Industrieverband Halbzeuge und Konsumprodukte aus Kunststoff e.V.

pro-K Fluoropolymergroup

Technical Bulletin 16

Articles on the new regulation on PFAS

Preface

A wide range of fluorothermoplastics was developed to make use of the benefits of plastics containing fluorine in many applications. The PFA and FEP fluorothermoplastics have very similar properties to polytetrafluorethylene (PTFE), which is still the most widely used fluoropolymer. In contrast to PTFE, however, PFA and FEP can be processed with traditional thermoplastics methods, i.e. injection moulding or extrusion. This can offer in particular economic advantages in application. Partly fluorinated polymers, such e.g. ETFE or PVDF, bridge the gap to the non-fluorinated types of technical polymers and high-performance materials. With respect to both the processing temperatures and the polymer properties, these have been refined towards the properties of the non-fluorinated types far enough to allow, for example, joint processing with polyamides (PA12, PA1012). Composite structures therefore form another, continually growing application variant that is capable of covering an even broader range of properties and applications. They consequently expand the range of applications for fluoropolymers even further.
As part of the new regulation on perfluoroalkyl and polyfluoroalkyl substances (PFAS), fluoropolymers and their applications are also being reviewed and new regulations put in place.

This Technical Bulletin reflects the current status of the new PFAS regulation process under consideration of the special situation of the fluoropolymers. The commissioned institutions are currently processing the input from the industry, in particular from companies, but also from associations and authorities, to generate an initial dossier, which will be published in July 2022. This will be followed by another phase for discussing and enhancing the draft.

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Important note:

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Fluoropolymergroup
The Fluoropolymergroup is an association of pro-K Industrieverband Halbzeuge und Konsumprodukte aus Kunststoff e.V. (industrial association for semi-finished and consumer plastic products),
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pro-K is a trustee association of the Gesamtverband Kunststoffverarbeitende Industrie e.V. (general association of the plastics processing industry).

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Introduction

Fluoropolymers play an important role in our society. With their special range of properties, fluoropolymers are virtually irreplaceable in many key industries. Fluoropolymers are safe, sustainable and durable and are used in critical applications that are crucial for human welfare, safety and the environment. Fluoropolymers are an essential contribution to the socio-economic status of Europe and play an important role for adding value in society. Restricting fluoropolymers could have a critical impact on the technological leadership of the EU and one has to ask the question whether the EU climate and energy targets can be achieved without fluoropolymers.

The European Commission adopted its chemicals strategy for sustainability on 14 October 2020. In this strategy, the Commission presents a comprehensive package of measures for regulating the PFAS substance category. The declared objective is to re-regulate and, if necessary, restrict the use of PFAS and the placing on the market of products containing PFAS. Exceptions are envisaged only for essential applications which are still to be defined as part of the restriction process. The authorities responsible for REACH in the Netherlands, Germany, Denmark, Sweden and Norway already started preliminary work on preparing a corresponding restrictions dossier last year and published their intention of submitting a PFAS restriction proposal on 15 July 2021.

The exact extent of the PFAS restriction proposal has not yet been defined, but currently includes all substances with at least one aliphatic CF2 or CF3 group in the molecular structure. According to the current OECD list for PFAS, this definition comprises at least 4,700 chemical compounds. As this list does not include all relevant substances, though, a much higher number of compounds can be expected in reality. The main reason given for this planned extensive restriction of PFAS is the high persistence of many of the representatives of this group of substances. Other reasons cited are the high mobility and the bioaccumulation potential of some PFAS substances.
The introduction of a materials cluster was initiated to account for the special properties of the different substance classes within PFAS. A final decision as to which material groups are to be introduced, however, has not yet been made at this time.

1 The significance of fluoropolymers

Fluoropolymers stand for the following, now and in the future: safety and reliability during use, durability in high performance applications and personal use in everyday life. Their durability, the water-repellent action, temperature resistance, chemical resistance, abrasion resistance, low dielectric constant and minimal signal attenuation in the gigahertz range make them crucial materials for many areas of application, now and in the future.

Fluoropolymers are indispensable for achieving the targets of the EU Green Deal. The same applies to achieving the UN Sustainable Development Goals (SDGs).

The following are examples of key industries that depend on the use of fluoropolymers:

- Mobility and transport
- Clean and green energy
- Chemicals and power plants
- Electronics
- Buildings
- Medical technology
- Data transmission; autonomous driving

2 Emissions during the life cycle of fluoropolymers

The main focus of the regulatory authorities for PFAS is on the emissions generated by fluoropolymers during their complete life cycle.

a. Start of the life cycle phase
- Sustainable production technologies
- Use of polymerisation processes that require no emulsifiers; use of fluorine-free emulsifiers or reduction of the required volumes of fluorinated emulsifiers
- Emissions monitoring, in particular regarding the low-molecular, fluorinated polymerisation aids, during production and processing using the best available technology

b. Use phase
- Emissions are not an issue during the use of the fluoropolymers in the intended applications
- Fluoropolymers are classified as “polymers of low concern” (PLC) [Henry et al., 2018]. This means they pose no threat to the environment and living beings.

c. End of Life phase

- Fluoropolymer products can be placed in landfill or incinerated in suitable plants (energy recovery). The various recycling processes should be prioritised, though: PTFE can be turned in to PTFE micropowder by means of thermomechanical or irradiation modification. Fluorothermoplastics can be recycled with the conventional thermoplastics recycling processes: crushing – cleaning – reuse for injection moulding or extruding. The newly developed chemical recycling process for PTFE and fully fluorinated thermoplastics (upcycling processes) allows polymers to be divided into their original substances – the monomers. After cleaning, these can be used for polymerisation again. This generates new polymers without any loss of quality.
- Other activities: End-of-life (EoL) project led by the American Chemistry Council (ACC) to understand the optimum conditions for mineralisation: Above 800 °C, fluoropolymers can be turned into non-critical mineral substances.

Fluoropolymers meet the REACH definition of persistence. Fluoropolymers are high-molecular and have unique physical-chemical properties. This means they form a separate class of solids within the mostly liquid or gaseous PFAS. They meet the OECD criteria for PLCs. They are non-toxic, biocompatible and insoluble and cannot enter the cells of living beings due to their high molecular weight, and therefore have no negative impact on humans and the environment.

3 Sustainability in production and processing

The main focus of the regulatory authorities with regard to the production of fluoropolymers is on the use of fluorinated polymerisation aids and their emissions. Potential emissions at the End of Life of fluoropolymers are another key issue of the regulation work.
50 – 60 % of the produced fluoropolymers do not require any fluorinated polymerisation aids. These include, in particular, partially fluorinated thermoplastics such as polypropylene fluoride (PVDF) and PTFE manufactured using the suspension process. For processes that require fluorinated aids, great efforts were made to reduce the emissions through air and water. In some cases, values of up to 1 % relative to the values from 2017 were achieved through this. In addition to this, the industry is working on fluorine-free emulsifiers.

The Fluoropolymer Group (FPG) of PlasticsEurope has committed to “responsible manufacturing”, which includes the following measures:

- Continuous improvement and/or development of the best available technology during the production process and the monitoring of emissions into the environment
- Starting R&D programs to improve the technologies that allow for replacing PFAS polymerisation aids
- Increasing the recycling content and reuse in fluoropolymers in connection with the objectives of a circular economy
- Measures for further reduction of fluorinated emulsifiers; wastewater treatment

- Recovery of emulsifiers through ion exchange technology Complete binding of gaseous emissions from the production process and introducing these into thermal oxidation. The objective is a recovery and thermal breakdown rate of 99.9 %.

According to the latest findings, 2.69 % of all PFAS emissions in the EEA are caused by fluoropolymers. Most of these emissions are categorised as fluorinated side chain polymers, which are used in consumer goods such as textiles or leather and paper treatments. It can be assumed that these substances remain in the environment.

The pro-K Industrieverband with its Fluoropolymergroup takes on a leading role in supporting the fluoropolymer processing industry in the monitoring and reduction of their emissions and waste with the following measures:

- Information and knowledge transfer
- Explanation of the scientific background
- Further development of suitable production methods

Individual fluoropolymer manufacturers also take on tasks for educating their customers with regard to safe processing, emissions monitoring and waste reduction.

4 Alternatives to fluoropolymers

Replacing fluoropolymers can be expensive and entails certain risks. Due to their unique combination of performance characteristics, fluoropolymers are very difficult to substitute in many key industries. Substituting fluoropolymers with alternative materials can result the following:

- Increased safety risks (e.g. due to flammability, lower temperature resistance)
- Prevention of technical progress (e.g. 5G data transfer impossible)
- Prevention of achieving the EU economic and green technology targets
- Socio-economic impact, e.g. reduced service life of systems, buildings, vehicles, reliable fire brigade, saving human life
- Higher carbon footprint due to reduced service life and lower reliability

Using alternatives to fluoropolymers usually means accepting additional disadvantages during the use and development of industrial solutions.

5 The important role of fluoropolymers in innovative applications

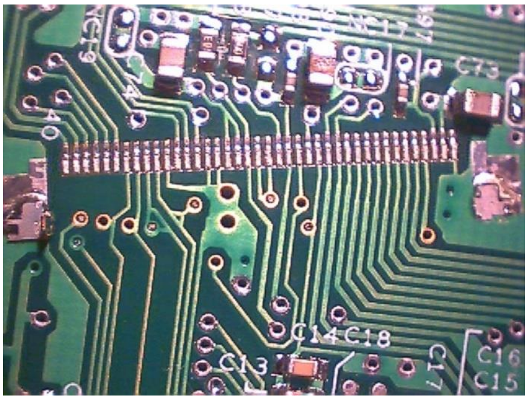
The following examples highlight the important role of fluoropolymer applications and products.

Construction of chemical plants

Fluoropolymer linings on construction elements made of fibre reinforced plastics ensure maximum purity of chemicals, ensuring that these are free from interfering metal ions.

Fig. 1: Fluoropolymer lining

Semiconductor industry



PCBs and high frequency components are possible only with the use of boards based on fully fluorinated polymers (PTFE and/or FEP).

Fig. 2: PCB

Pharmaceuticals and fine chemicals

Use of only metal free, fibre reinforced plastics that are lined with fluoropolymers on the inside, where they come into contact with high purity chemicals.

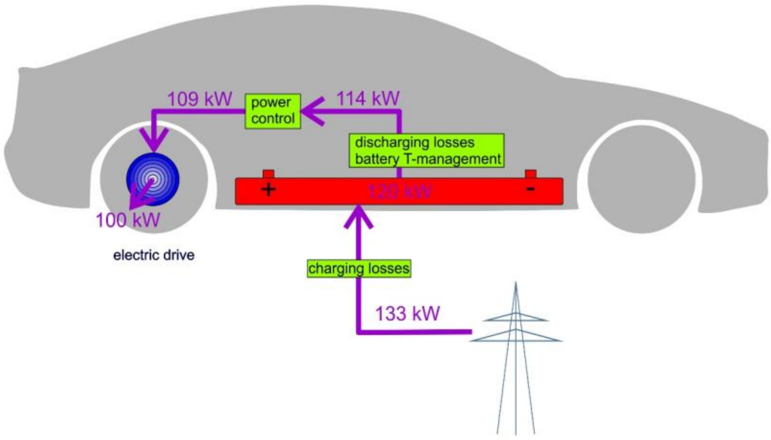
Fig. 3: Contact surfaces coated with fluoropolymers

Power of innovation and performance

Top quality with continuous quality control.

Fig. 4: Quality check inside a vessel

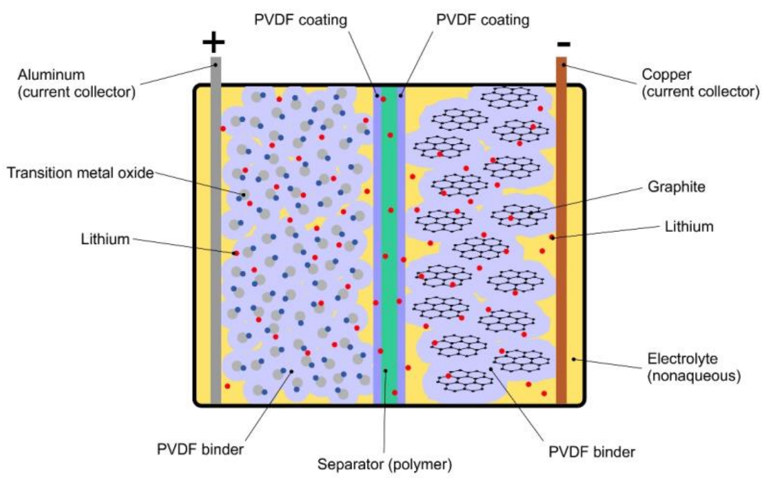
Mobility of the future



Megatrend e-mobility. E-mobility will expand the application options for fluoropolymers.

Fig. 5: Schematic diagram of the energy flow in a passenger car with electric drive (EV)

New applications: **PVDF** as a binder in the battery for anode and cathode, **ETFE** for cable insulation and **porous PTFE** for ventilation (function) and as a burst disc (safety).



PVDF in different applications in the battery pack

Fig. 6: Battery structure using PVDF

Energy source of the future: green hydrogen

The transition from internal combustion engines to electric drives will require more electricity. In the event of a complete switch from internal combustion engines to electric drives, the electricity requirement would increase by about 25 %. Green hydrogen H2 can be used as an energy carrier and as a buffer for strongly fluctuating renewable energies such as wind power or photovoltaics.

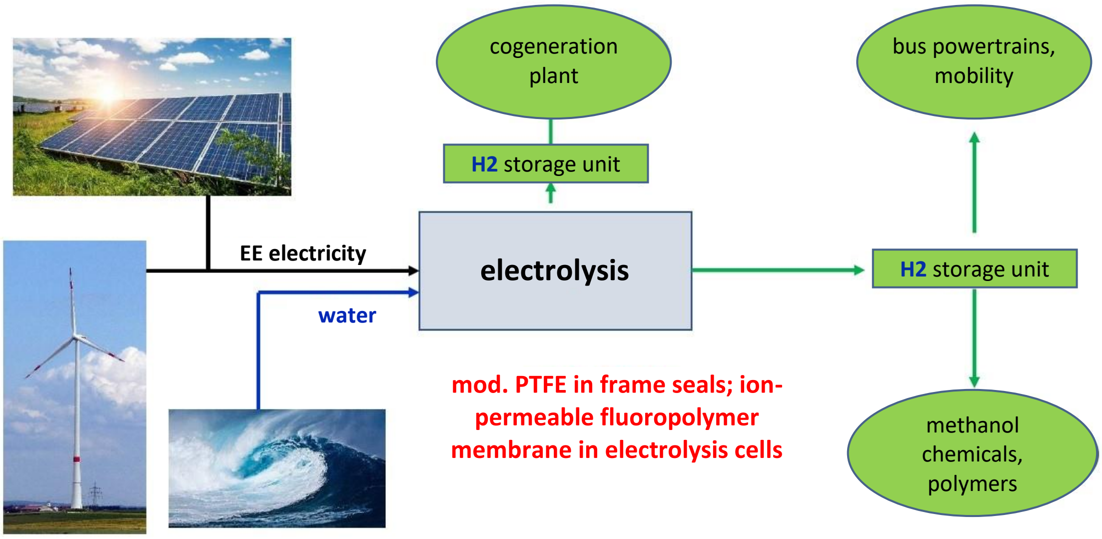


Fig. 7: Green hydrogen as an energy source of the future

With wind energy and photovoltaics, hydrogen is generated from water using electrolysis. Oxygen is produced as a byproduct. In the electrolysis cells, modified PTFE is used in frame seals and ion-permeable fluoropolymer membranes in electrolysis cells. Hydrogen storage tanks are then used to transfer the energy to cogeneration plants, as fuel for mobility in urban environments and local transport and as a raw material for the chemical energy in the production of a variety of chemical products.

6 Special properties of fluoropolymers within the PFAS group

PFAS is a very broadly defined category of substances with very different physical, chemical, environmentally relevant and biological properties. Fluoropolymers differ from the other candidates in the PFAS substance classes in a very characteristic way, which makes it necessary and justified to evaluate and regulate them separately. They have a very specific physical-chemical properties profile. They meet the OECD criteria for PLCs. They are non-toxic, biocompatible, insoluble and immobile molecules with a usually very high molecular weight (up to 10^8 g/mol in the case of PTFE). As inert substances, they only have a very minor influence on the environment and human health.

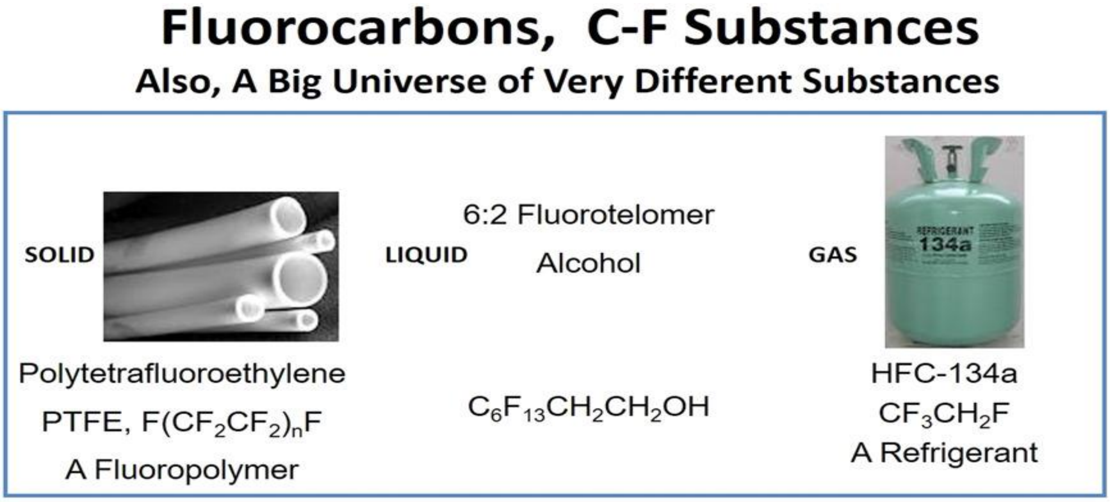


Fig. 8: Solid, liquid and gaseous applications form different PFAS product groups

The wide product range of the PFAS groups requires a differentiation and must not be considered a uniform, homogeneous group of substances. The following three product groups are examined here as an example:

- Semi-finished products in the form of tubes, hoses and profiles made of PTFE and modified PTFE
- Fluorotelomer alcohol, used e.g. in the production of side-group fluorinated polyacrylates
- Refrigerants for use in air conditioning systems

7 The use phase of fluoropolymers

Polymers of low concern (PLC)

This product group was created by the OECD Polymers Expert Group in 2009. PLCs are products with insignificant influence on the environment and human health. In 2018, Henry et al reported that four fluoropolymers passed the PLC suitability criteria upon extensive testing.
These are:

- Polytetrafluorethylene (PTFE)
- Fluorinated ethylene propylene (FEP)
- Ethylene tetrafluoroethylene (ETFE)
- Tetrafluoroethyleny copolymers with perfluoroalkoxy alkane (PFA)

In 2015, these four fluoropolymers made up approx. 70 – 75 % of the world's fluoropolymer market.
A number of the largest fluoropolymer manufacturers worldwide came to the conclusion that another 10 fluoropolymer candidates also meet the PLC suitability criteria.

In summary, fluoropolymers have the following defining properties:

- High chemical stability
- Thermal, photochemical, oxidative and biological stability
- Low-extractable, low-molecular content
- No significant functional groups

The unique properties of fluoropolymers can be traced back to the strong C-F bond. The generally have a very high molecular weight (> 100,000 Da). As a consequence, they cannot enter living cells, react with “target organs” or change these. This also includes the reproductive systems.
It therefore has to be assumed that fluoropolymers pose no significant threat to human health or the environment during their use in the intended application and within the recommended application limits.

8 Safe waste disposal, circular economy after End of Life, recycling and upcycling

Different recycling cycles have already been integrated into the life cycle of fluoropolymers and are general practice. These are, for example:

- Incineration of waste from monomer production and polymerisation, Ca(OH)2 waste gas cleaning for recovering flurospar, CaF2. It can be reused as a raw material for monomer production.
- Extension of the life cycle: thermomechanical degradation of off-spec batches, transforming PTFE into PTFE micropowder through treatment with high energy irradiation. The PTFE micropowder products start a “second life” in the additives sector. They can be used as an additive in lubricants, as a processing additive and as a dirt repellent top layer in paints or in plastics to improve their gliding properties

Mechanical recycling:

Swarf from the production of semifinished products and finished parts is collected, cleaned, crushed and used either for manufacturing semifinished products such as rods, tubes or plates using ram extrusion or as a PTFE micropowder after irradiation. If products are easy to clean once they have reached the end of their application, then they can be milled and either used as a raw material for ram extrusion or – after irradiation modification – as PTFE micropowder in additive applications. Fluorothermoplastics such as PFA, FEP or ETFE can be reused in injection moulding or extrusion after cleaning and milling, using state-of-the-art processes.

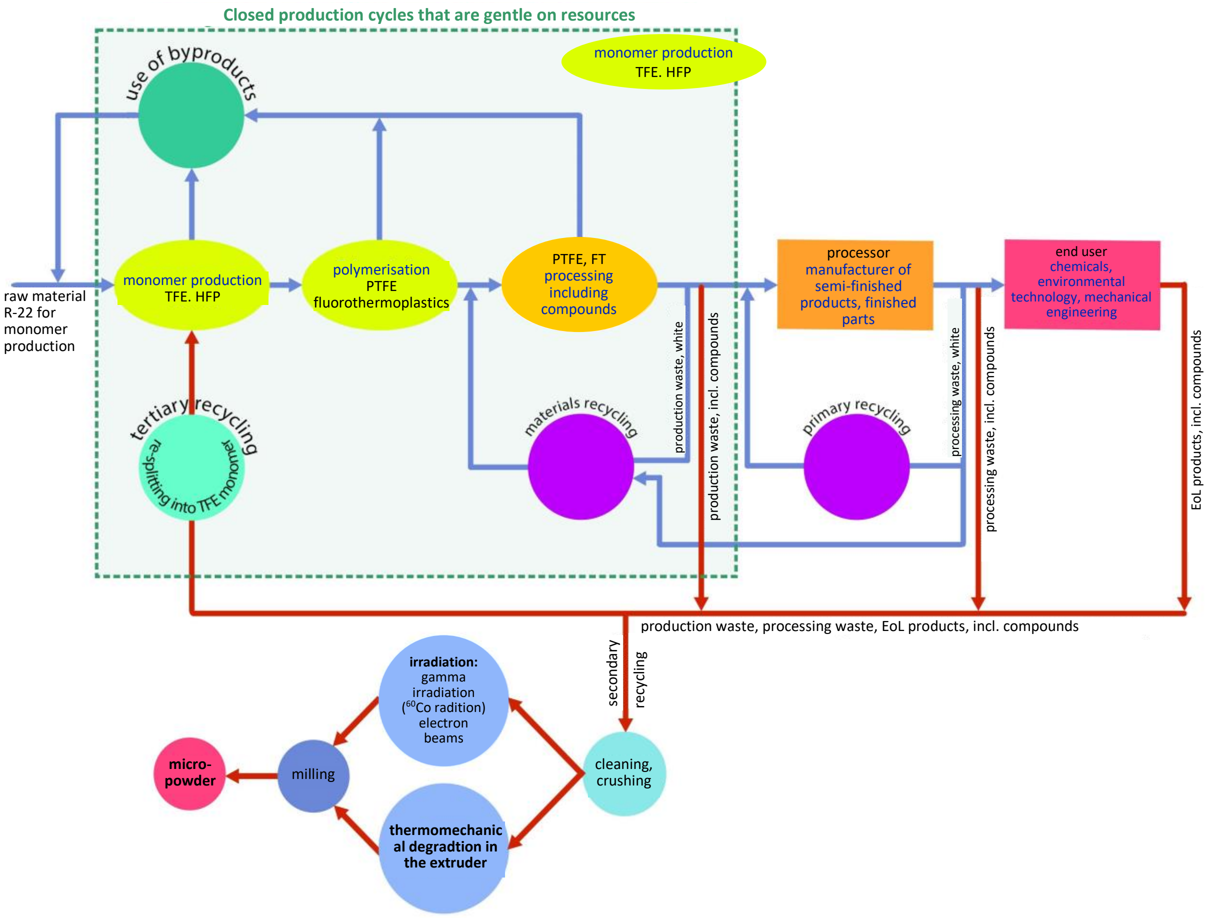


Fig. 9: Schematic diagram of the upcycling process, generation of micropowder

Chemical recycling:

This upcycling process is a new technology. It has been developed on an industrial scale since 2015 in an experimental industrial plant with a total capacity of approx. 1000 t/a and is now ready for market launch. The fully fluorinated polymers, PTFE, modified PTFE, PFE and FEP as well as some PTFE compounds can be recycled.

The recovery rate of cleaned monomers is approx. 85 %.

The upcycling process:

When the application has reached the EoL, the products are collected and thermally resplit into, in particular, the monomers tetrafluoroethylene (TFE) and some hexafluoropropene (HFP). This is equivalent to chemical recycling and, after cleaning, the produced monomers can be reused for polymerisation of new fluoropolymers. Polymers produced in this way show no reduced quality compared to the original polymers. So this recycling process transforms “old materials” into new ones. The quality is restored to the original level.

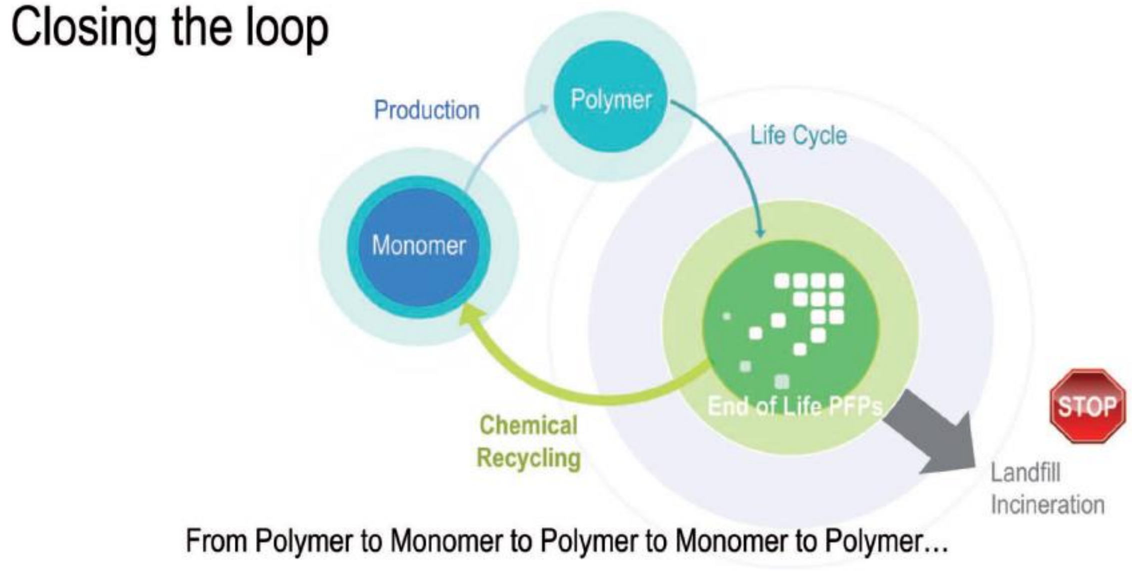


Fig. 10: Schematic diagram of chemical fluoroplastics recycling

9 Process sequence

The further sequence of the process is as follows:

A restrictions dossier will be submitted by 13 January 2023, after evaluation of the two surveys (call for evidence 1 + 2) and the completed expert discussions, e.g. pro-K/BAuA and BDI, VDMA, VDI, ZVEI, pro-K/BAuA.

This will be followed by another public 6-month consultation phase from March 2023 on the completed restrictions dossier.

Another comprehensive public consultation of around 2 months, in particular on the socio-economic impact, is scheduled for the middle of 2023.

The final statement to the EU Commission is planned for early 2024. The technical/scientific process will be completed by this point and the further consultations in the political sphere will take place subsequently.

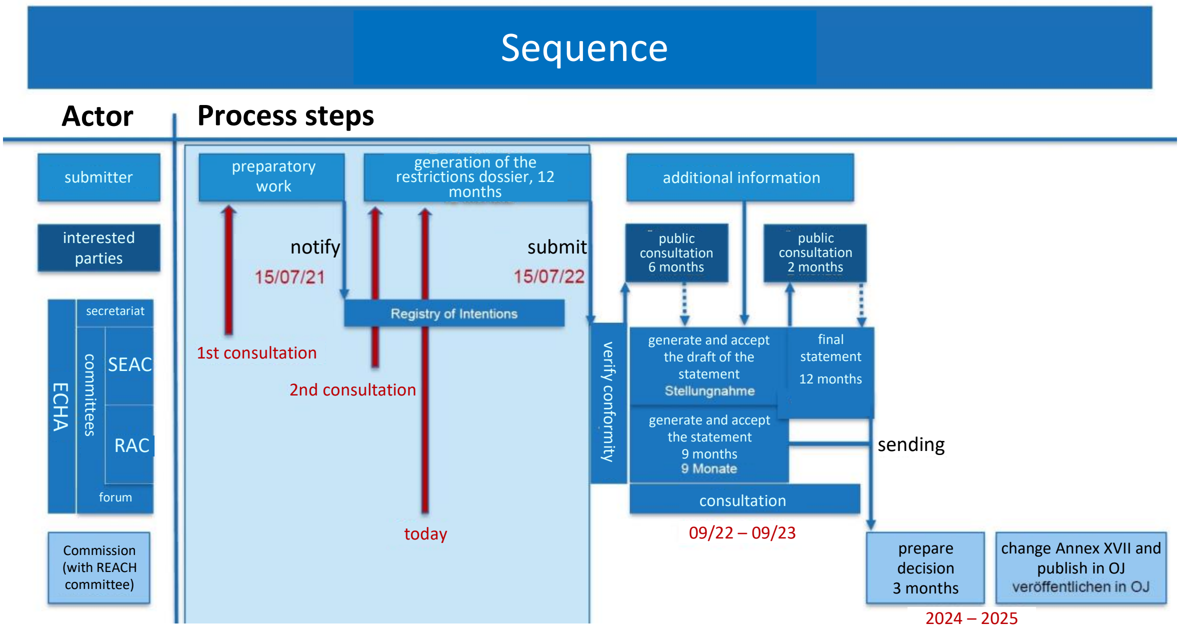


Fig. 11: Overview of the sequence of the PFAS regulation process

10 Conclusions

Fluoropolymers are very important for society and they are the prerequisite for the further development of new technologies and areas of application. In particular, they are indispensable for achieving the EU Green Deal targets.

The five countries that started the PFAS petition focus on potential emissions during production, the use phase of fluoropolymers and after End of Life.

Fluoropolymer manufacturers are constructively working on reducing emissions and using fluorine free polymerisation aids. The work on developing technologies with fluorine free polymerisation aids is progressing.

Almost all fluoropolymers meet the OECD criteria for polymers of low concern, which ultimately means that fluoropolymers pose no risks during their life cycle. Fluoropolymers do not form dispersing PFAS compounds while degrading. They are primarily used as materials in industrial processes. Fluoropolymers differ fundamentally from fluorinated side chain polymers which can be regarded as the main initiators of the emissions.

Polymer waste of fluoropolymer processors is collected and reused by means of different methods and therefore starts a “second life”. At 800 °C or more, fluoropolymers degrade completely and the formation of PFAS as a result of incomplete incineration is excluded through burning under energy recovery conditions. Fluoropolymer waste is inert and poses no risk to humans and the environment if it is disposed of in landfill.

How can fluoride emissions be avoided in the long term?

Establishing a circular economy for products after they reach their End of Life is one of the central aspects of the PFAS regulation process. The manufacturers of the fluoropolymers together with the processors, the parties placing them on the market and the end users have to jointly ensure that fluoropolymers do not end up in emissions after their End of Life.

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