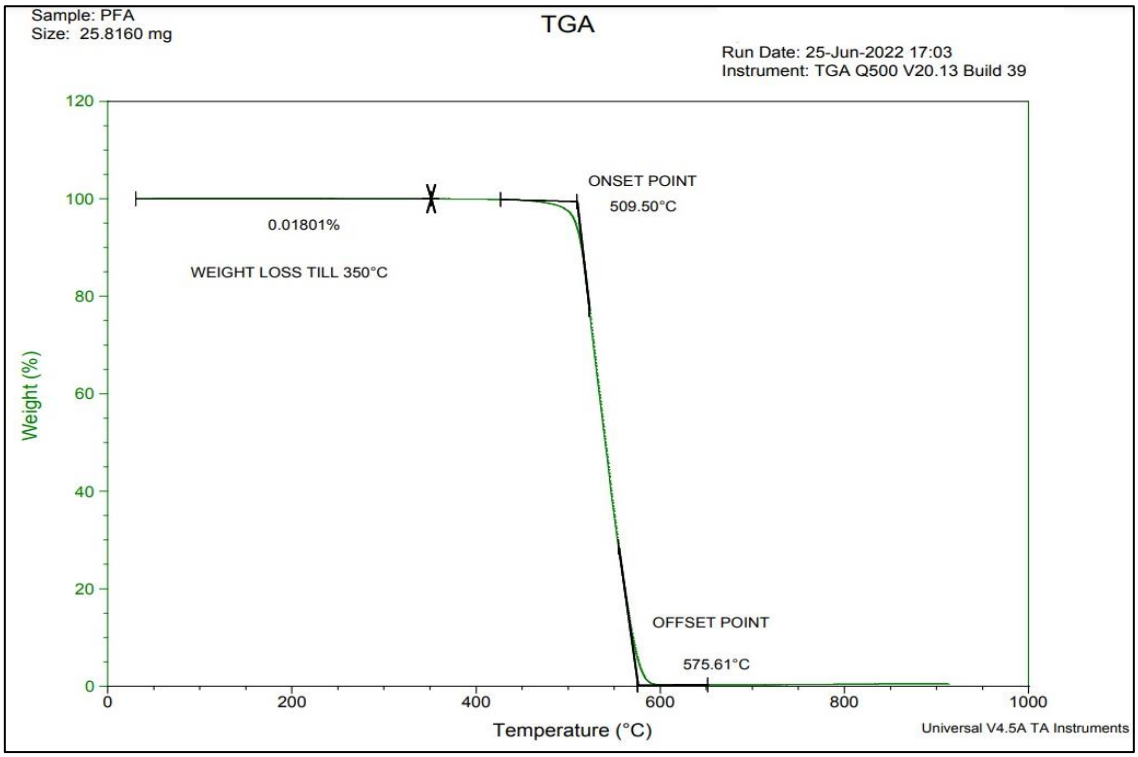


Figure 9. TGA analysis of Fluorinated ethylene propylene (FEP)

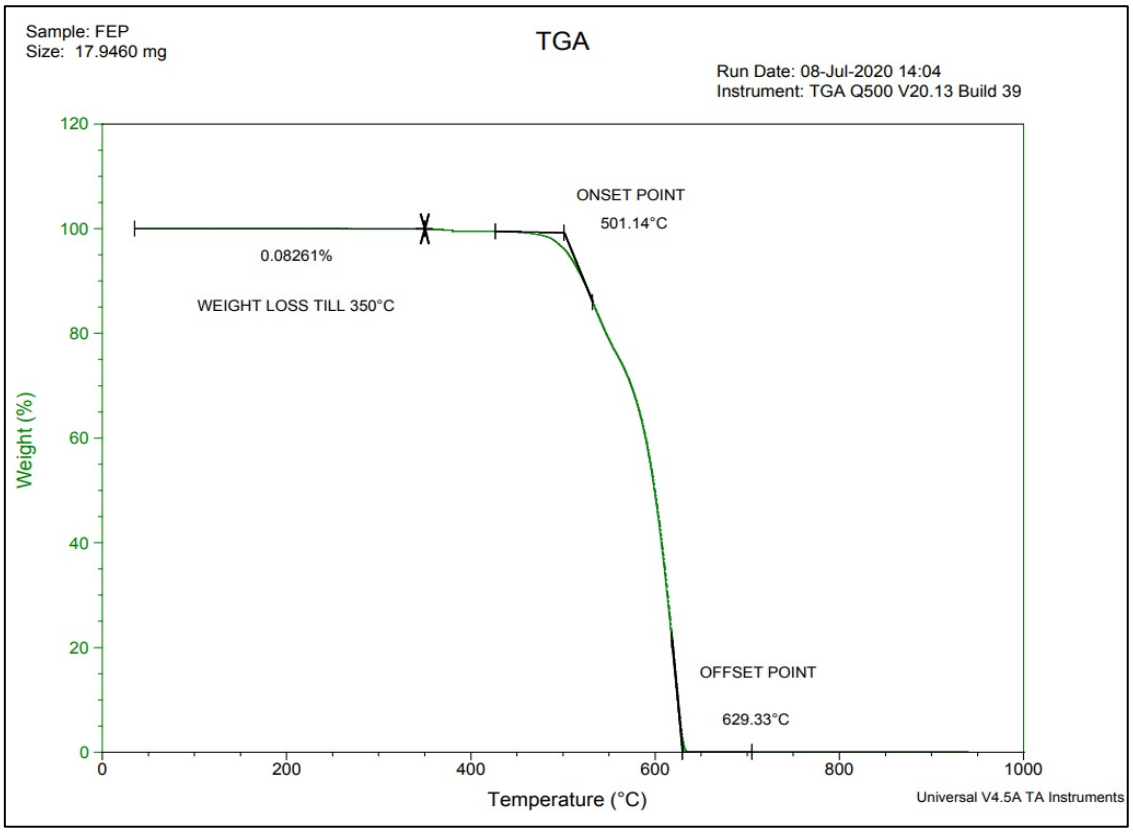


Figure 10. TGA analysis of Polyvinylidene difluoride (PVDF)

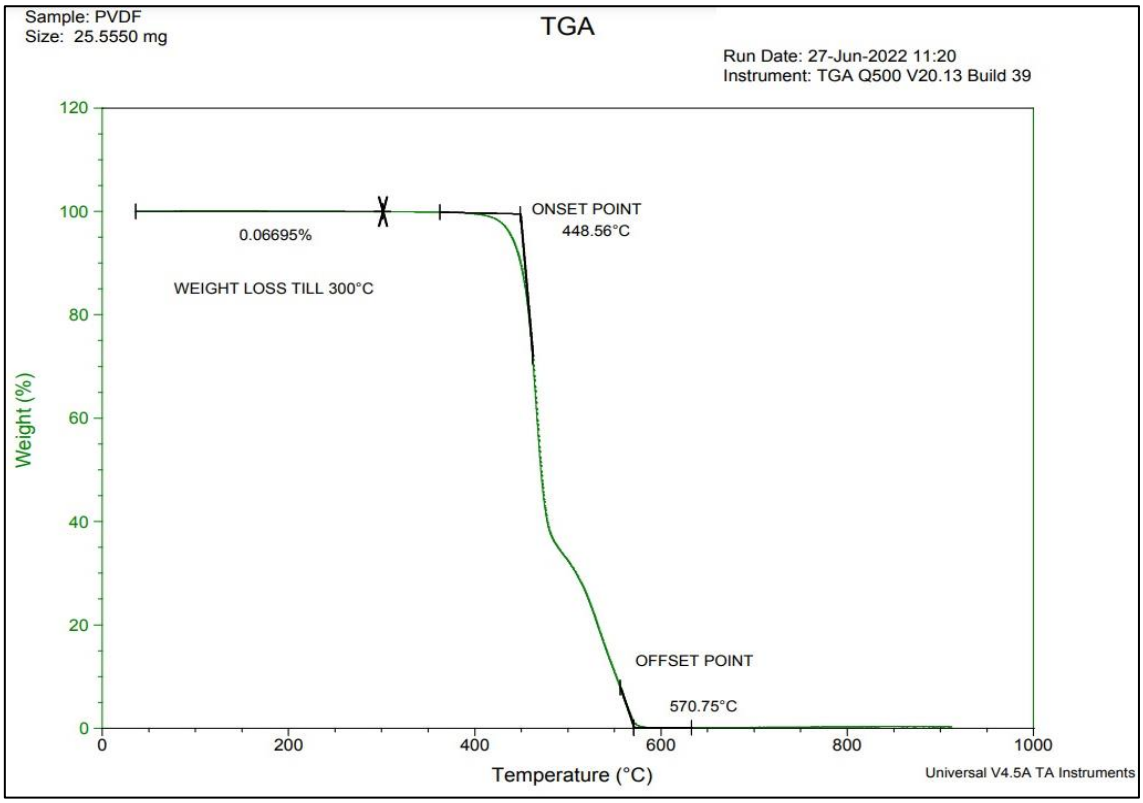
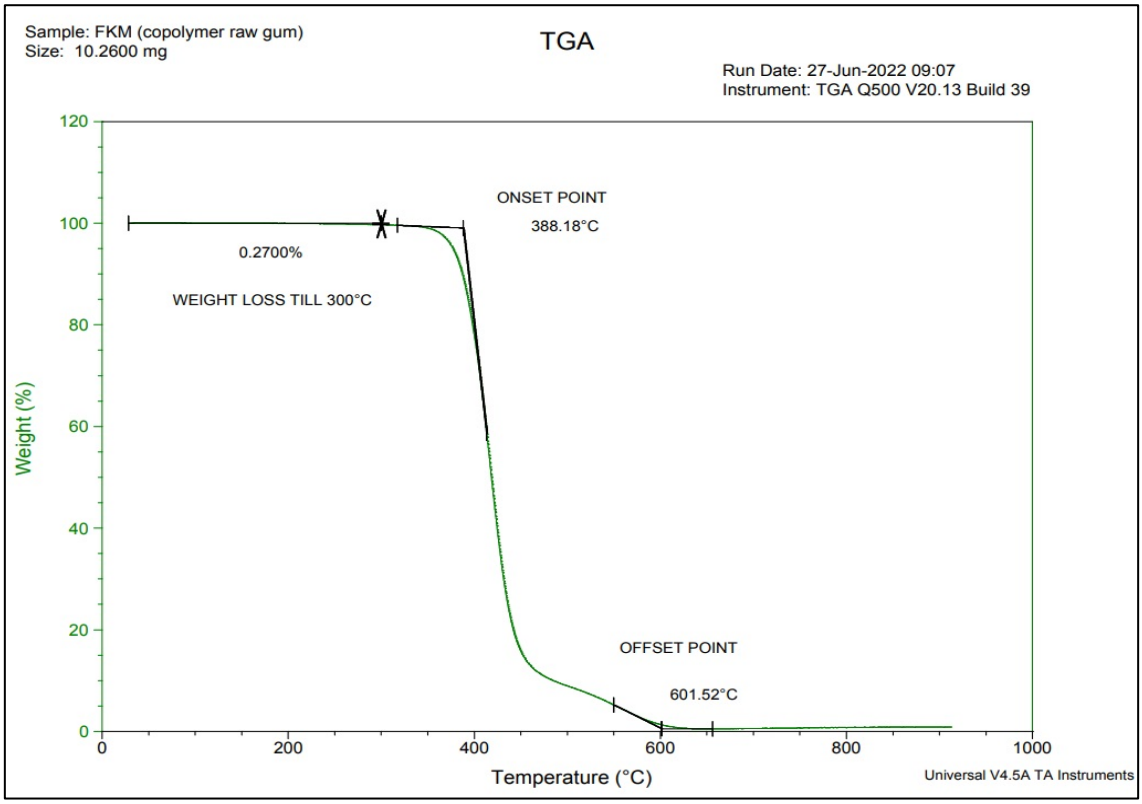


Figure 11. TGA analysis of Vinylidene fluoride-hexafluoropropylene copolymer (FKM)



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

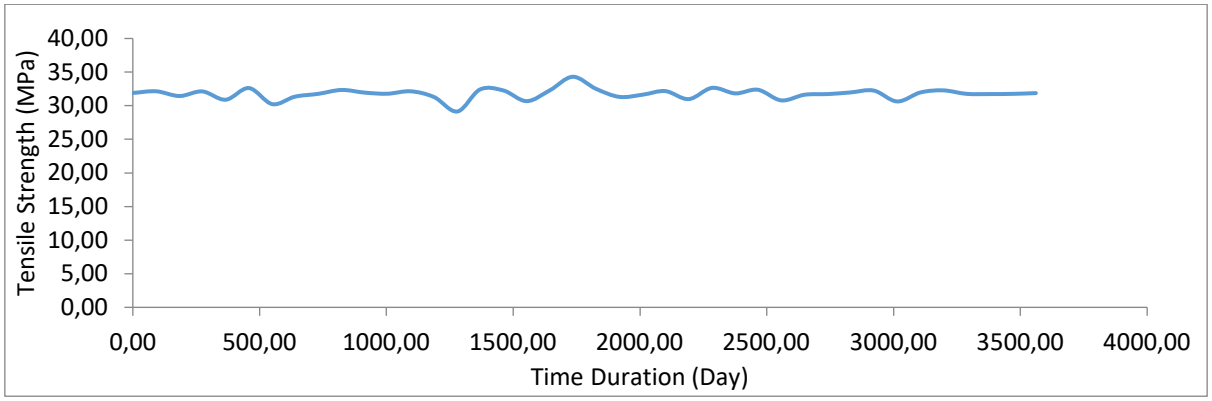


Figure 13. Effect of environmental conditions on Fine Powder PTFE - tensile strength

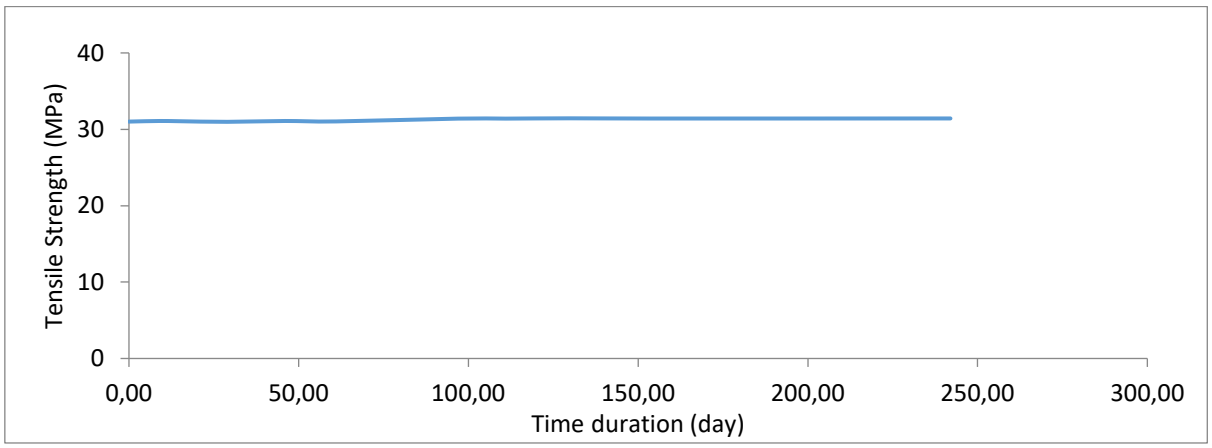


Figure 14. Effect of environmental conditions on Granular PTFE - elongation

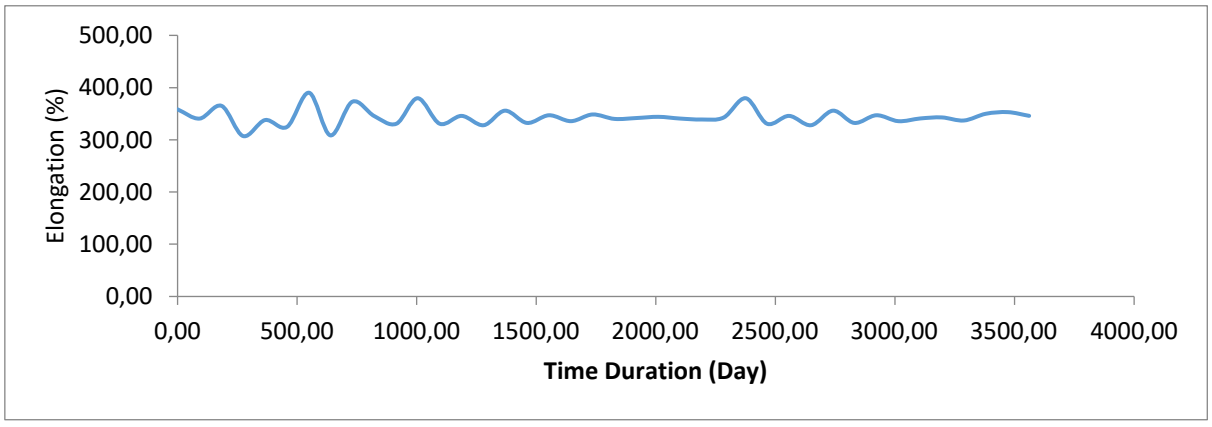
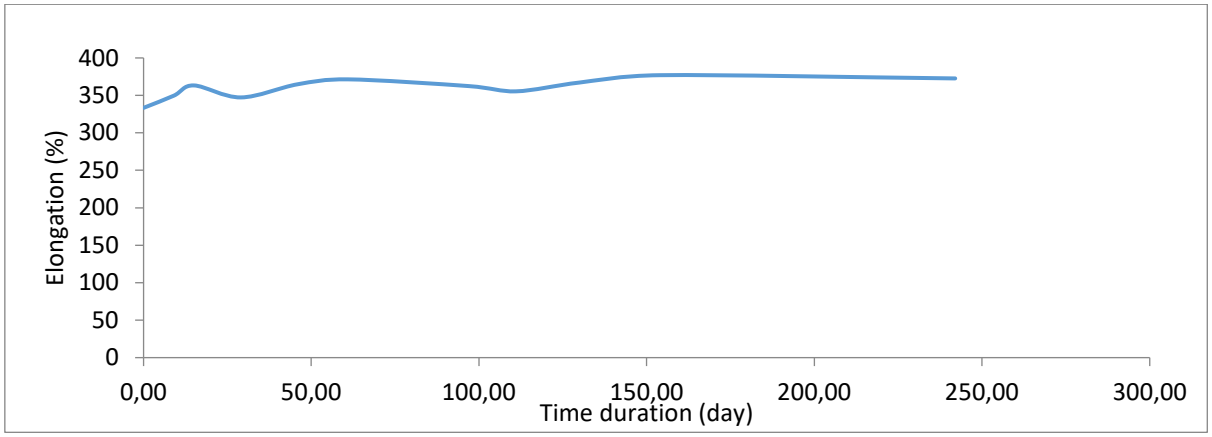


Figure 15. Effect of environmental conditions on Fine Powder PTFE - elongation



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