Review

Fluoropolymers as Unique and Irreplaceable Materials: Challenges and Future Trends of These Specific Perfluoroalkyl Substances

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Review

Fluoropolymers as Unique and Irreplaceable Materials: Challenges and Future Trends of These Specific Perfluoroalkyl Substances

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Abstract: In contrast to some low molar-mass per- and polyfluoroalkyl substances (PFASs), well-established to be toxic, persistent, bioaccumulative and mobile, fluoropolymers (FPs) are water insoluble, safe, bio-inert, durable niche high performance polymers which fulfil the 13 polymer of low concern (PLC) criteria in their recommended conditions of use. In addition, more recent innovations (e.g., the use of non-fluorinated surfactants in aqueous radical (co)polymerization of fluoroalkenes) from industrial manufacturers of FPs are highlighted. This review also aims at showing how these specialty polymers endowed with outstanding properties are essential (even irreplaceable since hydrocarbon polymer alternatives used in similar conditions fail) for our daily life (electronics, Energy, optics, internet of things, transportation, etc.) and constitute a special family *a part* from other "conventional" C_1-C_{10} PFASs found everywhere on the Earth and Oceans. Furthermore, some information reports the recycling (e.g. the unzipping depolymerization of polytetrafluoroethylene, PTFE, into TFE), end of life of FPs, their risk assessment, circular economy and regulations. Various researches are devoted to Environment involving FPs, though they represent a niche volume (with a yearly production of 330,300 tonnes) compared to all plastics (with 460 million tonnes). Complementary to other reviews on PFASs, which lack of such above data, this review presents both fundamental and applied strategies as evidenced by major FP producers.

Keywords: end of life; fluoropolymers; per- and polyfluoroalkyl substances (PFAS); polymerization aids; recycling; regulators; surfactants

1. Introduction

According to the Organization for Economic Co-operation and Development (OECD)[1-2], perfluoroalkyl (and polyfluoroalkyl) substances (PFASs) are artificial/anthropogenic products which contain multiple C–F bonds. [3-9] Because of their unique hydrophobic/lipophobic physicochemical properties, this specific group of chemicals displays quite different physical, chemical, and biological properties[5-9] than other hydrocarbon compounds and have been involved in many applications in different areas[5-10]. The OECD[1] has reported more than 4700 PFAS molecules and, according to the US Environment Protection Agency,[3,11] this number reaches more than 12,000 compounds.[12] However, PFAS molecules, especially those of low molar mass have been found in many soils, water, seas and oceans as reported by plethora of articles and reviews.[4-10] Thanks to the high electronegativity and small radii of the fluorine atom that confers a short and quite stable C-F bond, fluorinated products have remarkable chemical inertness and thermal stability (the dissociation Energy of this C-F bond worth ca. 120 kcal/mol). However, such characteristics further induce some limitations_since PFASs are known to be water soluble, mobile, toxic, persistent and bioaccumulable.[9,12-14] Since 2000, many regulations have been proposed, modified and multipled.[5-8,10,12-17] Various fluorinated compounds have been banned for several years and a continuous procedure from competent authorities still maintain their pressure to impose drastic legislations/regulations.[16]

Thomas et al.[17] comprehensively reported the global situation on the regulation of PFASs in both the scientific and legislative communities, and analyzed the different regulatory actions launched both in Europe and in the USA (including federal and state-level initiatives). These authors supplied

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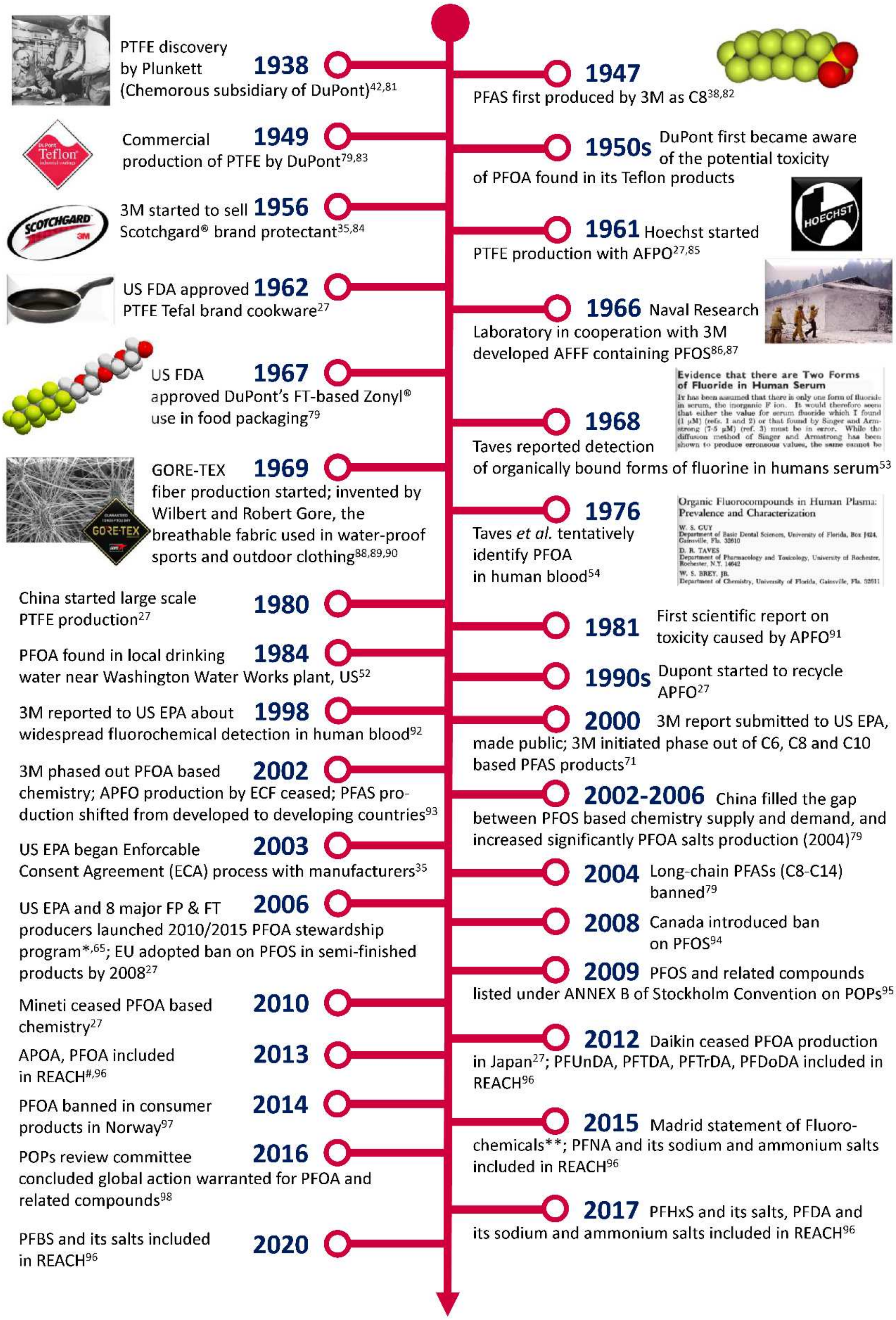
an exhaustive list of different dossiers of legislation and carefully reported how regulators have approached the concerns of PFASs from different perspectives. Last March 2023, China added PFOA and PFOS to its list of New Pollutants for Priority Management to modify their production, use, import, and export.[18] Presently, 152 countries have ratified the Stockholm Convention, that puts in place elimination and restriction of listed PFASs with exemptions for specific uses such as hard metal plating and firefighting foams (AFFFs). As of April, 5th 2023, Israel, Haiti, USA, Malaysia, and Brunei Darussalam have not ratified the convention. Although ratified, there is no indication that a number of the member nations have made efforts to regulate PFASs via other independent mechanisms.[17]

This review aims first at making a difference between various classes of PFASs, showing major issues from low molar mass-ones in contrast to the high molar mass fluoropolymers which display specific advantages (safety, bio-inertness, non-toxicity and fulfilling the 13 polymer of low concern (PLC) criteria in their conditions of use).

In addition, advanced technologies from industrial manufacturers of FPs have led to recent innovations such as the use of non-fluorinated surfactants in aqueous radical (co)polymerization of fluoroalkenes to yields FPs with similar performances. This an above comparison and these innovations have unprecedented been reported before. This review also aims at showing how these specialty polymers endowed with outstanding properties are essential (even irreplaceable) for our daily life (electronics, Energy, optics, internet of things, transportation, etc) and constitute a special family *a part* from other "conventional" C1-C10 PFASs found everywhere on the Earth and Oceans. Furthermore, some information report the recycling (e.g. the unzipping depolymerization of polytetrafluoroethylene, PTFE, into TFE), end of life of FPs, their risk assessment and circular economy. Various researches are devoted to Environment involving FPs, though they represent a niche volume. Complementary to articles on PFASs, which lack of such data above, this review gathers both fundamental and applied strategies as evidenced by major FP producers. Various features are still attracting a huge interest from both academic and industrial actors.

2. History of PFASs

Fluorinated products have been known for eighty-five years [14] and a brief historic sketch showing their extraordinary evolution is depicted in Figure 1, that includes gases, intermediates, monomers, oligomers and polymers. Among them, surface-active products (surfactants) are specific amphiphilic PFASs which display much lower surface tension and surface energy than those of hydrocarbon surfactants.[9,19] They are currently used in more than 200 applications (such as aqueous firefighting/film forming foams,[19-21] food packaging, cosmetics, photoacid generators,[9-10,19] paints, semiconductors, electroplatings[21] and as polymerization aids in the emulsion radical polymerization of fluorinated alkenes.[9;21] Many examples deal with PFAS production sites,[12] or storage areas such as military bases equipped with extinguishers[22-23] and airports[24-25] where many PFASs have been found. Ruyle et al.[23] analyzed groundwater samples from the fire training area between September 2007 and July 2021 (six time points; Figure 2). All groundwater measurements were from samples collected from the same well to control the hydrological variability. The samples represent concentrations in the upper 2−3 m of groundwater. These authors directly compared PFAS concentrations from those of samples collected in 2007. Their analyses were achieved in order to supply quantitative and qualitative information from complementary techniques such as liquid chromatography-tandem mass spectrometry (LC-MS/MS), combustion ion chromatography, high-resolution mass spectrometry, and a comparison of measured and library MS/MS spectra.



1938 PTFE discovery by Plunkett (Chemorous subsidiary of DuPont)[42,81]

1947 PFAS first produced by 3M as C8[38,82]

1949 Commercial production of PTFE by DuPont[79,83]

1950s DuPont first became aware of the potential toxicity of PFOA found in its Teflon products

1956 3M started to sell Scotchgard® brand protectant[35,84]

1961 Hoechst started PTFE production with AFPO[27,85]

1962 US FDA approved PTFE Tefal brand cookware[27]

1966 Naval Research Laboratory in cooperation with 3M developed AFFF containing PFOS[86,87]

1967 US FDA approved DuPont's FT-based Zonyl® use in food packaging[79]

1968 Taves reported detection of organically bound forms of fluorine in humans serum[53]

Evidence that there are Two Forms of Fluoride in Human Serum

It has been assumed that there is only one form of fluoride in serum, the inorganic F ion. It would therefore seem that either the value for serum fluoride which I found (1 μM) (refs. 1 and 2) or that found by Singer and Armstrong (7·5 μM) (ref. 3) must be in error. While the diffusion method of Singer and Armstrong has been shown to produce erroneous values, the same cannot be

1969 GORE-TEX fiber production started; invented by Wilbert and Robert Gore, the breathable fabric used in water-proof sports and outdoor clothing[88,89,90]

1976 Taves *et al.* tentatively identify PFOA in human blood[54]

Organic Fluorocompounds in Human Plasma: Prevalence and Characterization

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1980 China started large scale PTFE production[27]

1981 First scientific report on toxicity caused by APFO[91]

1984 PFOA found in local drinking water near Washington Water Works plant, US[52]

1990s Dupont started to recycle APFO[27]

1998 3M reported to US EPA about widespread fluorochemical detection in human blood[92]

2000 3M report submitted to US EPA, made public; 3M initiated phase out of C6, C8 and C10 based PFAS products[71]

2002 3M phased out PFOA based chemistry; APFO production by ECF ceased; PFAS production shifted from developed to developing countries[93]

2002-2006 China filled the gap between PFOS based chemistry supply and demand, and increased significantly PFOA salts production (2004)[79]

2003 US EPA began Enforcable Consent Agreement (ECA) process with manufacturers[35]

2004 Long-chain PFASs (C8-C14) banned[79]

2006 US EPA and 8 major FP & FT producers launched 2010/2015 PFOA stewardship program[*,65]; EU adopted ban on PFOS in semi-finished products by 2008[27]

2008 Canada introduced ban on PFOS[94]

2009 PFOS and related compounds listed under ANNEX B of Stockholm Convention on POPs[95]

2010 Mineti ceased PFOA based chemistry[27]

2012 Daikin ceased PFOA production in Japan[27]; PFUnDA, PFTDA, PFTrDA, PFDoDA included in REACH[96]

2013 APOA, PFOA included in REACH[#,96]

2014 PFOA banned in consumer products in Norway[97]

2015 Madrid statement of Fluorochemicals**; PFNA and its sodium and ammonium salts included in REACH[96]

2016 POPs review committee concluded global action warranted for PFOA and related compounds[98]

2017 PFHxS and its salts, PFDA and its sodium and ammonium salts included in REACH[96]

2020 PFBS and its salts included in REACH[96]

Figure 1. Historical scheme of the fluorochemicals from the discovery of polytetrafluoroethylene (PTFE) to REACH regulations (reproduced with permission from RSC, ref 9).

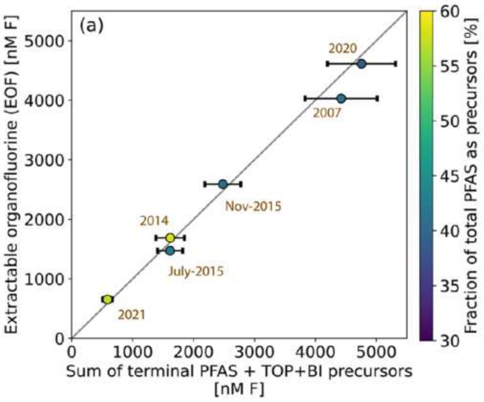


Figure 2. Mass budget for PFAS in groundwater below the fire training area at Joint Base Cape Cod, USA. (a) Comparison of detected extractable organofluorine (EOF) and PFAS concentrations. The x-axis represents the sum of terminal PFAS and oxidizable precursors inferred from the total oxidizable precursor (TOP) assay using Bayesian Inference. The sum of differences from duplicate extracts for targeted PFAS (9%; $n = 1$) and the standard deviation of inferred precursor concentrations are shown by x-axis error bars. Circles are shaded in purple by the fraction of EOF explained by oxidizable precursors. The one-toone line (gray) is used to compare the sum of terminal PFAS and precursors measured using targeted analysis and the TOP inference with EOF. [23] (Reproduced with permission from Amer. Chem. Soc.).

3. Issues on Mobility, Persistency, Toxicity and Bioaccumulation of PFASs

However, major concerns arise from their high-water solubility[26] and thus mobility, as well as their chemical stability, toxicity, persistence[25,27-29] and bioaccumulation in the Environment in the food chain and in humans.[5-6,10,12,22,27-30] A growing attention has been paid to PFAS as a specific chemical class[4,7,30] because of their adverse health effects, modes of action, and physical and biochemical properties,[4] mainly linked to their too stable small perfluorinated chain that cannot degrade or be metabolized.

Actually, modern powerful analytical apparatus and machines are able to detect very low chemical concentration (as low as several tenth of ppb[31] (or even hundreds of ppt); knowing that one ppb is a drop of water in an Olympic swimming pool!).

Globally, environmental officials from five-member states[16] launched actions to push regulatory agencies (as Registration, Evaluation, Authorisation and Restriction of Chemicals, REACH) and consequently EU to restrict PFASs (including FPs) with some plans to ban all PFASs by 2030 [32]. In addition, more than a dozen of states in the USA have been also influencing authorities to ban PFASs in the coming years (Maine and Minnesota have already started). Consequently, synthesizing alternatives to face perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) issues (since 2006, PFOA and PFOS, their salts and similar compounds have been banned in many countries) led to many research well-summarized in various review[20] or book chapters,[21,33] (though China is still currently using PFOA as polymerization aid as well as other PFASs containing shorter chain lengths). On the other hands, Chemours and Dyneon industrially produced hexafluoropropylene oxide dimer ammonium carboxylate (Gen®X or HFPO-DA) and 4,8-dioxa-3H-perfluorononanoate (Adona®), respectively, enabling to yield FPs, the quality and performances of which were similar to those of FPs obtained in presence of PFOA or PFOS. However, several years later, these surfactants had also been detected in soils and rivers probably because of their persistency and mobility issues.[9,33,34]

4. Different Categories of PFASs

PFASs have been categorized into two distinct families of fluorinated compounds, [4,7,26,35] the major differences being their molar masses (Figure 3) and dispersities for their separated uses.

4.1. Non-Polymeric PFASs

4.1.1. Introduction

Low molar mass-PFASs (< 1,000 g.mol^{-1}) including PFOA, PFOS and fluorinated telomers (Scheme 1)[9,36] have contaminated many places on Earth and oceans or decompose in the stratosphere leading to trifluoroacetic acid (that is extremely difficult to separate from water) and trifluoroacetate,[37] polluting waters and soils and thus bringing negative impact. These compounds also cross the cellular membranes of animals and human beings.[1,31,38]

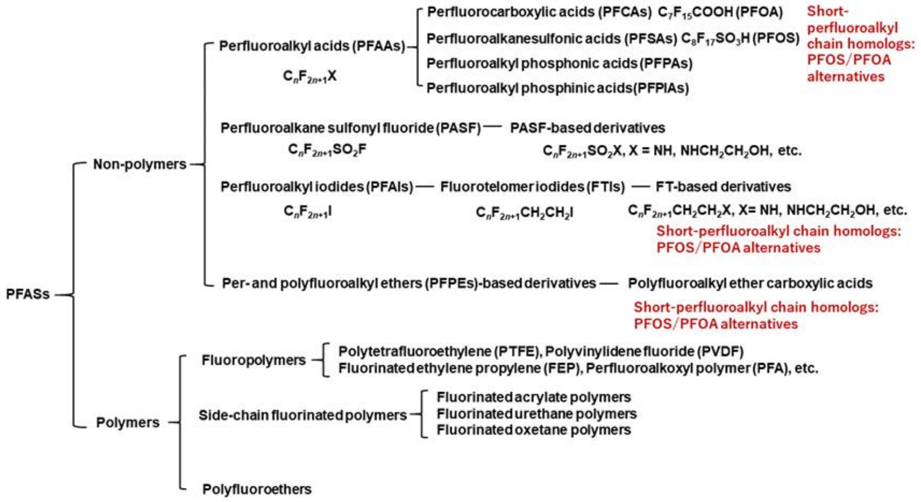


Figure 3. General classification of PFASs according to the Organization for Economic Co-operation and Development (OECD)[1].

4.1.2. Strategies to eliminate low molar- mass PFASs.

Beside the thermal,[39-41] biological,[42] microbial[43] degradation and that under subcritical water[44], well summarized by Mueller and Yingling[45] a variety of porous sorbents such as carbon-based materials, ion exchange resins or polycationic gels have been investigated to remove PFASs.[46-49] The adsorption behaviors of PFASs are dramatically affected by pH values of environmental conditions, as well as substances of several orders of magnitude higher concentrations than PFASs in natural water sources.[46-48] Therefore, selective PFASs separation under environmental friendly conditions sounds highly challenging.[49,50] Actually, thanks to the fluorophilicity feature, fluoropolymer nanoparticles (FPNPs) (e.g. star polymers with fluorinated nanogel cores and hydrophilic poly(ethylene oxide) arms able to remove PFOA from 10 ppm to ppb level[51-52]) are interesting candidates for PFASs adsorption, because they display strong and selective affinity to PFASs, FPNPs being highly resistant to non-fluorinated ions spread in the environment.

In addition, Song et al.[53] recently succeeded in eliminating FPAS by chlorine radical triggered electrochemical oxidation, while Chen et al.[54] synthesized original FPNP-embedded hydrogel for PFAS adsorption. These FPNPs were produced from tandem photo-mediated RDRP (Figure 4). The FPNPs showed significant adsorption performance to a many cationic, anionic, neutral and zwitterionic PFASs. The strong and selective affinity toward fluorinated compounds enabled clearance of PFASs at high environmentally relevant concentrations in water without being dramatically disturbed by acidic/basic conditions. Furthermore, such an FPNP-embedded hydrogel displayed good mechanical properties inclined to facilitate separation, regeneration and recycling of hydrogel.

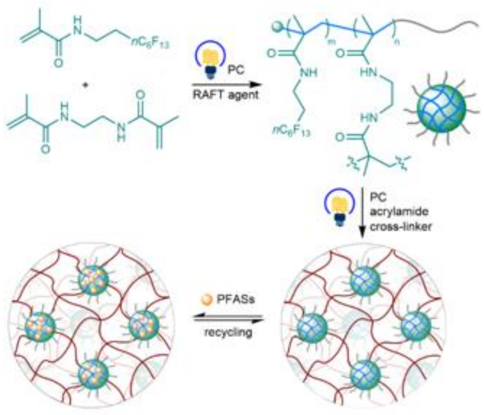


Figure 4. synthesis of fluoropolymer nanoparticles (FPNP)-embedded hydrogel and study on PFASs adsorption. Reproduced with permission from ref.[54] (copyright 2020 Amer. Chem. Soc.).

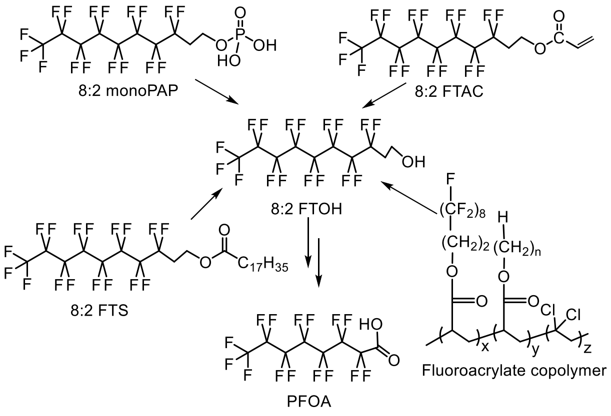
Beyond FPNPs, other fluorinated sorbents have been reported as relevant host molecules for PFASs guests. One example deals with cross-linked fluoropolymer gels,[46,49] β-cyclodextrin-based polymers,[55] granular activated carbon[41] are evidenced to capture neutral and/or anionic PFAS efficiently. The outstanding performance of those FPs further highlights that the fluorophilicity effect could be used as a basic feature to promote PFASs adsorption toward a sustainable society.

4.2. Fluorinated Polymers

4.2.1. FPs containing fluorinated side chain or Oxygen atoms

A wide variety of fluorinated polymers has been reported in some textbooks[56-59] and reviews.[60-64] While fitting the PFAS definition because of their chemical composition, structure, and presence of fluorine atoms,[4,7,64] FPs represent a specific family and are significantly different from other substances of PFAS category (Figure 3). Indeed, they can be composed of: i) polymers bearing fluorinated dangling chains such as poly[fluoro(meth)acrylate]s,[65-66] or fluorinated polyurethanes or poly[fluoro(oxetane)]s, ii) perfluoropolyethers, PFPEs, prepared by ring opening polymerization of either hexafluoropropylene oxide (HFPO) or oxetanes, or achieved from the photochemical polymerization of TFE and hexafluoropropylene (HFP) in the presence of oxygen[67] and finally iii) polymers containing Carbon and Fluorine atoms in their backbones.

Actually, polymers bearing (per)fluorinated side group have undergone major issue as evidenced by Liu and Avendaño[43] on their microbial degradation. It can be assumed that, because of their high chemical and ageing stability, to the best of our knowledge, no similar study has already been reported on FPs bearing fluorine atoms in the backbone. These poly(fluoroacrylate)s possessing ω-perfluorinated dangling moieties have led to 8:2 fluorotelomer derivatives (Scheme 1) while several studies have described the decomposition and releasing of the fluorinated side chain under various conditions.[66]



Scheme 1. Illustration of microbial degradation of poly(fluoroacrylate)s that generate 8:2 fluorotelomer derivatives.[43] (reproduced with permission from Elsevier).

4.2.2. Fluoropolymers (i.e. backbone containing C-F bonds)

4.2.2.1. Valuable Fluoropolymers with exceptional properties

This sub-section is devoted to polymers bearing C-F bonds within the backbone and it is divided into four parts. These unique specialty polymers are niche products (production: 330,000 tonnes/year[64] compared to >400 million tonnes/year of all polymers), known to be safe, bio-inert, persistent and not degradable under environmental conditions. These durable materials display outstanding properties,[56-64] prolong lifetimes, increase fire safety, reduce maintenance needs and keep good performances (even in extreme conditions or aggressive/corrosive media) where other materials fail. One example is the Challenger dramatic explosion in 1986, 73 seconds after liftoff, related to poly(thioether) seals which had too high Tg values. Since then, all shuttle packings and gaskets have been made of fluoroelastomers.[69]Advantageously, they are the unique candidates displaying the best heat and oil resistance (e.g. aircraft fluids as Skydrol®)[68] (Figure 5) and excellent flexibility. Essential for our daily life[63] and involved in many High-Tech areas, FPs are endowed with exceptional features,[56-64] their molar masses being able to reach several million g.mol^{-1} (as PTFE). Because of the growing need for higher requirements and engineering materials which combine specific properties for high-tech applications, FPs are currently undergoing an increasing development.[70]

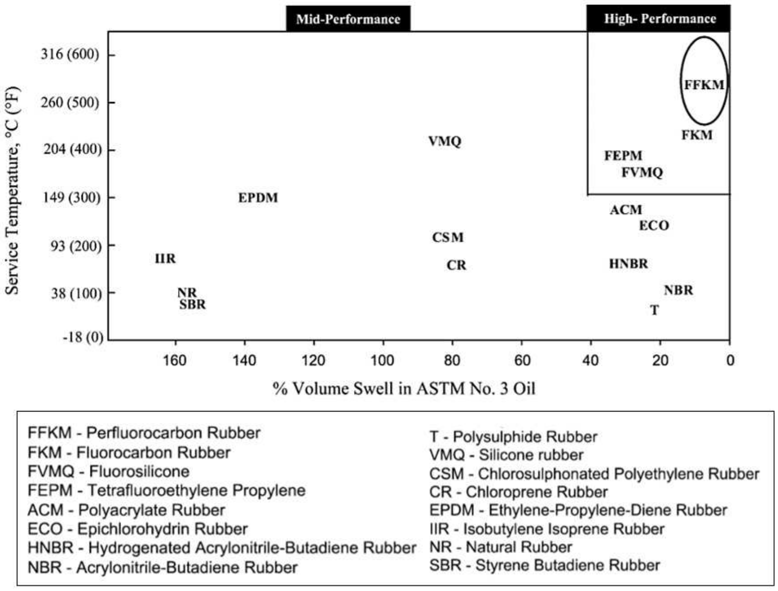


Figure 5. Compared relative heat and oil resistances of elastomers (ASTM D2000). Reproduced with permission from Elsevier [68].

One example is poly(vinylidene fluoride), PVDF, which satisfies stringent leachable limits and other national health regulations, ensuring that they are safe for use in water treatment. In addition, this FP is durable, withstanding high pressures while maintaining structural integrity.

Actually, these specialty polymers are also involved in specific UV and aging resistant coatings and have been involved in many other applications: i) wires and cables in wide domains such as aerospace (because of high limiting oxygen index value, PTFE coatings ensure fire retardancy to several hundred km-cables and connections in planes, insulation (insulation resistance ≥ 1500 MΩ.km), electrical and high frequency (5000 V) performance, coaxial cables for avionics and high temperature resistant cables for aero engine services.[71] The resilience and inertness of crosslinked elastomers provide in exceptional performance to gaskets in shuttles[72]); ii) materials for Energy storage and conversion (as key-candidates for the energetic transition: cathode binders in Lithium ion batteries, proton exchange fuel cell membranes, backsheets of photovoltaic panels, electroactive (piezoelectric and electrothermal) devices,[73] haptics, printed electronics, dielectrics, for virtual reality, actuators for artificial muscles, and are indispensable drivers of the European Green Deal], iii) chemical process industry (e.g., injection molded PVDF tower packing is used over and over in sulfuric acid and chlorine scrubber systems and does not lose its properties like other polymers when exposed to harsh chemistries and high temperature.), iv) transport (transmission fluids and specific seals and gaskets)[57,74], telecommunications (optical fibers among more than 4 million km of undersea cables are carrying information via a huge network),[75] food and water treatment, electronics,[76] pharmaceutical and medical devices.[77-82]

FPs should only be involved in uses required for health, safety, or are critical for the functioning of society and no alternatives are available. [9,63,64,83-84] In addition, searching alternative materials would reduce the time required for toxicological analyses.

The most prevalent materials are PTFE,[61] PVDF,[73,85] poly(chlorotrifluoroethylene), PCTFE,[86] and the copolymers based on tetrafluoroethylene, TFE, [87] and vinylidene fluoride, VDF,[88] which can be either thermoplastics or elastomers.[72] Usually, in their conditions of uses, FPs are safe, stable (thermally, chemically to UV and aging, and biologically), durable, non-toxic, non-bioaccumulative, insoluble in water and thus non-mobile, are hydrolytically stable, and are not subject to hydrolysis catalyzed or metabolized degradation. For these features, they are not considered as substances of very high concern (SVHC) and fulfil the 13 criteria (see section 4.2.2.3.).[35,89-90] Furthermore, their relevant combinations of properties are not matched by any of the alternative hydrocarbon polymers, [9,63,83-84] hence making them so unique and valuable.

The regulatory agencies, such as Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), [32] Toxic Substances Control Act (TSCA) and Japanese Existing New Chemical Substances Inventory (ENCSI) support initiatives aimed at regulating the substances of greatest concern. They will endeavor to contribute to the broad and complex scientific, technical but also economic forthcoming debate on those substances. Actually, FPs seem to be impacted by the upcoming restriction on PFASs under the EU REACH Regulation, published on February 2023.[32]

4.2.2.2. Improvement of FP production in more environmentally friendly processes

Because they are concerned about the negative aspects of fluorinated polymerization aids (FPAs or surfactants) currently used to replace PFOA, FP manufacturers have been overcoming the great challenge to produce FPs free from FPAs. They are currently searching solutions in both replacing such PFAs by non-FPAs and processing by reducing fluorinated effluents and gas emissions. Indeed, a few years ago, the Chemours and Dyneon companies developed and used Gen®ex and Adona®, respectively, though these FPAs have been found as traces in rivers and soils.[33] However, the regulatory agencies are currently pushed from various authorities in helping the industry to swiftly move towards sustainable technologies and many efforts from these FPs producers have been recently taken in two main strategies: i) absence of FPA, as well as matching the PLC criteria are more appropriate to specific syntheses (as FKM). Much progress has been observed in the last decade after several FP manufacturers modified their production using NFPAs (or surfactants) leading to major innovations by the whole industry (such as 3M,[91] AGC,[92] Arkema,[93] Chemours,[94-95] Daikin,[96] Gujarat Fluorochemicals[97-99], Solvay[100] and others in filing multiple patents claiming such a "NFPA Technology" for various products (Table 1).[101]

Table 1. Industrial developments of NFPA technology in the manufacturing of fluoropolymers.

Type of Fluoropolymer	Reference
PTFE Aqueous dispersions	89,93
PTFE Fine powders	90,94
PVDF	88,93,95
FKM	89,92,95
PFA	94

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FKM and PFA stand for poly(VDF-*co*-HFP), poly(VDF-*ter*-HFP-*ter*-TFE), and poly(TFE-*co*-perfluoroalkyl vinyl ether) copolymers, respectively.

However, the use of NFPAs in a specific recipe (for example, in aqueous radical polymerization of M1 fluoromonomer, e.g., TFE), does not necessary lead to the same success for that of another M2 monomer; e.g., VDF or a mixture of various fluorinated comonomers). The legislation process should be focused on the use of FPAs and the emissions of fluorinated derivatives. In this regard, a regulatory decision tree was suggested [101] (Figure 6), linked to the manufacturing FPs in presence or absence of such surfactants (with process abatement to get a PFAS concentration lower than 25 ppb[38]), essential use criteria in terms of safety, performance, health, improvement of the process and alternatives.

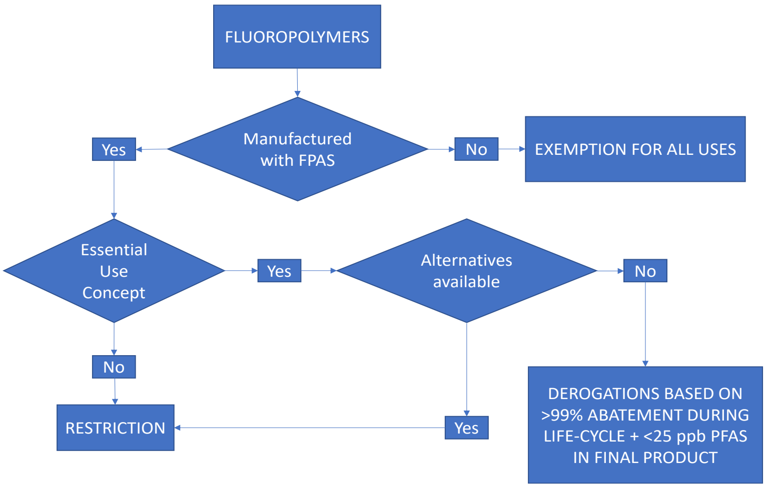


Figure 6. Regulatory decision tree for fluoropolymers (reproduced with permission from Lexxion[101]).

Hence, FPs produced without any FPAs should be exempted for all uses across all industries including consumer applications as they raise no risk to Environment, to mammal and to the human health, in addition to the fact that FPs also match the PLC criteria.

ii) Manufacturing modification. The second action taken by many FP manufacturers aimed at changing their process to eliminate fluorinated side-products such as residual reactants, oligomers, low molar mass-derivatives and intermediates, aqueous residues and volatiles. Actually, improving the abatement processes and PFAS recovery in the manufacture of FPs have enabled the reduction of 99% of fluorosurfactant emissions since the 1990s [102] while recent studies have brought it as high as 99.99%.[103] For example, though severe analyses were published in the last decade [104], the Arkema Company strongly reacted and announced that, since February 2023, this innovative solution made it possible to reduce C_6F_{13}-telomer sulfonates (6:2 FTS) emissions by more than 90% and that emissions of such a telomer now represents less than 1 kg per day [105] in the FP manufacture in Pierre-Bénite (France) without the use of any fluorosurfactants. Actually, by the end of 2024, a similar process will equip all its other production sites around the world.[105]

Other companies have also been modifying their process to significantly reduced their emissions, many of them having announced such strategies.[105-111] An abundant literature is available in relation to the control and treatment of emitted PFASs from industrial processes[43-45] while many studies are still ongoing.[39,113]

4.2.2.3. Polymer of Low Concern criteria

More recently, the American Chemical Council led the Fluoropolymer industry Group (*Fluoropolymergroup*) to investigate a similar study on 14 additional fluorinated (co)polymers.[90] FPs and the Stockholm Convention persistent organic pollutants (POP) criteria meet the persistence criterion only, but not the bioaccumulative, toxic, or mobile criteria.

According to OECD definition,[1,35,114] the criteria of polymers of low concern (PLC) that result from the combined experience and knowledge of global regulatory authorities on predictive parameters of health and environmental hazards induced by polymers have been extensively reported in several reviews.[114-116] Indeed, to be regarded as a PLC, a polymer must not have any known hazard classification while they also should commit to the following criteria:

i) a high average molar mass in number (M_n) and a minimum oligomer amount are the most important requirements for PLC assessment, as claimed by EU:[115] "*most potential health concern polymers have a low number average molecular weight, M_n, (< 1000 Da) and an oligomer content >1%*." The higher the amount of oligomers, the more the polymer eco-toxicological.[114] Actually, by comparing the potential health concern of polymers with varying the oligomer percentage, "*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*".[114]

ii) Reactive functional groups (RFG) requirements.;

iii) solubility in solvents and in water lower than 10 mg.L^{-1};

iv) other criteria such as a_low cationic density, not containing any CF_2 or CF_3 groups; being stable under the conditions in which it is used. The primary concern for such FPs is its degradation in the environment to release persistent, bioaccumulative or toxic products, not being a high molar mass water absorbing polymer (≥10,000 g.mol^{-1}) and not having any known hazard classification.

Indeed, regarding the RFGs and RFG ratio to M_n,[90,115-116] FPs fulfill the PLC criteria. PTFE most typically bears terminal $-CF_3$ groups[35] that is not considered as an RFG. Furthermore, M_n value is an important feature of biological effect because very large molecules (>1000–10 000 Da) are too big to cross the cellular membrane[117-119] and thus cannot react with "target organs," such as the reproductive system. Hence, as the M_n of a polymer increases, a reduced incidence of potential health concern effects might be expected,[114] and, as a proof, expended PTFE (e-PTFE) materials are currently used for stents, cardiovascular prostheses, and many other medical items. [80-81]

In contrast and as expected, a polymer is not suitable to the PLC criteria if it decomposes considerably, degrades or depolymerizes during use. In other words, it undergoes a deep modification into simpler, lower molar mass-chemicals as the result of oxidation, hydrolysis, heat, sunlight, attack by solvents or microbial action or any other reaction(s). Indeed, FPs are resistant to such reactions/decompositions. [59] Based on such relevant features and above PLC criteria, Henry et al.[35] supplied key-evidences on four main FPs (PTFE, FEP, PFA and ETFE) matching the 13 PLC criteria.[120] By gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) analyses, these authors characterized the extractible fractions from these FPs and detected less than 2 ppm leachable from PTFE (Table 2).[35] As expected, since the monomers are gases, they were not detected.

Advantageously, as most FPs, PTFE is insoluble in water and, therefore, is not mobile in the environment. Using the descriptive solubility table for the US Pharmacopeia,[121] the water solubility of PTFE would be classified as insoluble (10^{-5} mg.L^{-1} or 0.01 mg.L^{-1}) to very slightly soluble (10^{-4} mg.L^{-1} or 0.1 mg.L^{-1}).

Table 2. Results of gas chromatography/mass spectrometry and liquid chromatography/mass spectrometry analyses of extractible fraction from PTFE to match the PLC criteria (readapted with permission from Wiley) [35].

Final PTFE Results		
Properties of Interest	**Concentration**	**PLC Criteria**
*% oligomer	Not detected	< 2% wt/wt (20,000 ppm)
**residual monomers	Not detected	No Limit Established by OECD, 2009
low molar mass leachables & extractables	#2 ppm	No Limit Established by OECD, 2009

*Polymers with potential health concern have an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content (OECD, 2009). The table lists the lower limit, 2%.

**The data set used by OECD[114] to establish the PLC criteria was insufficient to establish a universal limit for all residual monomers, though residual monomer content was established as a PLC criteria.[108] According to U.S. EPA's Safer Choice criteria (SCP, 2015), TFE is a residual of concern, which is not allowed to be present in Safer Choice recognized products at 0.01% or higher. There is no specific limit on residual monomer in the PLC criteria.[114]
#Isopar K, an unavoidable ambient air contaminant adsorbed to the PTFE fine powder, was detected at $\leq$ 2 ppm.

The polymer policies of 10 countries, including the EU REACH handling of polymers, were examined[114] and concluded that "Polymers with <1% of M_n <1000 Da and low water extractivity are not able to cause systemic effects which are toxicologically or ecotoxicologically relevant." In the case of high molar mass-FPs, such characteristics are not observed (Table 2).

Among all FPs, PTFE is not a substance currently registered under REACH regulations supplying the 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*".[122] But, because PTFE, as all FPs, is an identifiable organic substance, the suggested Universal Basic Asset (UBA) framework for assessment using the proposed PMT criteria (persistent, mobile and toxic) would be applicable. Moreover, PTFE is highly stable in the environment and is resistant to thermal degradation. Being stable for years at temperatures up to 260 °C; [35,123,124] it is stable to hydrolysis, oxidation, and light, as well as to anaerobic and aerobic degradations.[125] Therefore, PTFE would fulfill the UBA's proposed persistence criterion.

As stated by USEPA, regarding PFAS and PFCA, the regulatory agency suggests 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*)."[126] Surprisingly, the key characteristic is the presence of a $-CF_3$ group that is attached to, or forms part of, the polymer backbone and "*this link (between the polymer backbone and the $-CF_3$ group) is susceptible to degradation and cleavage*."[126] Thus, in a USEPA's report, the presence of $-CF_3$ group is relevant since it is a structural alert to consider potential degradation products.[127] This statement is quite surprising since a CF_3 end-group prevents from depolymerization by unzipping.[59]

As listed in Table 2, these FPs are not subject to degradation.

Another advantage of PTFE deals with its non-toxicity. Thanks for a too high (several million) average M_n of PTFE mentioned above, it cannot cross the cellular membrane, indicating it is not toxic or bioavailable. Indeed, this polymer has been extensively tested in the European Union and USA to allow commercial applications for global medical device regulations, food contact, and surgery.[77-81] Furthermore, FPs contain none or tiny monomer(s) (which are gaseous), oligomer(s), and leachable amounts and no reactive functional groups with high toxicity (Table 2). [35] These comparisons of PLC and various regulatory assessment criteria demonstrate that, in contrast to conventional PFASs, high molar mass-FPs display quite different characteristics. Therefore, they should fall in a separate class of materials that must be determined on their own features.

More recently, the American Chemical Council led the Fluoropolymer industry Group (*Fluoropolymergroup*) to investigate a similar study on 14 additional fluorinated (co)polymers.[90] FPs and the Stockholm Convention persistent organic pollutants (POP) criteria meet the persistence criterion only, but not the bioaccumulative, toxic, or mobile criteria. Actually, their physico-chemical properties prevent bioavailability, bioaccumulation, toxicity, and degradation. Presently, 96 % of FPs fulfill these 13 PLC criteria.

4.2.2.4. Recycling, End of Life and Reuse of FPs

Recycling is the re-introduction of utilized compounds (or polymers) into the cycle of products (i.e., polymers in the context). They are collected, sorted and refined to be re-used as materials or energy source. Recycling should help to preserve resources and to avoid waste.[128-130] Indeed, the recycling of plastics is a real challenge[131-133] since only ca. 9% of polymers is recycled, less than three time more that of FPs.[134] The global plastics production was 460 million tonnes (Mt) in 2021,[131] predicted to reach 1120 Mt annually by 2050[132] and should increase up to 1231 Mt by 2060. In the 2000-2019 period, the growth of plastics has outpaced that of economic growth by almost 40%. MacLeod et al.[133] highlighted the global threat induced by the plastic pollution, based on the high environmental persistence of plastics. In contrast to commodity polymers, the consumption of FPs represents a quite small volume (estimated to 330,300 metric tonnes in 2021[64], hence representing less than 0.1% among all polymers). In 2015, its global consumption was 270 kt evidencing a 22.2 % increase since then. Actually, the global situation on the fate of FP waste is as follows: 83.5% of incineration, 13.1% landfill and 3.4% of recycling,[134-135] briefly summarized hereafter.

i). *Different techniques of recycling.* FP waste from commercially available and industrial waste manufacturers are either pre-sorted or arise from dismantling processing or can also be incinerated for energy recovery. Fractions of pre-sorted FP waste are devoted to recycling, either to be exported for recycling in various countries[134-136] or to domestic recyclers. Other recycling includes sintering, re-grinding or chemical recycling of FP materials. Four main ways of recycling are possible:[128] i) primary (or mechanical) recycling; ii) secondary recycling; iii) tertiary recycling and iv) quaternary (or energy) recycling.

ii) Decomposition and recycling of FPs

Several examples are supplied here after:

PTFE. The thermal degradation and pyrolysis of PTFE was studied by many authors. In 1947, it was pioneered by Lewis and Naylor (under vacuum at 600 °C);[137] 9 years later, by Wall and Michaelson (at 450-510 °C, under the presence of various gases),[138] then reported by Simon and Kaminski[139] (who pyrolyzed PTFE at 500–600 °C in a fluidized bed reactor, the primary products of decomposition being TFE and $^\bullet CF_2^\bullet$ bisradicals) and comprehensively described by Ellis et al.,[140] followed by Schlipf and Schwalm,[141] further up dated by Puts and Crouse,[142-143] carefully reviewed by Lakshman and Chakraborty in 2015 in a book.[144] Puts and Crouse,[142-143] could deeply detect and quantify the released fluorinated compounds (especially fluoroolefins and octafluorocyclobutane, OFCB) in the pyrolysis of PTFE from 35 °C to 800 °C in presence or absence of various metals or salts. These authors highlighted that, in absence of salts, TFE was produced in 98% while the nature of the salt induced other released gases with the influence of inorganic oxides of Al, Cr, Co, Cu, Fe, Ga, In, La, Mn, Ni, V, Zn and Zr (Scheme 2).[142-143]

Industrially, while various thermal processes (smoldering, pyrolysis, open burning, etc) were claimed in the patent literature (recently summarized),[136] reuse of fluoromonomers have scarcely been reported, as scaled up in a pilot plant at Dyneon Company,[145-146] (Figure 7) via a robust process so-called "*FP upcycling technology*" yielding more than 90% TFE/HFP. This technology was scaled-up into a new demonstration plant (capacity is presently >500 tonnes year).

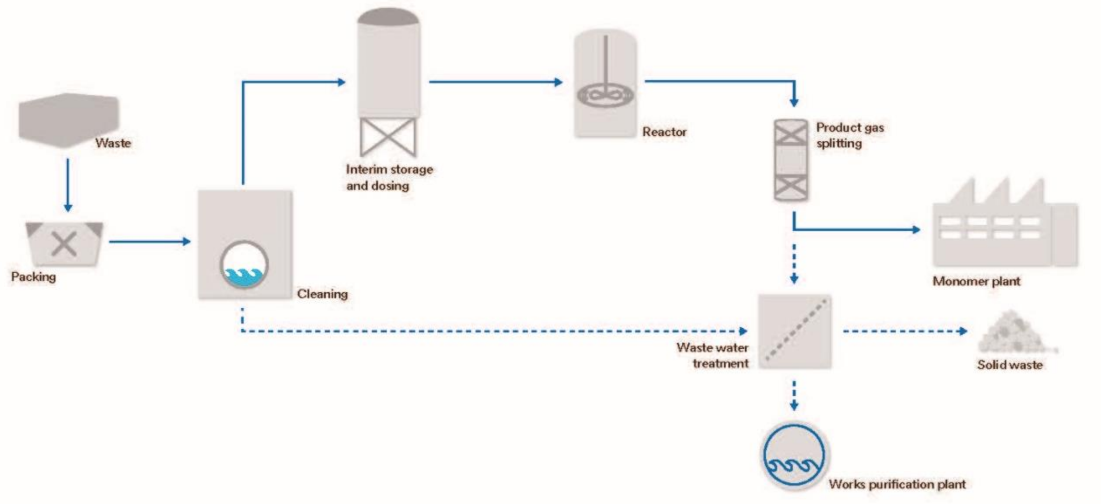


Figure 7. Sketch of the world's first pilot plant for recycling perfluorinated polymers in Germany[145] (with courtesy from 3M/Dyneon).

Recycling of other thermoplastics. The Arkema Company[141-142] claims to use PVDF copolymers as processing and recycling aid (PPRA) for polyethylene and polypropylene films, pipes, cables, and injection molded parts. Such a PPRA increases output and flow, enhances surface finish, reduces extruder pressure and allows a steady gauge control and a processing at lower temperatures. This company has involved a process which enables 20-30% only of recycled materials before losing some feature and being reprocessed up to 90 or even 100% recycled materials to make such above items.[147] Materials already containing the PPRA recycle behave almost the same as a virgin material in which polymer processing aid (PPA) was added as a master batch at the extruder.[148] PVDF and VDF copolymers are currently assisting the reprocessing of high-volume polyolefins as a PPRA. In addition, Takahara's group [149] reported that PVDF used for fishing lines could not be degraded by UV radiation and biodegradation and thus, may be recycled after use.

Recycling of Fluorinated Elastomers. The recycling of fluorinated elastomers has been reported in a few studies, well-summarized by Schuster et al.[150] These authors reported only two relevant methods to achieve the recycling of poly(VDF-*ter*-HFP-*ter*-TFE) terpolymers (also named FKM) in an industrially acceptable way by i) milling FKM into fine powders to be mixed to virgin FKM and ii) the mechanical devulcanization of FKM, followed by successive compounding with virgin rubber. Both techniques give suitable thermostable products by preserving the mechanical features of original FKM. Indeed, these authors' review cites many patents mainly while the quoted articles just refer to the degradation and not to de-vulcanization. These authors concluded that recycling FKM is possible and leads to products with competitive properties to those obtained in presence of virgin FKM. But, as known, Schuster et al.[150] stated that fluorinated elastomers are usually crosslinked and thus recycling is rather complex in addition to the fact that they also contain fillers and additives.

Degradation and recycling of perfluorosulfonic acid membranes. Another key-functional FP is a copolymer based on TFE and a perfluoroalkyl sulfonyl fluoride vinyl ether further processed into proton exchange membranes for fuel cells, PEMFC, such as Nafion®, Flemion®, Fumion and Aquivion®, called perfluorosulfonic acid (PFSA) membranes (Figure 8).[151] These high performance polymers are also involved in chloro-alkali process to produce chlorine and sodium hydroxide from brine, desalination for drinkable waters, and electrolyzers able to produce "clean" hydrogen from water. Though the thermal degradation of Nafion® N117 membrane was reported by Feng et al.[152] or by Zaton et al. [153], its recycling is really challenging.

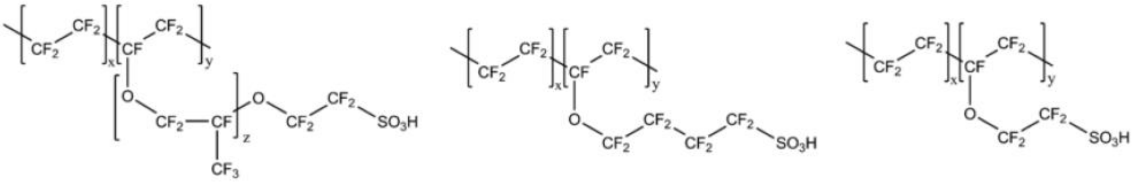
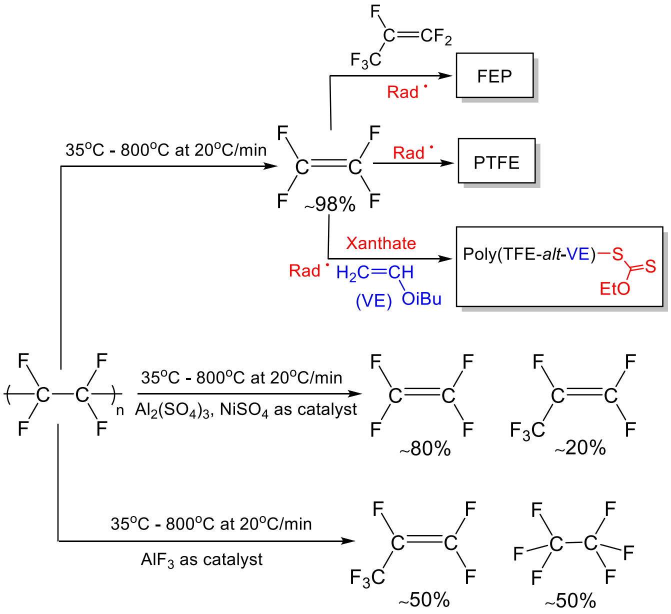


Figure 8. various types of perfluorosulfonic acid (PFSA) for PEMFC membranes used in fuel cells and electrolyzers.

Nowadays, no alternative is foreseen to be able to substitute such highly performance materials,[9,59,63,83-84] essential to the functioning of the hydrogen value chain and electrolyzers. These are produced and used in a highly controlled industrial environment, where their emissions are negligible and, due to their high initial price, their reusability and recyclability are actively investigated. So far, a patent from Grot[154] (by dissolving the membrane and separating the components), a report from Park [155] and a British Research and Innovation project, called Frankenstack[156] (dealing with the recovery and reuse at the end of the lifecycle membrane) are the only documents describing the recycling of PFSA membrane.

4.2.2.5. Chemical recycling to monomer and reuse of the released fluoromonomers. The chemical recycling of FP to fluoromonomer (CRM) is a real challenge. One example is illustrated by Scheme 2 that represents the depolymerization of PTFE into TFE or other fluorinated compounds according to the conditions. Actually, the generated TFE could be involved in various reactions enabling to close the loop: i) in radical homopolymerization initiated by peroxides or persulfates to lead to PTFE[157]; ii) by conventional radical copolymerization of either HFP[158] or isobutyl vinyl ether (iBuVE)[159] to produce either poly(TFE-*co*-HFP) copolymer (or FEP) or alternated poly(TFE-*co*-iBuVE) copolymer (as commercially available Zeffle® homologues[160]), and finally iii) under reversible addition–fragmentation chain-transfer (RAFT) copolymerization of TFE and iBuVE, controlled by a xanthate, to yield well-defined poly(TFE-*co*-iBuVE) copolymers.[159]



Scheme 2. Thermal decomposition of PTFE in absence or presence of various metals or salts to lead back to TFE (and other fluorinated compounds). [142-143] The recovered TFE was homopolymerized, [157] or copolymerized with HFP[158] or isobutyl vinyl ether (iBuVE)[159] to produce either PTFE, poly(TFE-*co*-HFP) copolymer (i.e. FEP) or alternated poly(TFE-*co*-iBuVE) copolymer.[159.]

Anastasaki et al.[161] reported the catalyst-free depolymerization of poly(2,2,2-trifluoroethylmethacrylate), PTFEMA, at 180 °C. This polymer was previously synthesized by reversible addition–fragmentation chain-transfer polymerization (RAFT) of TFEMA controlled by a trithiocarbonate (TTC). The kinetics of depolymerization, monitored by ^{1}H NMR spectroscopy, evidenced the unzipping reaction and evidenced that at the end of the reaction only TFEMA and the TTC remained in the flask (Figure 9). Though it required heat, that reaction did not need any toxic reactants.

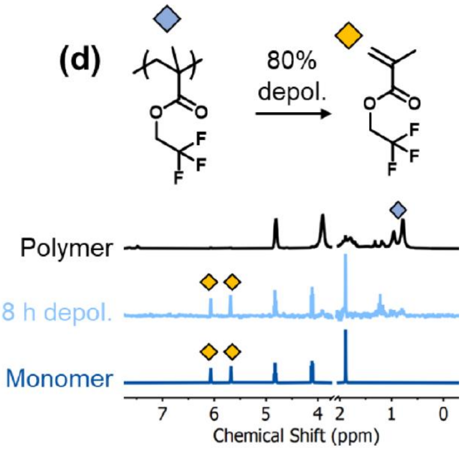


Figure 9. reaction scheme of the thermal depolymerization of poly(2,2,2-trifluoroethylacrylate), PTFEMA, and ^{1}H NMR spectra of PTFEMA (up), of the total product mixture after 8 hrs (middle

spectrum) and of TFEMA after depolymerization (bottom). (copyright reproduced with permission from Amer. Chem. Soc)[161].

4.2.2.5. Reuse of degraded FP

Bai's team [162] described that commercially available FKM elastomer [poly(VDF-*co*-HFP) or poly(VDF-*ter*-HFP *ter*-TFE) fluoroelastomers, Mn > 300,000 g.mol^{-1}], the average molar mass in number and dispersity of which were Mn=134,000 g.mol^{-1} and PDI=3.7 (while the VDF:HFP molar ratio was 3:1) could undergo a tertiary recycling yielding to cooligomers. The Mn of these latter were ranging between 3,300 and 10,400 g.mol^{-1}. This reaction occurred in presence of sodium hydroxide, hydrogen peroxide and triethyl ammonium chloride. These transparent dicarboxyl telechelic cooligomers were first chemically changed into diacrylates and then photocrosslinked. The resulting network exhibited suitable mechanical and hydrophobic properties.[162]

A more recent work on the use of FEP waste for transparent soils was achieved by the coating of specific terpolymers onto such waste (thanks to Fluorine-Fluorine interactions). The growing of lettuce roots was monitored by optical system and the roots were able to live in such an environment. [163]

4.2.2.6. Incineration

Incineration is the last method to process end of life of FPs. Recent studies on the disposal of end-of-life PTFE have highlighted the incineration to be an appropriate way to dispose of FP too, with no environmental concern. It is a high-temperature flaming process, happening in open air space, whereas smoldering is a flameless combustion process that occurs on the surface of a condensed fuel. While both methods can be utilized to decompose fluorinated waste, the main difference is that smoldering is self-sustaining and, hence, is more energy efficient compared to incineration which needs a continuous energy input.

The incineration or combustion, differs from thermolysis in that a source of fuel is used in order to purposefully favor a complete degradation of FPs (as a source of trifluoroacetic acid or acetate, TFA, and chlorodifluoroacetic acid, CDFA).[140] Furthermore, due to the high temperatures and oxidizing conditions used, it is unlikely to produce environmentally significant levels of TFA or TFA precursors. On the other hand, low-temperature burning of domestic waste, as an important source of furans and polychlorinated dioxins to the atmosphere, may analogously be a huge source of fluorinated acids.

Incineration has been adopted by various countries. [134-135,164-165] In the case of Norway,[165] though the municipal solid waste incineration (MSWI) conditions are achieved at about 850 °C, emissions of FP degradation products from household waste incineration have not been investigated yet. However, on the laboratory scale, the decomposition of PTFE and other FPs was comprehensive studied in the 700-1050 °C temperature range, yielding various main released products such as CF_4, CHF_3, C_2F_6, TFE, HFP and OFCB (Table 3). [124, 140,165-171]

Table 3. FPs and their main decomposition products at various temperatures from in the literature. In parenthesis: PFC-code[165] (reproduced with permission from Norwegian Institute of Air Research).

Polymer	T (°C)	Main products	References
PTFE	450	COF_2. HF	124
	400~500	TFE, HFP, PFIB	166
	500	HFP, TFA	140
	530	CF_4, C_2F_6, TFE, HFP, c-C_4F_8 (c-OFCB)	167
	550	CF_2O, C_2F_6, CF_3CFO, C_5F_4, CF_3CF_2CFO, $(CF_2)_3O_2$	168
	600-700	TFE, OFCB	169
	750-800	HFP	169

	850-900	PFIB	169
	800 °C	CF_4	124
	>900 °C	C_2F_6	124
	850	HFP, TFE	170
	750-1050	C_2F_6, CF_4	170
ETFE	350	COF_2, PFBE, TFE, CO	124
ECTFE	500	TFA, CDFA	124
FEP	400	COF_2, HFP, TFE, PFIB	124
PFA	400	COF_2	124
PEEPE	500	TFA	140
CPTFE/PCTFE	500	CPFP, CDFA	124
PTFE/PFA + PTFE/FEP	800	CH_4, CHF_3 (HFC-23), C_2F_6 (PFC-116)	171

Most of these substances are non-toxic, but highly toxic ones like perfluoroisobutylene (PFIB) or fluorophosgene may possibly be released under some severe conditions.

Wang et al. [172] suggested that PFASs may be generated from FP waste via a MSWI process, probably at temperatures lower than 500 °C. Thanks to its high thermal and chemical stabilities, PTFE is inert in the environment and Taylor et al.[173] found that municipal waste incinerators operating with an average gas temperature of 1000 °C can be used to totally decompose PTFE.

In contrast, in Germany, Aleksandrov et al.[174] reported that the incineration of PTFE, using best available techniques (BAT), did not release any PFAS. By comparing with the possible formation of 31 PFAS compounds as references, these authors noted that PTFE could almost fully decomposed into fluorine (as HF) and concluded that the municipal incineration of PTFE should be considered as an acceptable form of waste treatment. They tested for the presence of 31 different PFASs and 11 of these were detected but deemed to be due to contamination from the environment. A constant mass flow of wood pellets was utilized while these authors added PTFE into the reactor to maintain a consistent thermal profile, as shown in Figure 10.

Furthermore, the Dutch Institute for Public Health and Environment (RIVM) [164] drew slightly fewer concrete conclusions, mentioning that, although it can be assumed that the polymers are destroyed with the gasification process, this does not provide enough information on the kind and degree of by-products formed and on the rate of mineralization.

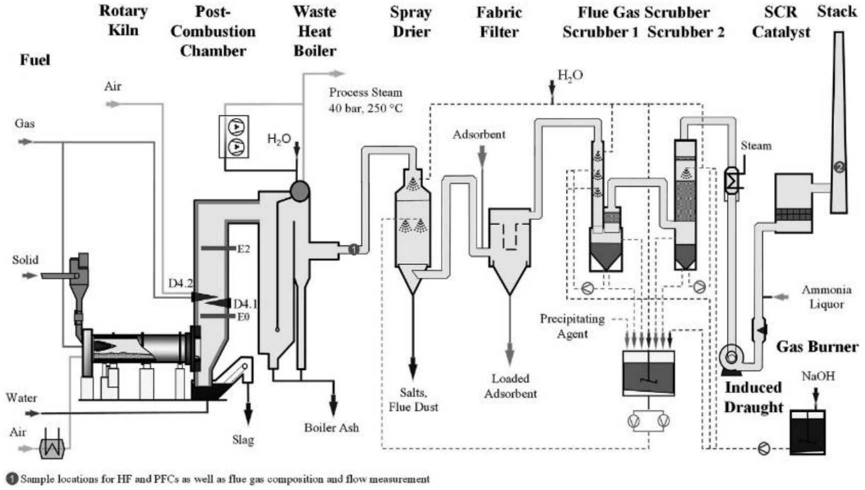


Figure 10. Engineering drawing of the German acronym for "*Brennkammer mit Dampfkessel*" (BRENDA) pilot combustion facility at Karlsruhe Institute of Technology.[174] (Reproduced with permission from Elsevier).

In EU, the overall situation of the fate of collected FP waste involved in recycling, recovery, reuse and landfill, proposed in the Conversio Report, is illustrated in Figure 11[134-135] indicating that, globally ca. 23.5 kt of FP waste were collected in 2020 (< 0.01% of the total waste). To compare, ca. 29,450 kt of plastics were collected in 2020 (<5% of the total collected waste excluding mineral fractions). Moreover, about 84% (20.4 kt) of the total FP collected waste in Europe in 2020 is either thermally or (co-)incinerated destructed while 3.1 kt (13.1%) were landfilled. Finally, 0.81 kt were collected separately for recycling whereas a significant amount was exported for recycling (e.g. to Asian countries).[130]

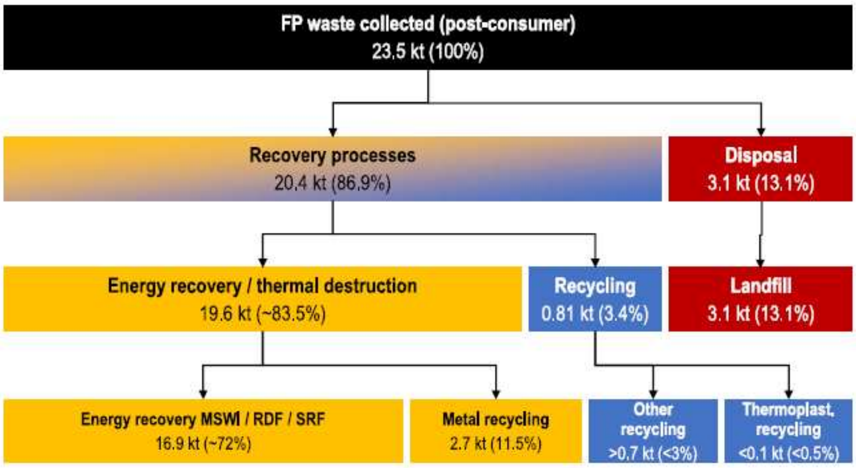


Figure 11. Fate of collected FP waste and tonnages (percentages) involved in recycling, recovery, reuse and landfill in EU.[135.]

Beside incineration, more severe degradation of FPs can be obtained by various methods including smoldering, pyrolysis. These are efficient to treat fluorinated waste,[136] the first one being self-sustaining. As a high-temperature process used for thermal decomposition, pyrolysis is similar to incineration except it is achieved in an inert atmosphere. For an efficient degradation, a temperature greater than 900 °C is preferred. These techniques enable to lead to total destruction of released hazardous PFASs. Several studies have tested the efficiency of these methods to determine if they reach temperatures high enough for a sufficient duration enabling a complete degradation.[174-175] Other techniques of incineration [136] such as mineralization (vide infra) of FPs during thermal treatment, or a plasma-based water treatment, are also being investigated as they may be safer and more efficient to treat waste.

4.2.2.7. End-of-life

Several authors have studied the end of life of FPs.[136] Actually, when a FP has fulfilled its intended use and will be disposed of, the fate of FPs must be investigated.

Many reports have concluded that FPs such as PTFE do not degrade in the environment and do not release any hazardous compounds toward mammals, human beings and for Environment.[102,123,165,176,177] Thus, the downstream, end-of-life process of incineration should lead to more studies.

In addition, though FPs match the PLC criteria (section 4.2.2.3.), circular economy of FPs deserves more interest, and to our knowledge, Wahlström et al.[165] have comprehensively proposed an overall situation including several flows (Figure 12) ranging from the manufacture of FPs to their use and their recycling (also analyzing the depolymerization of PTFE into TFE as explained in sections above).

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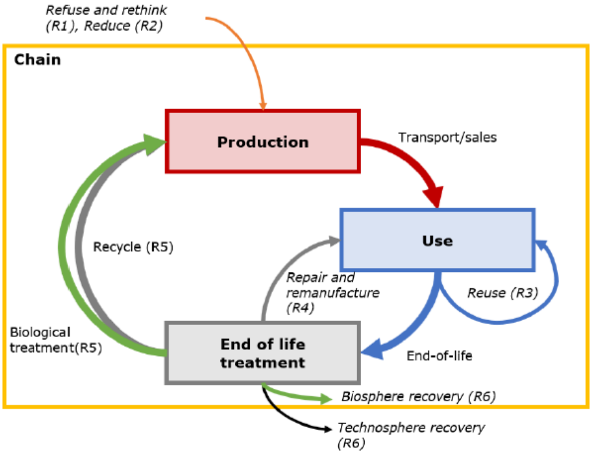


Figure 12. Sketch of flows of materials in a circular economy[165] (reproduced with permission from the European Topic Centre Waste and Materials in a Green Economy).

The Conversio report[134] extensively provided the results of the treatment of FP waste by industry segments (automotive, aerospace, semiconductors, electronics[76] and chemical industries) in the EU in 2020 regarding collected waste, energy recovery, landfill and recycling as well as co-treatment of FP and associated waste streams. Figure 13 represents the overall circular economy situation of FPs in EU, involving pre-consumer processing losses during the manufacturing of FP products and applications. [134-135] Most FP are (co-)incinerated in MSWI plants or dedicated hazardous waste incineration plants which are treating different wastes from chemical waste producers. Indeed, two main ways of recycling have been used (Figure 13): the mechanical and the chemical ones enabling to recycle melt processible FPs (such as PVDF or PFA) or non-melt processible ones (as achieved at Dyneon[145-146] or Karlsruhe Institute of Technology[174]) or virgin raw FPs.

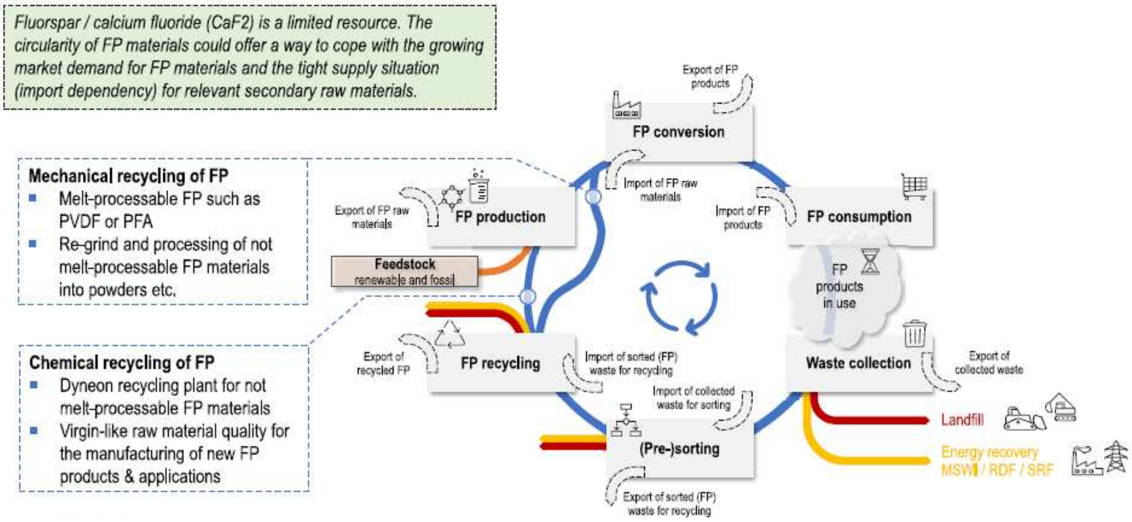


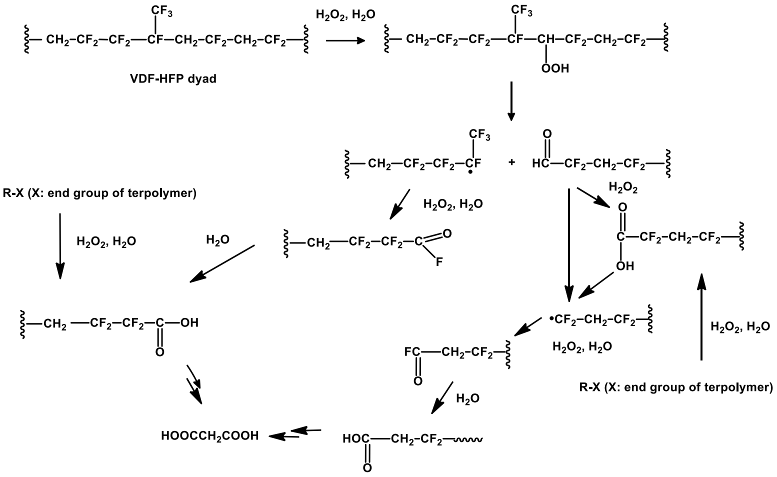
Figure 13. Circular economy situation of FPs: lifecycle of FPs from feedstocks extraction to end of life in EU[134].

The processing of FP materials such as the machining of PTFE rods and cubes for the manufacturing of various milled and drilled parts results pre-consumer FP processing losses. Actually, ca. 20 - 25% of FP producers claim to get their own internal re-processing steps for their process losses. These are the cases for Dyneon, [145-146] Arkema[147-148] and other companies. Then, 30 - 35% report to send their pre-consumer FP waste to external material re-processing companies while 15% exported their pre-consumer wastes to other companies inside the EU. 5 - 10% mention that their FP processing losses are exported outside the EU for re-processing, e.g., to Asian countries. [130] Finally, 5% of them state that they do not have any information on their process losses. These companies usually sub-contract waste companies.

4.2.2.8. Mineralization

A totally degradation of FPs is desired to avoid any release of oligomers that imparts severe persistent and toxic issues. The mineralization, that yields to fluoride anions, appears as an attractive and environmentally friendly method. As reported for low molar mass-PFASs,[44] the mineralization of FPs has been deeply studied by Hori's group since more than 10 years, by means of subcritical (or superheated) water.[178] These conditions can be reached at the critical temperature (374 °C) and pressure (> 22.1 MPa) of water[178-184] for which this fluid displays low viscosity, high diffusivity, and ability to hydrolyze and mineralize many organic compounds. Indeed, reactions requiring subcritical water are considered environmentally benign with the goal at recycling the fluorine element. In the case of FPs, from this technique, Hori's team mineralized PVDF,[179-180] (decomposed into F^- and CO_2) as well as VDF copolymers: poly(VDF-*co*-HFP),[180] poly(VDF-*co*-CTFE),[179] poly(VDF-*co*-PMVE)[181] and poly(VDF-*co*-MAF)[182] copolymers (where MAF stands for methacrylic acid) and poly(VDF-*ter*-HFP-*ter*-TFE) terpolymer[183]. This led to a *quasi*-complete mineralization of PVDF performed at 250 ºC as well as for poly(VDF-*co*-HFP) and poly(VDF-*co*-CTFE) copolymers.[179-180]

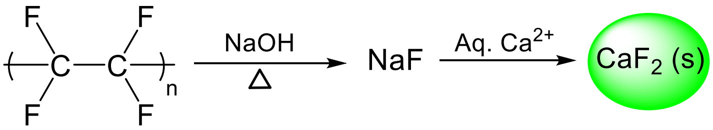
Scheme 3 supplies a suggested mechanism of the decomposition of poly(VDF-*co*-HFP) copolymer. Advantageously, by reacting Ca^{2+} cations onto such released fluoride anions, these authors examined the CaF_2 formation[180-183] to close the loop on the fluorine element, since CaF_2 is the source for all fluorinated compounds.



Scheme 3. Proposed mechanism for the H_2O_2-induced decomposition of poly(VDF-*co*-HFP) copolymer.[180] Reproduced with permission from Elsevier.

These authors also extended that strategy to the mineralization of ETFE[180] and PFSA membranes[184] in much more attractive conditions than those reporting the degradation of PFSA membranes generating perfluoroalkanoic acids[151] and perfluoroalkane sulfonic acids.[185]

A different approach from another Japanese team[186] involved molten alkaline metal hydroxide at 400-600 °C to mineralize PTFE. This two step-process allowed an efficient mineralization by chemical recycling. However, that process appears surprising since PTFE can be etched by liquid sodium and also degrades from 500 °C as seen in section 4.2.2.4. First, PTFE (as well as PVDF, PCTFE, and poly(VDF-*co*-HFP) copolymer) was decomposed into soluble alkaline fluorides via a degradation in such molten hydroxides at high temperatures and atmospheric pressure. Then, CaF_2, considered the main source of the organofluorine chemistry, was produced by treatment of the former aqueous solution with $CaCl_2$. When PTFE was heated with a large excess of NaOH at 500 °C, 74% yield of CaF_2 was obtained (Scheme 4) with respect to the initial PTFE amount.



Scheme 4. Proposed procedure for the mineralization of PTFE by molten NaOH[186] (readapted from Royal Society of Chemistry).

Indeed, such high temperatures are not far from thermal conditions to favor the unzipping depolymerization of PTFE [102,137-144,157] and, consequently, for other less thermostable FPs than PTFE, the degradation should also happen, even without any base. These authors noted that i) there was no decomposition with molten NaOH below 400 °C whereas ii) from 600 °C yields of CaF_2 fell down to 46% (from 67% and 74% at 450 and 500 °C, respectively).

More recently, Sheldon et al.[187] reported that a nucleophilic magnesium reagent (Figure 14 and Scheme 5) could enable defluorination of PTFE powder under mild conditions (room temperature and 1 atm), releasing a molecular soluble magnesium fluoride coordination product (2) that was separated from the surface-modified FP. This kinetically stabilized species could be utilized as fluoride carrier and appeared more reactive than inorganic metal fluorides, MF(s) or MF_2(s), which suffer from high lattice enthalpies and high stability. This proof-of-concept evidences that the Fluorine atoms in PTFE can be harvested and reused in coordination synthesis.

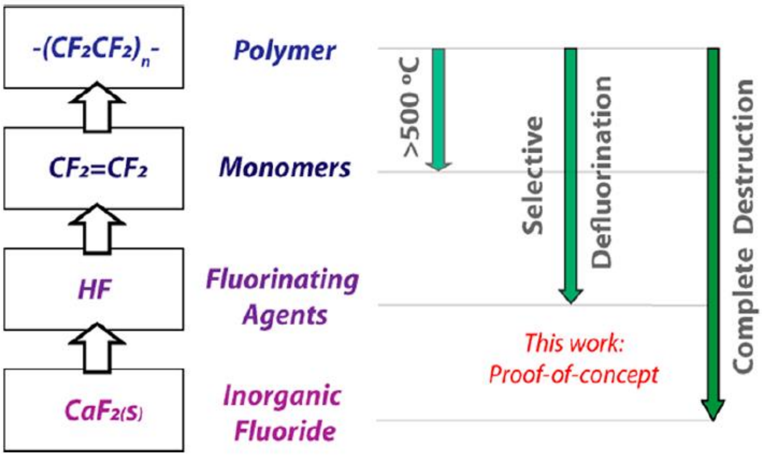
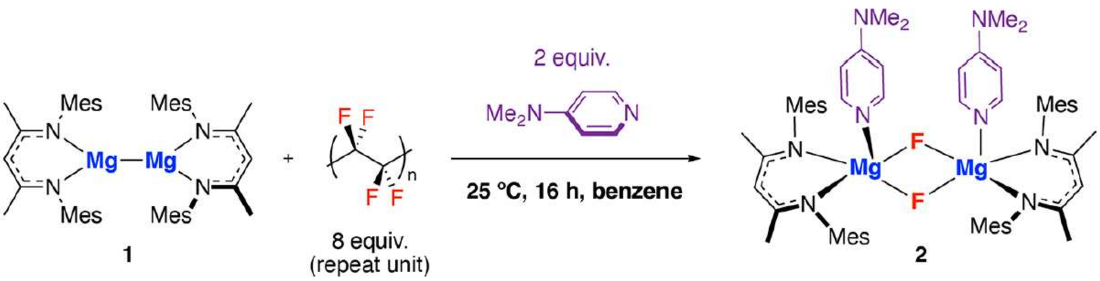


Figure 14. Cycle of Fluorine Chemistry from Fluorspar (CaF_2) to PTFE, along with potential routes for recycling, including the thermal depolymerization (above 500 °C), the selective defluorination[187] to form fluorinating agents, and complete destruction back to inorganic metal fluoride. (Reproduced with permission from Amer. Chem. Soc.).



Scheme 5. Room temperature reaction of a nucleophilic magnesium reagent (**1**) with PTFE to generate an organometallic fluorinated magnesium complex (**2**).[187] (Reproduced with permission from Amer. Chem. Soc.).

Conclusions and Discussion

PFASs cover more than 12,000 synthetic compounds containing a carbon-fluorine bond. With such a broad scope, all PFASs are not the same and it is likely that the impact on the global industry of a possible restriction on PFASs will be a shocking prospect, particularly since the recent proposal does not differentiate between substances that may have different toxicity profiles, and applications. Indeed, the justification to launch a restriction on PFAS as a group is based on 'persistency and other concerns' related to these chemicals, and the fact that previous initiatives to regulate PFAS chemicals individually has resulted in substitution of one PFAS molecule by another molecule that also matches the PFAS definition, and may exhibit similar toxicological properties.

While most PFASs have not yet undergone toxicology assessments or been linked to health harms, many efforts have been devoted to the detection and remediation in both solid and aqueous media to ensure that contamination is limited to safe levels.

Because of their chemical composition, structure, and molar masses, fluoropolymers are significantly different from other substances in the PFAS family. The only main reason for concern associated to FPs is the use of non-polymeric PFASs as polymerization aids during the manufacturing process (the emulsion or suspension polymerization in aqueous medium requires a surfactant that has been a hydrocarbon one since a couple of years).

Furthermore, FPs have high molar masses (several million for PTFE) and thus cannot cross the cellular membrane, which means they are not bioavailable or toxic. Moreover, since recent improvements in their manufacturing without any use of fluorinated surfactants in addition to their high chemical, thermal and aging stabilities, they contain no or quite tiny oligomer or organic leachables. In addition, their physico-chemical properties prevent from bioaccumulation and degradation. Advantageously, as most FPs, PTFE is insoluble in water and, therefore, is not mobile in the environment. Consequently, the outcomes of such features (in addition to others of the 13 requirements) are that ca. 96% of the global commercial FPs satisfy the accepted OECD PLC criteria.

FPs display exceptional properties while preserving their high performance even in aggressive chemical and thermal conditions. These niche technical polymers are stable to hydrolysis, UV, oxidation and to biodegradation. Their applications deal with health, safety, performance and functioning of the society and are used in strategic sectors and High-Tech industries (e.g., aerospace, electronics, energy, optics, medicine). Their relevant combinations of outstanding features are not observed by any of the alternative hydrocarbon polymers [9,63,83-84] hence making them so unique and valuable. Presently, alternatives to FPs, which should be assessed based on the criteria such as *performance, safety, accessibility, resource efficiency, waste generation, cost, availability, stability and lifetime,* do not exist. Furthermore, data show that FPs (especially PTFE) have been extensively tested to satisfy US, Japanese[130] and EU food contact and global medical device regulations, e.g., US Food and Drug Administration, China Food and Drug Administration, Korea Ministry of Food and Drug Safety, Japan Pharmaceutical and Medical Device Agency, including ISO 10993 biocompatibility testing and preclinical animal testing.

As presented throughout this review, FPs could potentially present environmental challenges across international borders. Since their inception and widespread commercial and industrial utilizations, these materials have become essential for many everyday applications and are not considered to be a health hazard during their typical life cycle. At end-of-life, possible low molar mass compounds which are dependent upon conditions may become an issue that needs to be easily detected and removed from the environment. Many techniques on remediation of PFASs have already been achieved.

FPs and the Stockholm Convention persistent organic pollutant (POP) criteria meet the persistence criterion only, but not the bioaccumulative, toxic, or mobile criteria.

Furthermore, the main concerns have been recently addressed, both in using NFPAs and controlling >99 % PFAS emissions linked to appropriate abatement technology of the industrial FP productions. As a result, FPs produced with NFPA technology has led to a commercial success and further motivates the industry to work harder in this direction. In addition, various solutions are searched for recycling, reuse, circular economy and life cycle analysis. In this vein, several occidental companies have already found strategies to depolymerize, recycle ("close the loop" even on pilot plant) or reuse FPs. In case of recycling (including PTFE and FP recycled plastics), among the annual plastic production of more than 460 million tons,[131] only 9 % has been recycled while the data fall down to 3.4% for FPs (for a yearly production of 330,300 tonnes[64]). Though the recycling of clean FPs (e.g., PTFE), FEP, PFA and PVDF waste or scraps generated in the production has already been achieved (e.g. by Dyneon on a pilot scale[145-146], at Karlsruhe Institute of Technology[174] or by Arkema company[147,148]), that of FPs in consumer articles is not well established, since these FPs are typically contaminated by other fillers and substances, which makes recycling difficult.

Various studies have shown, on small and pilot (500 tonnes/year[188]) scales, the ability to upcycle FPs back to their monomers (*via* the recycling to monomer) and to use the generated fluoromonomers (e.g., TFE) for further (co)polymerizations. Though such an approach to a closed loop economy for FPs has already been scaled up, it is expected that additional studies on recycling and reuse of FPs are currently continuing.

To overcome limitations of incineration (especially HF release), recent alternative processes regarding the thermal treatment (mineralization to release fluoride anions, precursor of CaF_2 as the starting point of the Fluorine Chemistry chain) of FPs either under subcritical water or with molten sodium or a Magnesium complex are quite relevant to close the loop and deserves to be further scaled up.

Research is requested to determine the possible emissions from thermal disposal of FPs. Furthermore, methods of the thermal degradation and waste treatment of polymers containing PFASs can be greatly expanded on to enable environmentally safe and conscientious processes. In addition, PTFE is known to undergo a quite low decomposition above the application temperature of 260 °C for months. However, to favor a major degradation, temperatures above 400 °C are needed. Hence, incineration is one of only a few techniques that can potentially decompose FPs and from 850 °C, a total degradation occurs without generating any PFAS. In December 2020, USEPA[127] reported the decomposition and disposal of PFASs. This active area of research enables to evaluate effective destruction temperatures and treatment time, the potential to generate products of incomplete combustion, stack gas analyses, deposition onto land, and other risk factors. Furthermore, on melt processible polymers, reactive extrusion has been reported to be a versatile technology to recycle such materials[189] and could be adapted to FPs.

Although there are sufficient data to demonstrate that FPs such as PTFE do not degrade in the environment or release substances of toxicological or environmental concern, the downstream, end-of-life (EoL) process of incineration deserves future actions. In addition, they must be appropriately marked or labelled to inform both the users as well as the EoL actors. This labelling should comply with eco-labelling standards and thus help the EoL managers in identifying and sorting the hazardous fluoropolymer waste from other plastic waste during the EoL treatment.

Though the demand of FPs is still increasing,[190] future works should deal with FP manufacture highlighting the safety, health, and environmental management practices, under applicable regulations. It should also assess substances used in FP manufactures, their human health and environmental attributes.

FPs could be impacted by the upcoming restriction on PFASs under the EU REACH Regulation, the proposal of which was published on February 2023.[32] Much progress has been made in industry over the last years in relation to control of PFAS emissions due to their use in fluoropolymer production. The FP representative industry[191], the *FluoroProducts and PFAS for Europe* group (which represent producers, importers, and users of fluorinated products and PFASs across Europe) have issued a six-point action plan, which includes derogations in key applications which are not time limited.

In addition, the FP industry in Europe[192-193] evaluated the contribution brought by the FP manufacturers regarding revenue, investment and employments, while many more significant benefits can be released along the value chain via the use of FPs in many High-Tech applications.

For these reasons and because of their usefulness, inertness, non-toxicity, non-bioaccumulation, non-mobility and growing interest even in coming-up technologies, FPs cannot be in the scope of the

PFAS restriction. Moreover, the main concerns linked to the industrial productions of FPs have been addressed (improvement of abatement techniques, removal of PFAS polymerization aids and introducing alternative technologies). They show that these high value-added polymers must be separated from conventional PFASs, are essential for everyday life and are irreplaceable materials.

Hence, the data presented demonstrate that the FP class of PFAS is well-defined, safe and an essential subset of PFAS. Though the dossier is still under evaluation,[32] the restriction of FPs under REACH regulations may hamper the EU strategic sustainability ambition[194] as well as the Ecological transition. For example, in the hydrogen sector, such a PFAS ban without granting any exemption, would have catastrophic consequences on the industry's €30-billion worth of investment in a decade[195] (only including electrolyzers and fuel cells). Such a ban would also jeopardize up to 200,000 direct jobs and over 260,000 indirect ones within 10 years in a market with a potential value of € 820 billion employing 5.4 million people by the middle of the century.

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