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Recycling and End of life assessment of Fluoropolymers: Recent Developments, Challenges and Future Trends

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Abstract

A non-exhaustive state of the art on the recycling, reuse, thermal decomposition (from thermolysis, thermal processing, flash pyrolysis, smoldering, open burning, open air detonation, and incineration), and life cycle assessment of fluoropolymers (FPs, ranging from poly(tetrafluoroethylene), PTFE, poly(vinylidene fluoride), PVDF and various fluorinated copolymers based on VDF and TFE) is presented. FPs are niche specialty polymers endowed with exceptional properties which have found many applications in High Tech industries. In contrast to other polymers, reuse of FPs has not yet been well-established and is still at its infancy. However, recycling them has led to a growing interest and has already reached a pilot scale. In addition, and recently, a few studies deal with vitrimers regarded as polymers ranking between thermosets and thermoplastics. Though many articles have reported the thermal degradation of these technical polymers, intensive efforts have been developed to avoid releasing low molar mass-oligomers and per- and poly-fluoroalkyl substances (PFAS, and especially polymerisation aids such as perfluorooctanoic acid (PFOA) and its alternatives) while various publications report the complete decomposition of PTFE leading to TFE (and hexafluoropropylene or octafluorocyclobutane to a lesser extend). Incineration is one of only a few technologies that can potentially degrade FPs and completely PTFE and other PFAS from 850 °C. More recent studies on the mineralisation of FPs under subcritical water represents an interesting approach to close the loop of the fluorine chemistry cycle. Because of their high molar masses (several million for PTFE) and their thermal, chemical, photochemical, hydrolytic, inertness and biological stability, it has been clearly evidenced that FPs satisfy the 13 accepted regulatory assessment criteria to be considered as Polymers of Low Concerns.

1. INTRODUCTION

Nowadays, plastics have invaded our daily life. Population growth and higher incomes have driven up global plastics production, which doubled between 2000 and 2019, reaching 460 million tonnes in 2021,[1] predicted to reach 1.12 billion tonnes annually by 2050[2] and should increase up to 1231 Mt by 2060. This situation is appealing and worrying since we are surrounded by plastic waste which are making the "6th Continent".[2] In the 2000-2019 period, the growth of plastics has outpaced that of economic growth by almost 40%.. MacLeod et al.[3] recently highlighted the global threat induced by the plastic pollution. These concerns were based on the high environmental persistence of plastics. Among them, and in contrast to commodity polymers, fluorinated polymers (FPs) are niche materials, the consumption of which was estimated at 320,300 tonnes in 2018,[4] hence representing only 0.1% among all polymers. Its global consumption in 2015 was 270 kt, showing a 18.6 % increase over this period. The recycling of plastics is a real challenge[1,3,5-8] since only ca. 9% of polymers are recycled while for FPs, recycling accounts for 3.4%.[9]

Thanks to the electronegativity and small radii of fluorine atom which confer to the C-F bond to be short and exceptionally strong, FPs are specialty polymers endowed with outstanding properties. They bring safety and performances where other materials fail, are essential for our daily life and involved in many High-Tech areas.[10-14] Because of the growing need for higher performance-materials possessing such specific properties for high-tech applications, fluoropolymers have undergone rapidly an increasing development. Specifically, FPs are used in core and cladding for optical fibers, specific UV and aging resistant coatings, wires and cables in wide areas, including aerospace (several hundred km of tubes and connections as fire retardants in planes and gaskets in shuttles) and in materials for Energy [proton exchange fuel cell membranes, backsheets of photovoltaic panels, binders at cathode in Lithium ion batteries, electroactive (piezoelectric) devices] in plastics/polymer bonded explosives and in munition components such as gaskets, wiring sheaths, tubing, and seals. The most prevalent materials are poly(tetrafluoroethylene), PTFE, poly(vinylidene fluoride), PVDF, poly(chlorotrifluoroethylene), PCTFE, and the copolymers based on tetrafluoroethylene (TFE) and vinylidene fluoride (VDF) (that can be either thermoplastics or elastomers).[13] Usually, in their conditions of uses, FPs are non-toxic, non-bioaccumulative, non-mobile, insoluble in water, stable –thermally, chemically and biologically-, durable, are hydrolytically stable, and are not subject to hydrolysis catalysed or metabolised degradation. For these features, they are not considered as substances of very high concern (SVHC).

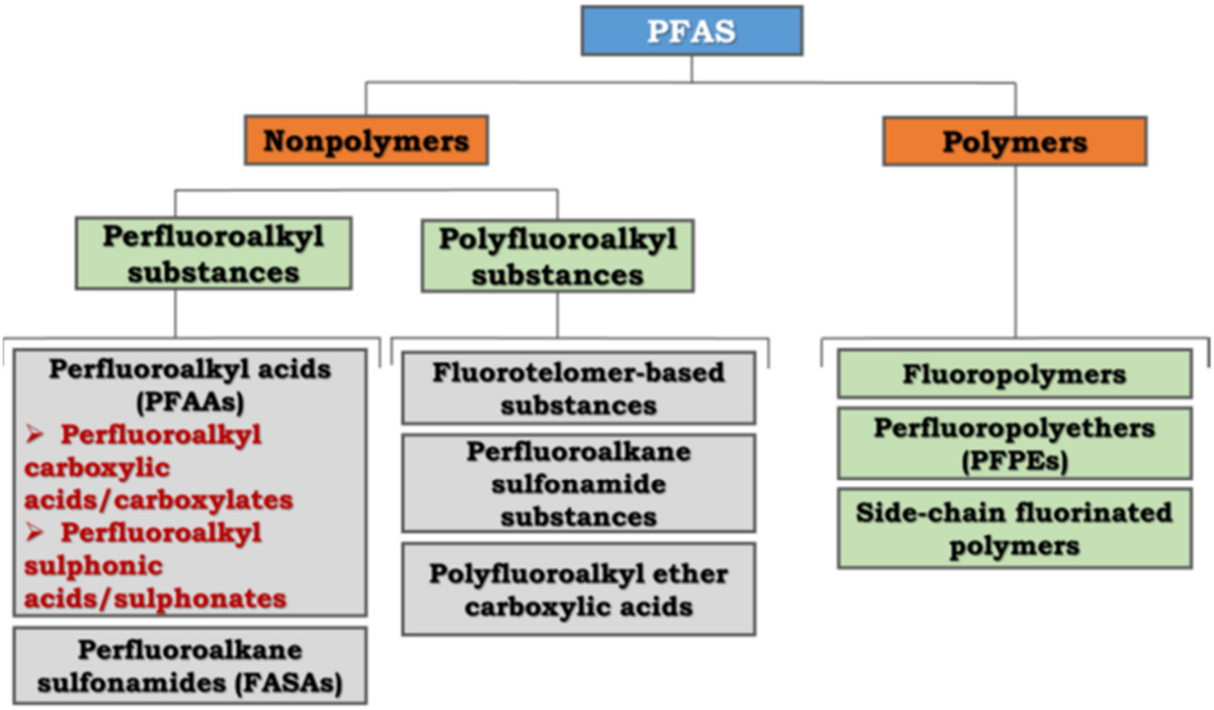


Fig. 1 Per- or poly-fluoroalkyl substances (PFAS) are gathered in various distinct families[15] (reproduced with permission from Wiley).

Though FPs are also regarded as per- and poly-fluoroalkyl substances (PFAS)[15,16], they represent a special family in the polymeric PFAS, composed of: i) polymers bearing fluorinated side chains such as poly[fluoro(meth)acrylate]s[18-21], poly[fluoro(oxetane)]s[3] or fluorinated polyurethanes[3], ii) perfluoropolyethers, PFPEs, obtained from the ring opening polymerisation of either hexafluoropropylene oxide (HFPO) or oxetanes, or achieved from the UV catalysed photopolymerisation of TFE and hexafluoropropylene (HFP) in presence of oxygen[22] and iii) polymers bearing Carbon and Fluorine atoms in their backbones (Figs. 1 and 2).

More than 200 use categories and sub-categories are identified for more than 4,730 individual PFAS while it reaches more than 9,000 compounds according to the US Environment Protection Agency.[23] The regulatory agencies (as Registration, Evaluation, Authorisation and Restriction of Chemicals, REACH, or Toxic Substances Control Act, TSCA) support initiatives aimed at regulating the substances of greatest concern and will endeavor to contribute to the broad and complex scientific, technical but also economic forthcoming debate on those substances that may concern it.

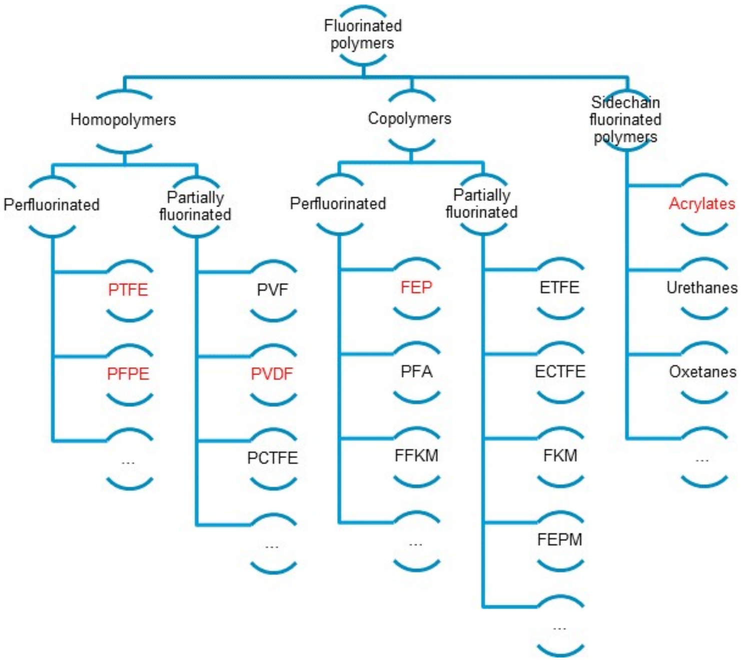


Fig. 2 Classification of FPs from the type of monomer base units[3] (reproduced with permission from European Topic Centre Waste and Materials in a Green Economy) most acronyms are detailed at the end of this review.

Regarding their biotic stability (aerobic, anaerobic and in vivo), FPs like PTFE are biologically inert and do not degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic conditions); in vitro and in vivo studies (on PTFE) demonstrate the absence of acute or subchronic systemic toxicity, irritation, sensitization, local toxicity on implantation, in vitro and in vivo genotoxicity, hemolysis, complement activation, or thrombogenicity.[24-28] In vivo degradation involves the breaking of the polymer bonds due to bacteria and other enzymes and oxidants. For example, PTFE hernia patches explanted from patients and examined by scanning electron microscopy, attenuated total reflectance Fourier transform infrared spectroscopy, modulated differential scanning calorimetry, and optical microscopy showed no degradation in vivo.[29] In addition to these properties, their thermal stability is excellent and therefore, these FPs require high temperatures for decomposition.[14]

In 1997, less than 1% of all polymers were used in areas of elevated temperatures, a grouping composed primarily of FPs. The sub-category of plastics known as engineering plastics, in particular FPs, operate at the extreme of polymers' temperature performance. PTFE, for instance, will endure 260 °C for several months[10-13] and even years until failure due to degradation. FPs are, largely, either recycled or degrade in situ, resulting in research on the toxicity of the decomposition products. The onset of thermal degradation of FPs is known to initiate cleavage of the backbone and subsequent rearrangement to produce significant amounts of trifluoromethylated species.

A classical method for plastic disposal involves burying the plastic in landfill.[1-3] Landfilling of FPs has led to contamination of leachates with PFAS and can contribute to releases of plastics and microplastics.[30] Wahlstrom et al.[4] published an intensive report on toxic free economy and the global scan of fluorinated compounds (including fluoropolymers) from the extraction of fluorspar (and related environment health and impact) to the synthesis and applications of fluoropolymers, including municipal waste and landfills of European countries (Fig. 3).

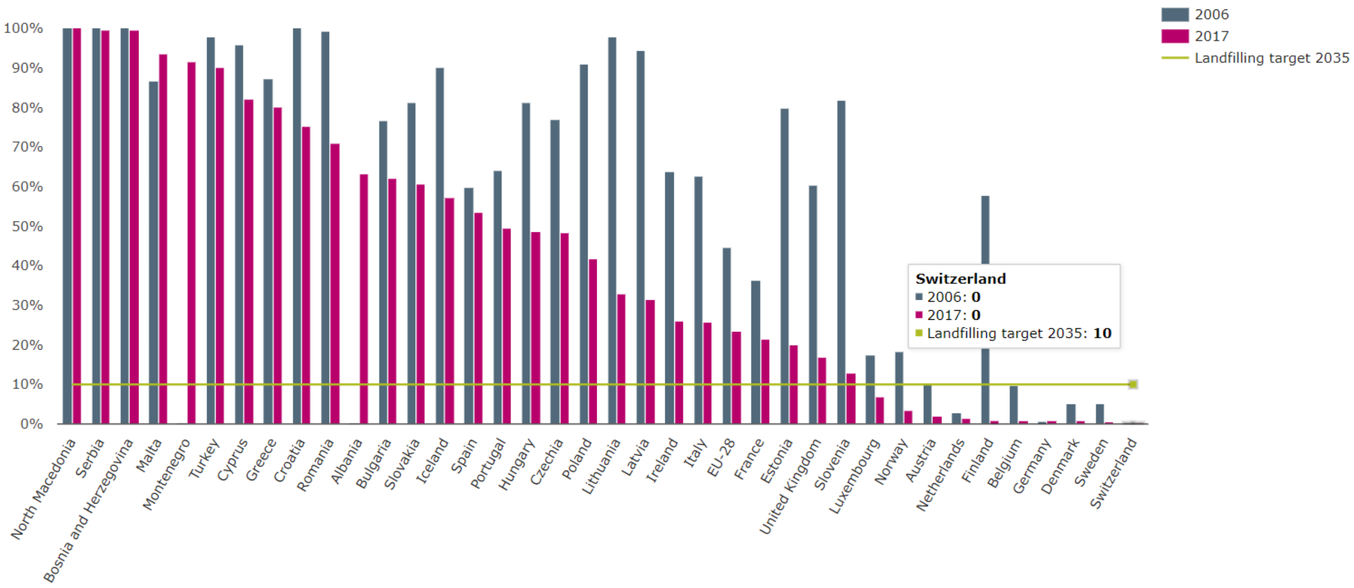


Fig. 3 Landfill rates in member and cooperating countries of the European Environment Agency, 2006 and 2017, %. Cluster columns chart shows development in landfill rate in European countries in 2006 (blue) and 2017 (red). Data is presented in descending order according to 2017 data values. Line chart represents landfill target for 2035 (Landfilling rates of municipal waste related to waste treated)[4] (reproduced with permission from European Topic Centre Waste and Materials in a Green Economy).

Even with an exceptional chemical and thermal stability, FP particles will be decomposed into microplastics by physical stress, which enables further dispersion and increased bioavailability.[31] Storage in abandoned mines and oil extraction fields is an option not routinely explored (except when court-ordered), but is costly and logistically complicated.

The objectives of this review aim at supplying a non-exhaustive state-of-the-art on the recycling, reuse, thermal decomposition, and life cycle assessment of FPs, as well as reprocessable new fluorinated vitrimers. A first part deals with the reuse of FPs (though quite a few information is found); followed by the recycling of these technical polymers (even produced in a pilot scale), including definitions of several recycling stages. Current efforts in recycling FPs deal with mechanical recycling, which requires extensive sorting and the addition of harsh chemicals, and the mechanical processing of the refined material typically leads to the reduction in molar mass and the degradation of the mechanical properties. The third part will summarize the thermal degradation of these FPs and will be classified into several sub-categories (thermolysis, thermal processing, flash pyrolysis, smoldering, open burning, open air detonation, and incineration, that last one being one of a few technologies that can potentially decompose FPs (PTFE and PFAS).[32-33] Among these thermal techniques, mineralisation of FPs under subcritical water, showed promising interest to close the loop, releasing CaF_2 as the starting point of the Fluorine chemistry. Finally, the concept of polymer of low concern (PLC) that FPs satisfy will also be discussed.

2. REUSE

Reuse, recycling, and closed loop systems are alternative options at the end of life. Recent work has shown, on a small scale, the ability to convert FPs back to their monomers (also called chemical recycling to monomer, CRM) for capture.[34-36]. This approach to a closed loop economy for FPs merits additional work and discussion, as does the recycling and reuse of melt-processible FPs, such as FEP, PFA or PVDF.

The five step-waste hierarchy defines the priority order in waste prevention and management legislation and policy: a) avoidance, b) preparation for the re-use, c) recycling, d) other recovery (e.g. energy recovery) and e) disposal.

Recovery can also be achieved and several ways of the material recovery of fully fluorinated thermoplastics have been done (Fig. 4).[37]

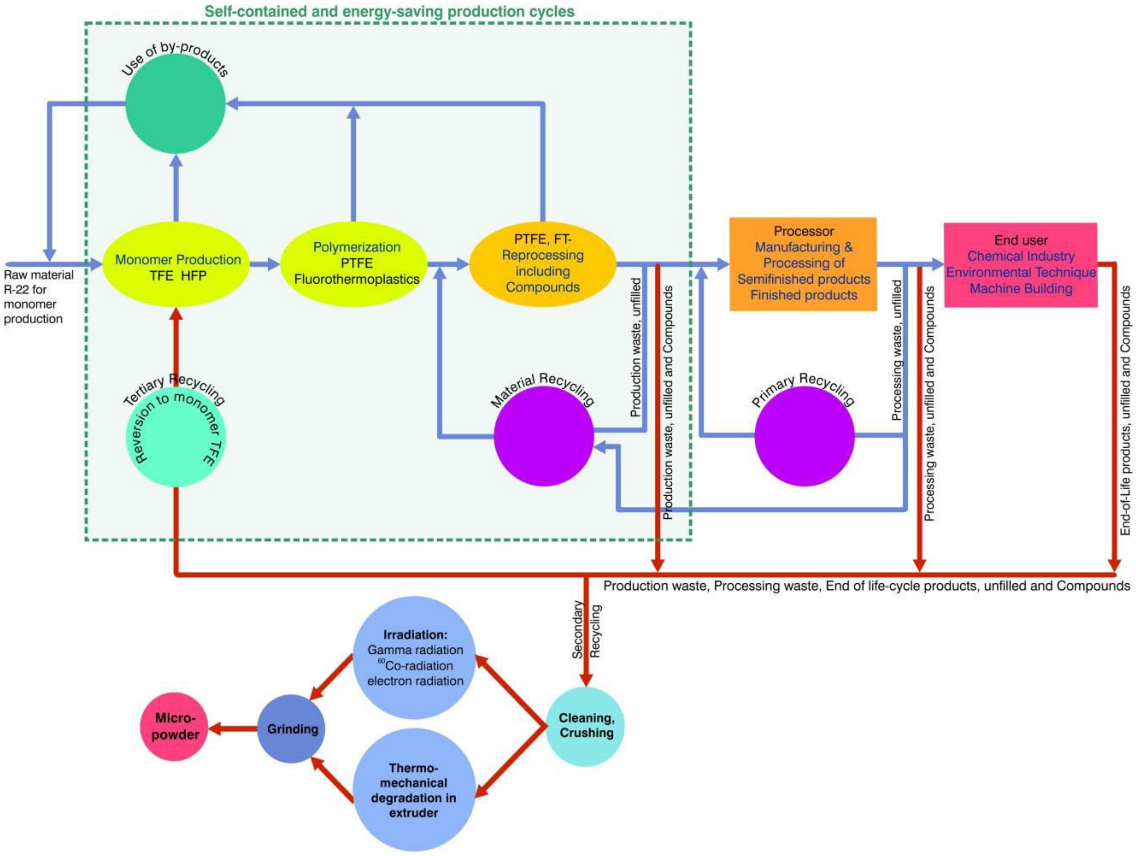
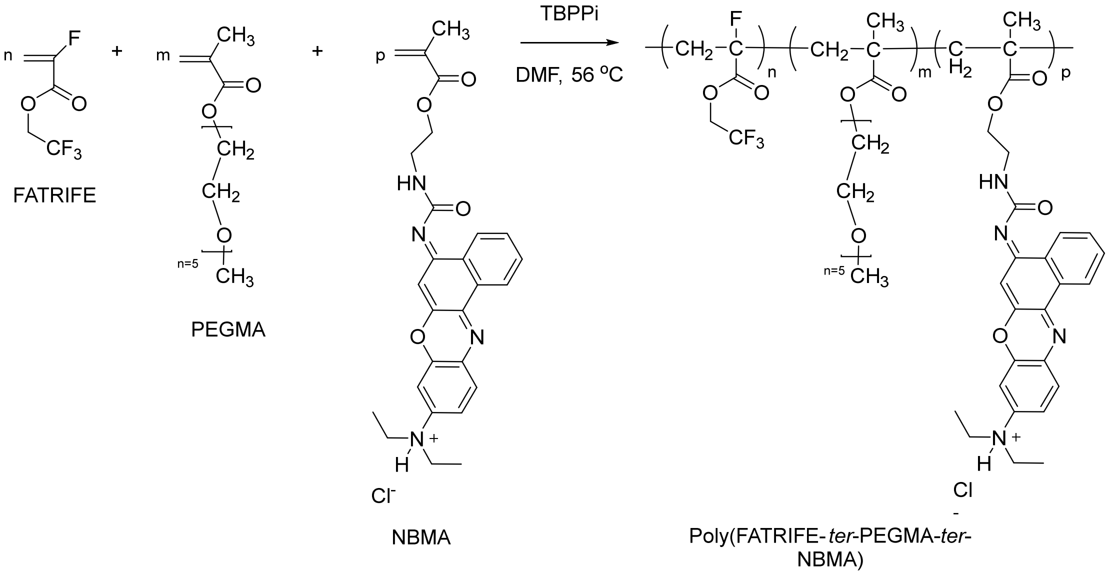


Fig. 4 Recovery cycle of PTFE and fluorinated thermoplastics[9,37] (reproduced with permission from *Recycling of fluoropolymers,* FPGroup).

To the best of our knowledge, because of their inertness, FPs are difficult to be reused. One case study deals with the coating of FEP waste on which a terpolymer based on poly(ethylene oxide) methacrylate (PEGMA), Nile Blue methacrylate and 2,2,2-trifluoroethyl α-fluoroacrylate (FATRIFE) (Scheme 1) was coated on it[38-39] thanks to Fluorine-Fluorine interactions.[40-43] The choice of these three monomers was for hydrophilicity (PEGMA) for water soluble nutriments brought to the plant, ii) sensor (NBMA) to observe the growing roots of the plant in a transparent soil and iii) adhesion onto FEP (FATRIFE) via such F-F interactions. The kinetics of terpolymerisation was not studied though it is assumed that the α-fluoroacrylate was the most reactive monomer. The morphology of such resulting materials was a core-shell in which the core was made of FEP while the terpolymer contributed to the shell, with the objective to prepare transparent soils to make and to observe growing roots of lettuce plants.



Scheme 1 Conventional radical terpolymerisation of 2,2,2-trifluoroethyl α-fluoroacrylate (FATRIFE) with poly(ethylene oxide) methacrylate (PEGMA) and Nile Blue methacrylate (NBMA) initiated by *tert*-butyl peroxypivalate (TBPPi) and resulting terpolymers coated onto FEP to produced transparent soils.[38-39]

3. RECYCLING

Usually, five common approaches can be identified for addressing the production of waste plastics: landfilling, incinerating, recycling, biodegradable polymers, and chemically recyclable polymers.

3.1. Show to manage FP waste and disposal?

A peculiar example is supplied by Germany which has the following stages of waste regulation.[9,37] According to the "*Kreislaufwirtschafts-/abfallgesetz* (KrWG)" (i.e. closed substance cycle waste management), waste disposal is only allowed if material or thermal recycling is not possible, due to economical, technical or ecological reasons. According to §§ 6 – 8 KrWG (dating from 2012), five stages in waste-management have to be suggested:

*3.1.1. Stage 1: Prevention of waste (*Qualitative and quantitative prevention of waste, repeated use or longevity applications) and as examples: - Increased use of isostatic molding processes. Chipping waste is minimised when a pre-shaped form, close to the final dimensions is used.

- Based on the durability e.g. of pumps and containers which are made of fluoroplastics can be re-used in a further application while export restrictions must be considered.

3.1.2. Stage 2: Preparation for re-use; Collect sorted disposal, avoid contamination, clean for re-use.

Examples: - Grouping of processing machines and exhaust systems according to FPcategories;
- Machining without use of lubricant and cooling liquids to prevent contamination.

3.1.3. Stage 3: Collection of waste; Collection of products with similar material properties, cleaning and processing, conversion into reprocessed PTFE, respectively PTFE micropowder. The collection of PTFE waste can be separated into standard and modified PTFE. In addition, processing for using as pre-sintered pellets for ram extrusion[44] or, after radiation-induced degradation, for the manufacturing of PTFE micropowders.

It is difficult to use as a molding powder because recycled PTFE is not easy to deformation by compression. The Daikin industries, Ltd.[45] claims PTFE mechanical recycling as a molding powder. Indeed, recycled PTFE was blended with virgin PTFE to improve the mechanical property and productivity of compression molding. Virgin PTFE could fill the voids between recycled PTFE and a modified PTFE was more suitable for this method in terms of development of mechanical property.

- Fully fluorinated disposal of fluorinated thermoplastics is cleaned, pelletised and re-used either as pure regrind or blended regrind material for thermoplastic processing.
- Up-cycling (thermo-chemical) of end of life products made of PTFE, PFA or FEP.

3.1.4. Stage 4: Other use; Other material recycling: PTFE and other perfluorinated polymers may not be used as substitute fuel for thermal incineration if its caloric value is below 11.000 kJ/kg (required according to §8 KrWG). Several examples are: - For sintered FP waste, the possibility to use it as flux in the cement or steel industry;

- For un-sintered lathe chips, possibility of re-use as molding powder provided that the waste can be milled to powder and the products are free of lubricants or cooling liquids.

3.1.5. Stage 5: Waste disposal; Incineration with insufficient energy use.

As an example, nowadays, waste from PTFE-compounds can only be disposed at high costs. To promote the re-utilization, § 9 KrWG additionally requires to collect specific waste (like metals polymers etc.) separately. If the fluoropolymer waste is contaminated, it might fall in the class of dangerous substances. In this case, providing supporting documents about the disposal chain (§50 KrWG) is obligatory: "*The producer, owner, collector, carrier and disposal companies have to prove the correct disposal of dangerous waste to the responsible authorities as well as among each other*."

Depositing is only allowed if the considered waste does not release any harmful substances, e.g., organic components or soluble heavy metals and its caloric value is less than 6.000 kJ/kg. This is mainly the case with PTFE waste as its caloric value amounts to ca. 5.500 kJ/kg. If the caloric value exceeds 6.000 kJ/kg, incineration of this waste is required.[37] In this case, it is requested that the incineration plant chosen is equipped with an acid scrubber and the combustion temperature is above 800 °C. Metal pieces containing PTFE which do not emit leachable components may be disposed in underground storage or in landfills belonging to class II. Furthermore, it is possible to remove PTFE in-liners mechanically and to use them as feedstock for Up-Cycling (see section below). The remaining metal parts may be utilised as scrap metals in blast furnaces.

Waste from the manufacture and processing of S- and E- PTFE is usually sorted and can easily be recycled. The re-processing is performed by specialised companies[37] (e.g. Invertec[35]). Typical products are micropowder and regenerated material for ram extrusion.[49]

However, at the end of their life-cycle, PTFE products are often contaminated with various other substances. In such cases, a separate pre-treatment is necessary to prepare them for recycling.

Since PTFE also contain fillers, techniques of recycling are limited.

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3.2. Different techniques of recycling

Recycling (or recovery) is the re-introduction of used materials (or polymers) into the cycle of materials/polymers. They are collected, sorted and refined to be re-used as material or energy source. Recycling should help preserving resources and avoiding waste. [1,46-48] From the annual production of more than 460 million tons of plastics in 2021, only 9 % has been recycled [9,48] while that percentage fell to 3.4% for FPs (yearly production of 320,300 tons in 2018).[9]

FP waste from commercial and industrial waste producers are either pre-sorted or result directly from dismantling operations or can be mainly incinerated for energy recovery. Some fractions of pre-sorted PF waste are sent to recycling, either to domestic recyclers or exported for recycling in various countries. Other recycling includes for example re-grinding and sintering as well as chemical recycling of FP materials. Table 1 lists four main ways of recycling:

ASTM D7209 definitions (withdrawn 2015)	ISO 15270 :2008 standard definitions
Primary recycling	Mechanical recycling
Secondary recycling	Mechanical recycling
Tertiary recycling	Chemical recycling*
Quaternary recycling	Energy recovery

Table 1: various ways of plastic recycling. [1,46] (*also including chemical recycling to monomer, CRM)

3.2.1. Primary (or mechanical) recycling

Primary recycling involves extruding preconsumer polymer or other "mechanical" processes (Fig. 5) or pure polymer streams. As an example, sintered PTFE waste are collected, sorted and ground into a free-flowing powder. Reprocessing of pre-sintered PTFE can be only achieved if temperature and pressure are simultaneously applied (Fig. 5; e.g. in ram extrusion[49]). The mechanical properties (e.g. tensile strength, elongation and cold flow) of such a resulting PTFE differ from those of virgin PTFE. Appropriate recycling companies (and their addresses) are listed in the Supporting Information.

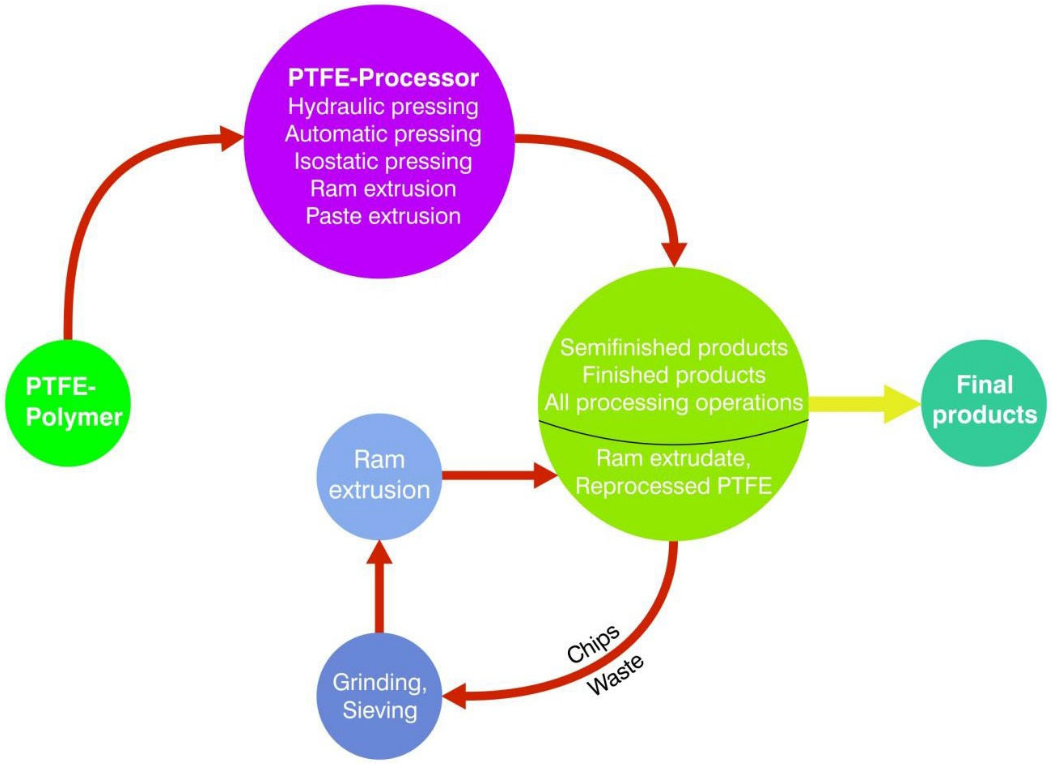


Fig. 5 Primary recovery circuit[37] (reproduced with permission from *Recycling of fluoropolymers,* pro-K Fluoropolymergroup).

3.2.2. Secondary recycling

In contrast to the primary recycling, the secondary one needs sorting of polymer waste streams, reduction of polymer waste size, followed by processing (extrusion, sintering or others). With a suitable control over processing conditions, many polymers can undergo several cycles of primary and secondary mechanical recycling without limitation of performance loss. For FPs, an example of recycling enables to degrade high molar mass-PTFE into PTFE-micropowder. This can be produced either by thermo-mechanical degradation or by degradation using irradiation with high energy radiation (Fig. 6 and section 5). Typically, radiation sources implemented in medical technology are either Gamma-radiation of a ^{60}Co-source or β-radiation (or electron-Beam).

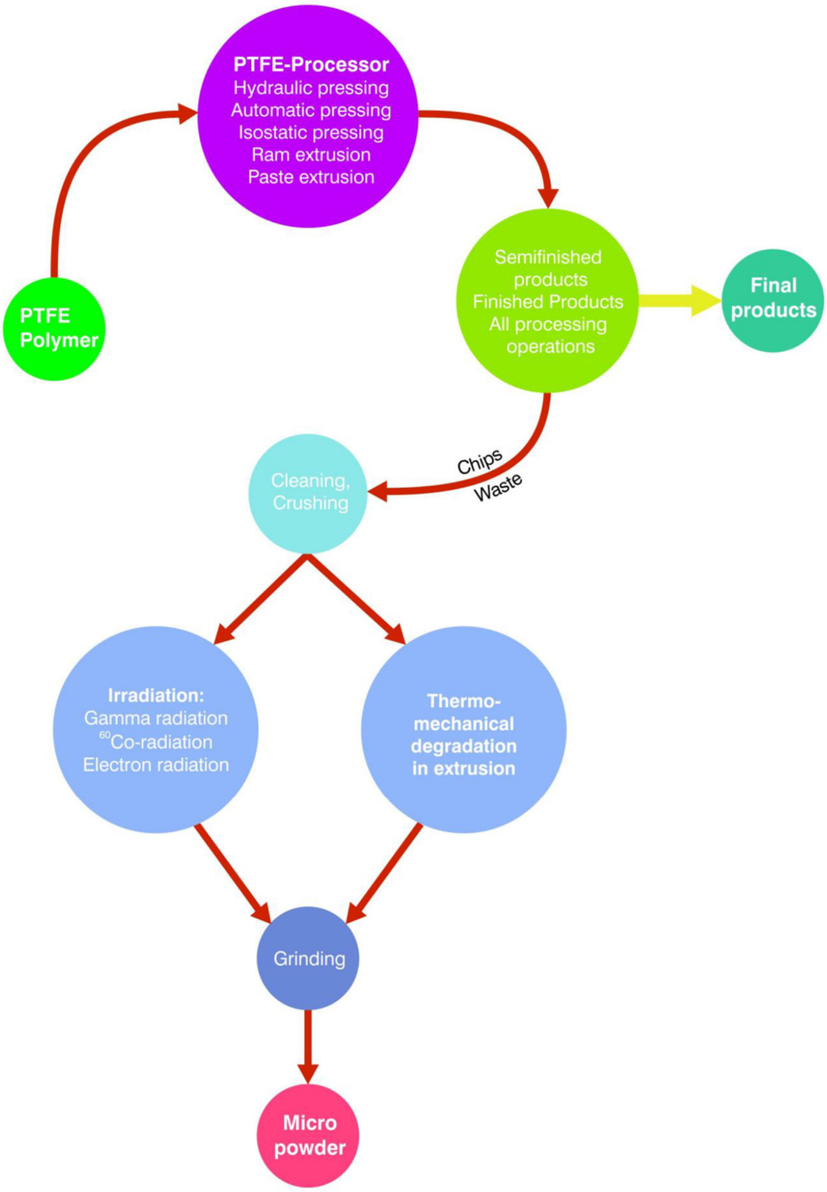


Fig. 6 Secondary recovery circuit[37] (reproduced with permission from *Recycling of fluoropolymers,* pro-K Fluoropolymergroup).

The irradiation process (Fig. 6) is supplemented by a grinding step to obtain the desired particle size. Thanks to this process, which strongly reduces the molecular chain to around 1% of their original chain length, the properties of the degraded PTFE change remarkably. Therefore, the resulting products cannot be used for typical PTFE applications. However, the PTFE micropowders manufactured according to such processes (either by irradiation or thermomechanical degradation in extrusion, followed by grinding, Fig. 6) can act as additives for manifold applications. The resulting micropowders can be involved in the following sectors:

- Non-PTFE plastics to improve the gliding properties;
- Non-PTFE plastics to enhance the processing properties;
- Lubricants to increase the lubrication properties;
- Elastomers to improve the non- stick properties;
- Printing inks to reduce the stickiness/soiling of the surface;
- Coatings and paints to enhance the processing and non-stick properties.

3.2.3 Tertiary Recycling

Tertiary recycling is applied on polymers no longer appropriate for these straightforward mechanical recycling methods.[2,46] This chemical recycling is often complementary to conventional recycling techniques, and can retain significant value if this process is selective (by degrading the polymer to its monomer, i.e. chemical recycling to monomer, CRM) instead of non-selective (as in pyrolytic or hydrocracking strategies). Also called "Up-Cycling",[49-50] this thermo-chemical process (often achieved by pyrolysis) splits the polymer back into the corresponding monomers (e.g. the pyrolysis of PTFE under inert atmosphere, produces monomers like TFE and HFP in a high amount (Fig. 7)[49] and when cleaned, can be re-used for polymerisation). The advantage of this process is that not only homogenous PTFE but also perfluorinated thermoplastics like FEP or PFA can be processed (section 3.3). Advantageously, FPs containing mineral fillers can also be recycled that way.

Since this recycling process can only be operated within an existing infrastructure for the recovery of fluoromonomers, only companies which are correspondingly equipped are qualified.

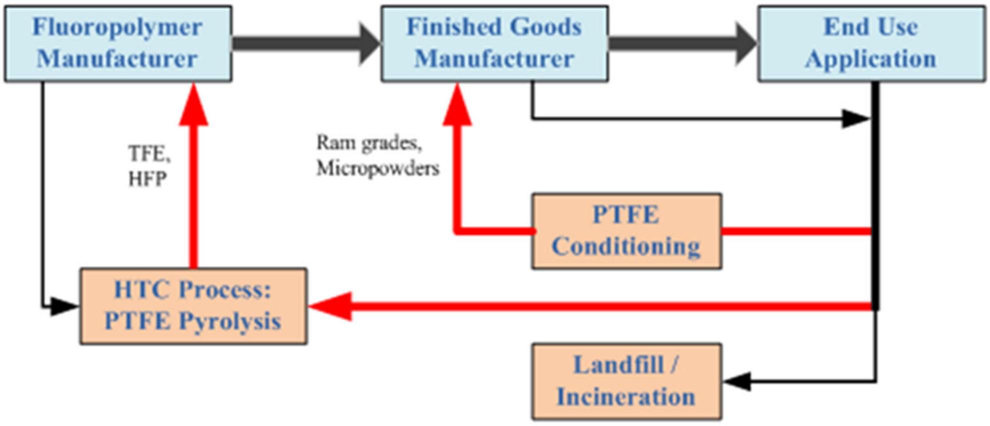


Fig. 7 Upcycling-Closing the loop[49] (reproduced with permission from The Royal Society of Chemistry).

3.2.4. Quaternary recycling

Quaternary recycling is applied to polymers which are non-suitable for any other method of recycling and are utilised for energy recovery via pyrolysis,[2,46] mainly described in section 4. Specific examples of FPs are summarized in the following sub-sections.

3.3. Recycling of Fluorinated thermoplastics

In 2015, Lakshmanan and Chakraborty[51] reviewed the recycling of PTFE while two years later, Dams and Hintzer[49] further reported that of FPs in a book chapter. According to the EU-Legislation, fluorinated thermoplastics should be recovered thermally if mechanical recycling is not possible.[37] Several modifications of the primary recycling have been studied. During film extrusion, trimming waste is directly pelletised and re-fed into the film extruder. Startup and shut-down materials, which may differ in their properties from the finished products, are collected as mono fraction, cleaned pelletised and directly used in the thermoplastic processing and may not be suitable for all applications. In the meantime, these products have already found some applications, as tubes and clamping systems in the architecture and power plant construction, to name a few.

If, for technical or other reasons, a primary recycling for fluorinated thermoplastics (PTFE, PVDF and copolymers of VDF or TFE as FEP and PFA) is not possible, they may be used in the tertiary recycling or Up-Cycling.

Other recycling includes for example re-grinding and sintering as well as chemical recycling of FP materials.

Poly(tetrafluoroethylene-*co*-perfluoropropylvinylether) copolymer (PFA) is involved in many applications ranging from aerospace and biomedical to corroding environments in the chemical industry. Despite a low share in end-of-life products, PFA processing can lead to up to 30%-waste. Thus, understanding how recycled FPs affects the performance of product, it is essential to ensure primary recycling, besides economic and environmental reasons. Romoaldo et al. [52] used the feasibility of PFA waste materials to study recycled PFA (PFAr) in closed-loop recycling. These authors studied the effect of PFAr loading (5–100 wt.%) in virgin PFA on the thermal, mechanical, rheological, color properties and chemical resistance, the two last ones showing no significant changes in all ranges of PFAr content tested. The addition of higher loads of PFAr (≥50 wt.%) led to a reduction in mechanical properties, particularly stress-strength analysis and elongation at break. However, elastic modulus and hardness had improved with an increase in the degree of crystallinity. Romoaldo et al.[52] noted a decrease of viscosity and yellowing of the samples probably linked to a polymer chain degradation. Nevertheless, the addition of up to 10 wt.% of PFAr proved to be an effective alternative to reusing PFA residues based on mechanical recycling.

In addition, thanks to its performance and wide range of processing methods, PVDF is also an outstanding polymer for durable and sustainable solutions in a circular economy. With the ability to be processed and reused up to five times, PVDF does not lose any appreciable mechanical or physical properties.[53-54] While processing, it is common to use up to 20% reprocessed material in the manufacture of injection molded and extruded products. Moreover, a 3D printing producing park bridges out of PVDF reprocessed material has been reported.[53] Furthermore, exposed PVDF materials is claimed to be safe to reuse in the current form.[54] PVDF copolymers have been found to be effective as a polymer processing and recycling aid (PPRA) for polyolefin films, cables, pipes and injection molded parts.[54] Each of these processing methods has a different need, but using a PPRA can improve surface finish, increase output, reduce extruder pressure and die build up, improve flow, steady gauge control and allow processing at lower temperatures. FPs and fluorinated elastomers have been used for years to impart all of these above features to polyethylene and polypropylene, but with more insight on the recycling, the same benefits given to virgin resins are found to be more advantageous in recycling. The Arkema Company claims that processes which enable 20-30% only of recycled materials before losing some performance can now be reprocessed using up to 90 or even 100% recycled materials to make items such as films, cables, pipes and injection molded parts.[53] This company also has reported that materials already containing the PPRA recycle behave quasi the same as a virgin material in which polymer processing aid (PPA) was added as a master batch at the extruder.[54] PVDF and VDF copolymers assist in the reprocessing of high-volume polyolefins as a PPRA.

3.4. Recycling of Fluorinated Elastomers

The recycling of fluorinated elastomers is also quite challenging and to the best of our knowledge, quite a few studies have been reported on that topic, well summarized by Schuster et al.[55] However, these authors have forgotten to cite a tertiary recycling of commercially available poly(VDF-*co*-HFP) fluoroelastomers (average molar mass in number, Mn=134,000, dispersity, PDI=3.7 and VDF:HFP=3:1 mol.:mol.) into cooligomers, the Mn of which ranged between 3,300 and 10,400 g/mol.[56] This reaction occurred at -10 °C in presence of sodium hydroxide, hydrogen peroxide and triethyl ammonium chloride. Then, these transparent telechelic dicarboxyl terminated cooligomers were chemically changed into diacrylates which were further photocrosslinked without any high pressure, toxic solvent and high temperature. The resulting materials displayed satisfactory hydrophobic and mechanical properties.

Actually, recycling methods involved in the field of conventional rubber cannot be systematically adapted to fluorinated elastomers. From Schuster et al.'s review,[55] only two relevant methods have been proposed to achieve the recycling of poly(VDF-*ter*-HFP-*ter*-TFE) terpolymers (FKM) in an industrially acceptable way: i) the milling of FKM into a fine powder to be mixed with virgin FKM and ii) the mechanical devulcanisation of FKM, followed by successive compounding with virgin rubber. Both techniques provide satisfactory thermal stability by maintaining the mechanical properties of original FKM. Indeed, in this review, for FKM, only patents were supplied. As a matter of fact, cited articles often just refer to degradation and not to de-vulcanization. These authors concluded that recycling FKM is possible and leads to products with competitive properties to those obtained with virgin material. However, as known from engineering on disassembling, Schuster et al.[55] concluded that elastomers and therefore fluorinated elastomers should be vulcanized for the goal to further facilitate devulcanization.

3.5. Which Companies recycle FPs?

Companies involved in the recycling of PTFE and those operating on Up-Cycling of PTFE, selected TFE-based thermoplastics are listed in the Supporting Information.

On March 2015, the Dyneon Company started the world's first pilot plant for recycling perfluorinated polymers in Germany (Gendorf Chemical Park, Burgkirchen, Fig. 8).[50] It established a milestone towards sustainability with a closed loop in FP production. By regaining resources, this pilot plant not only helps making production processes more efficient but also reduces the need for mining with chemicals and the transport of heavy loads, as well as the overall energy requirements of Industry, thus inducing a positive impact on the environment.

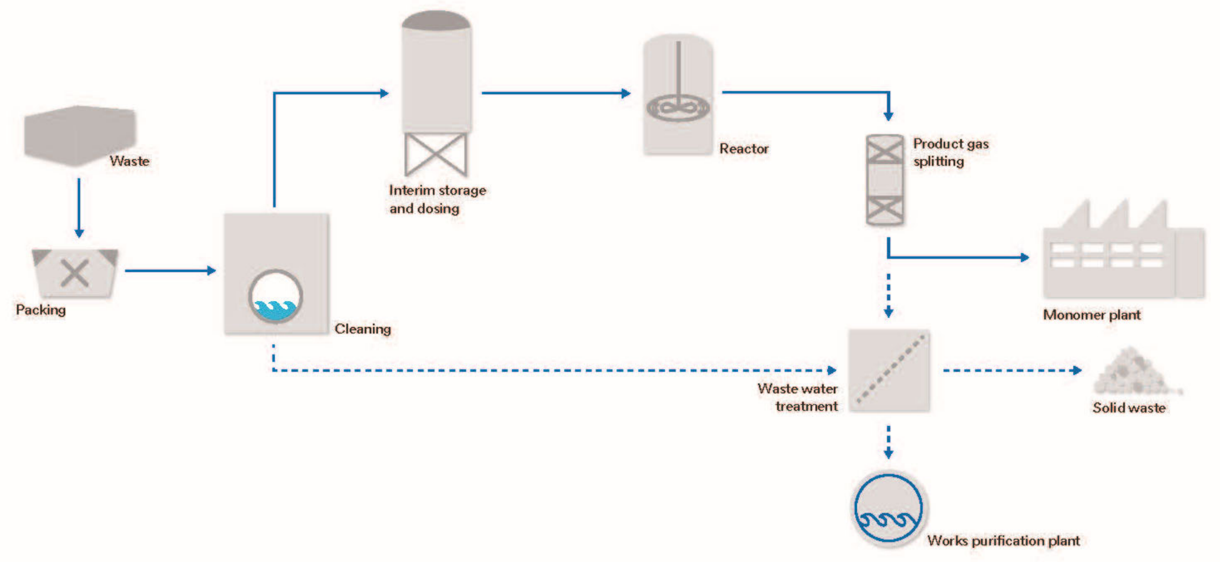


Fig. 8 Sketch of the world's first pilot plant for recycling perfluorinated polymers in Germany (Gendorf) [50] (reproduced with permission from 3M Dyneon and image curtesy of 3M Company).

On the industrial scale, recycling of "clean" PTFE waste or scraps generated in the production has already been achieved (e.g. by Dyneon[50] or as a pilot scale by Karlsruhe Institute of Technology, see section 4.4), often by converting these waste into PTFE micropowder *via* vacuum pyrolysis (so-called fluoroadditives). This process regenerates gas-phase monomers from end-of-life industrial-scale fluoropolymer products (i.e. CRM).[34] They were also used to reduce wear rate and friction.[57] This has the unintended consequence of spreading FPs into more uses, and complicating any efforts of controlling and reducing their losses from the technosphere. On the other hand, the recycling of fluoropolymers in consumer articles is not well established, as those FPs are typically contaminated by other substances and fillers, making a difficult recycling.[34,37] Fluoropolymers applied to metal articles (e.g., nonstick frying pans) might end up in metal recycling streams, leading to their uncontrolled breakdown in metal smelters at high temperatures. Commercial bakeries regularly remove fluoropolymer coatings from their baking forms after 12−24 months of use either *via* burning or blasting, with unknown emissions of PFAS and FP particles to air, water, and soil, and then have the forms recoated.[30] In Sweden, every year some 20 000 baking pans are "recoated" with a total baking surface of 500 000 m^2. Stripping the old coating is performed by either "burning off" at 450 °C for 4−5 h to "break down" the coating followed by grit blasting or by water blasting at 1500 bar; it is unclear whether emissions are controlled.[15,58-59]

3.6. Caloric values of FPs

The caloric values for PTFE is 5400 kJ/kg while it worthes 5020 kJ/kg for PTFE Glass compounds.

Furthermore, Dams and Hintzer[49] reported the environmental /raw material savings per 1000 tonnes TFE produced by High Temperature conversion process (Fig. 9).

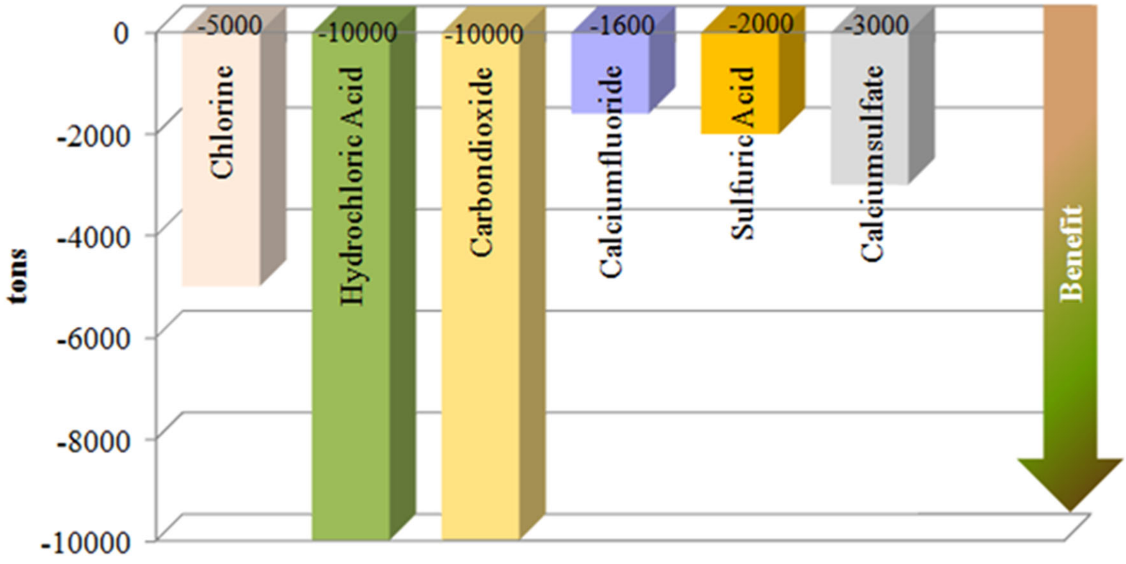


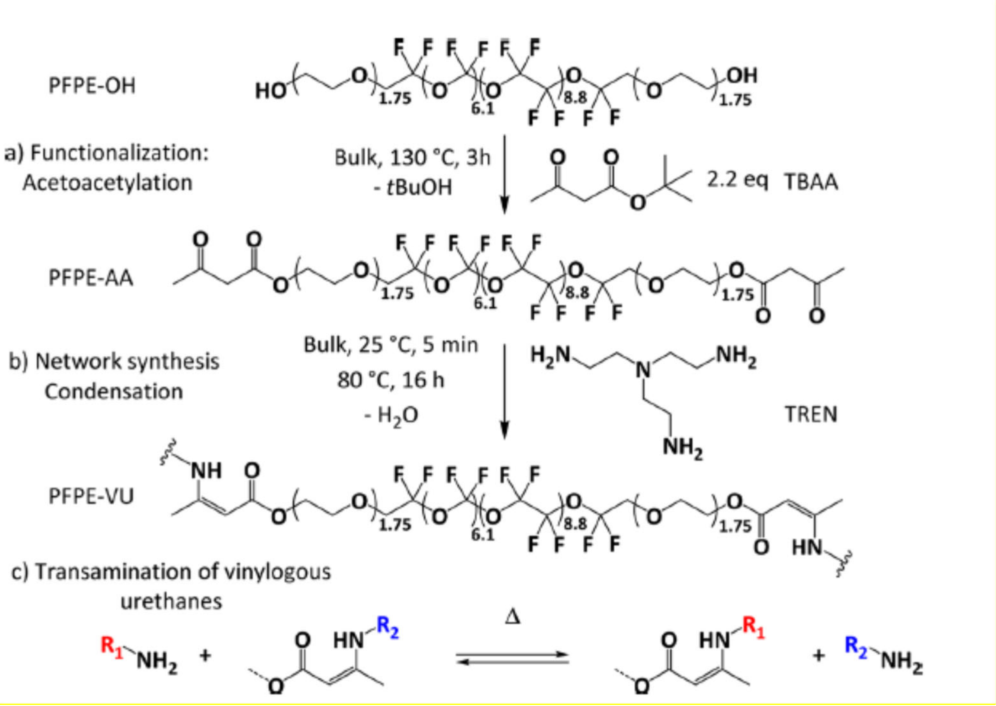
Fig. 9 Environmental benefit (environment /raw material saving per 1000 ton-TFE) from depolymerising perfluoropolymer back to TFE produced by high temperature process[49] (reproduced with permission from Royal Society of Chemistry)

3.7. Vitrimers

The above parts summarize the non-exhaustive situation of recycling, reuse, end of life of thermoplastics and elastomers. Indeed, a third class of polymers, called *vitrimers*, invented by Leibler et al.,[60] has shown a growing interest. They mainly combine three features: i) the mechanical properties, ii) the solvent resistance of 3D thermosets, and iii) the reprocessability of linear thermoplastics. They constitute a fascinating class of polymer materials ensuring the preservation of their properties after numerous reshaping processes. Their key features, i) an insoluble 3D-network able to flow, ii) a chemical resistance, iii) a unique rheological behaviour and iv) reshaping ability, make them promising materials for innovative industrial applications. They behave according to two profiles: a dissociative one in which the crosslinking density decreases whereas the associative one maintains the crosslinking density constant.[61] They should play the role of sustainable materials with a prolonged useful lifetime as the main requirements for a more circular economy. This unique behaviour is due to the triggering of certain covalent exchange reactions that allow the network to rearrange upon application of a stimulus. They represent a novel family of permanently crosslinked polymers which exhibit a liquid feature upon heating while the macroscopic deformation is controlled by the rate of such internal chemical bond exchange reactions.

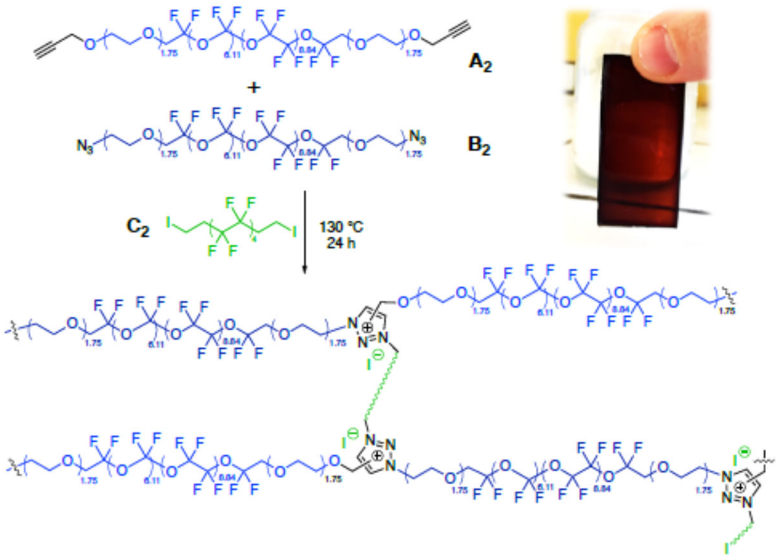
Du Prez's group[62] reviewed the recent developments to understand and control covalent adaptable networks and dynamic crosslinking reactions within vitrimers, and how tuning this chemical reactivity can be utilised to favor the material properties.

Actually, to the best of our knowledge, vitrimers based on FP (including PTFE, PVDF and copolymers of TFE, CTFE and VDF) have never been reported, though a few ones containing either perfluorooligoether (PFPE) or CF_2 and CF_3 moieties are exemplified hereafter. Guerre et al.[63] studied a catalyst-free fluorinated vitrimer elastomer, achieved by polycondensation of a telechelic bis(acetoacetonate) PFPE (obtained from the PFPE diol, Scheme 2a) and tris(2-aminoethyl)amine (TREN) (Scheme 2b) wherein two competing bond exchange mechanisms co-exist, each of them showing a strikingly different temperature dependence. This contributes to a highly unusual dual viscosity profile for such a new class of vitrimer materials: a very gradual decrease in viscosity at lower temperatures, intercepted by a much sharper drop in viscosity at higher temperatures.



Scheme 2 a) Functionalization of a telechelic PFPE diol into a bis(acetacetonate)-PFPE (PFPE-AA), b) network synthesis via polycondensation reaction of acetoacetate and amine leading to vinylogous urethane bonds and c) general scheme for transamination of vinylogous urethanes[63] (reproduced with permission from American Chemical Society).

Another strategy also involving low glass-transition temperature (T_g) PFPE led to electrolytes for lithium ion batteries.[64] Ion-conducting vitrimers were prepared from a concomitant thermal initiated-Huisgen polyaddition of telechelic PFPE-diyne (A2) and bis(azido)-PFPE (B2) and an *in-situ* *N*-alkylation in the presence of a fluorinated telechelic 1,12-diiodoTFE telomer crosslinker (C2) (Scheme 3). The creep behaviour at elevated temperature was typical of a viscoelastic liquid and the relaxation times ranged from 2.5 h at 170 °C to 4 min at 210 °C. The network was stable under both acidic and basic environments and could recover its mechanical properties after two recycling steps. Three PFPE-based vitrimers were obtained by varying the diiodo-crosslinker contents and the most stable displayed a suitable thermal stability (5%wt loss, $T_d^{5\%}$ = ca. 300 °C), a water contact angle of 136°, and ionic conductivities (as non-doped materials) ranging from 0.5 to 1.0 x 10^{-6} S cm^{-1} at 27 °C.



Scheme 3 Synthesis of the fluorinated network by thermally initiated polyaddition of PFPE-diyne **A2** and PFPE-diazide **B2** in combination with *in-situ* *N*-alkylation in the presence of 1,12-diiodo-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane **C2**[64] (reproduced with permission from American Chemical Society).

The reprocessing was achieved at 170 °C at 200 bar for 48 h (Fig. 10).

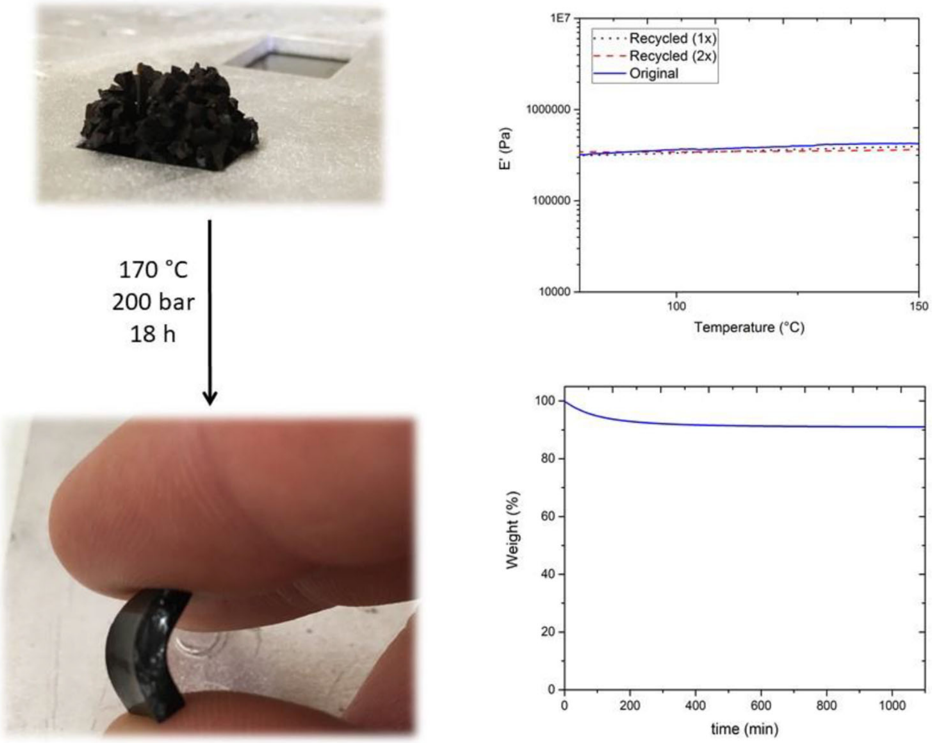
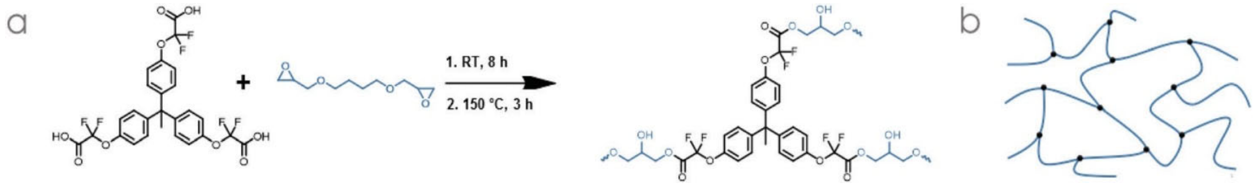


Fig. 10 Sample made from A2+B2+C2 (1:1:1 mol:mol:mol) cut into small pieces and remolded (left). Storage moduli E' of original and recycled samples (right). (where A2, B2 and C2 stand for telechelic diyne-PFPE, bisazido-PFPE and 1,12-diiodo-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane, respectively) [64] (reproduced with permission from American Chemical Society)

Cuminet et al.[65] reviewed various strategies to overcome the issue of high catalyst loadings in conventional vitrimers**.** They suggested internal catalysis, neighboring group participation able to favor the reshaping ability of such materials. These authors summarised the influence of the activating groups and the different types of exchangeable bonds on the exchange reactions in vitrimers.

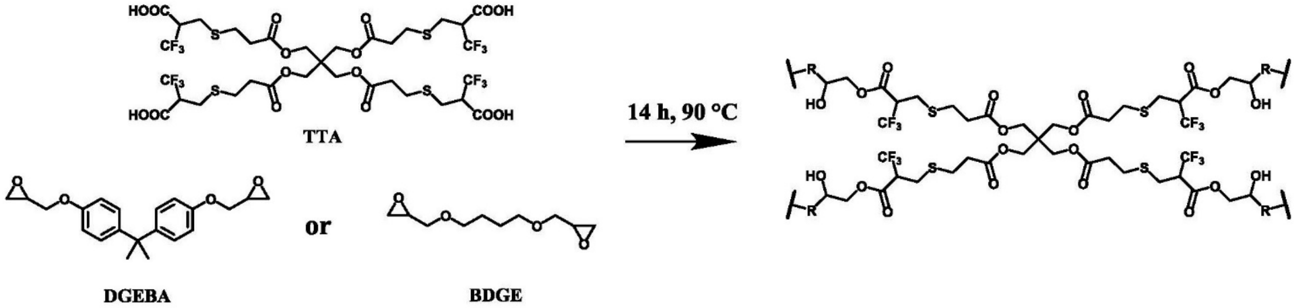
A peculiar example from the same group[66] dealt with the synthesis of catalyst-free transesterification by inserting of a difluoromethylene activating group adjacent to the ester functions. First, they modified 1,1,1-tris(4-hydroxyphenyl)ethane by bromodifluoroethyl acetate (Scheme 4). After saponification, the resulting aromatic trifunctional CF_2CO_2H reacted onto telechelic 1,4- butanediol bis(glycidyl) ether (DBGE) without any catalyst thanks to the high electron-withdrawing CF_2 groups hence favoring the epoxy-acid polymerisation, and remarkably the transesterification on adjacent esters (with a gel time of 1 h 20 min).



Scheme 4 (a) synthesis of a network from 1,1,1-tris(4-hydroxyphenyl)ethane and 1,4-butanediol bis(glycidyl) ether and (b) schematic representation of the network[66] (reproduced with permission from The Royal Society of Chemistry).

Surprisingly, no information of possible cationic ring opening polymerisation of the epoxides initiated by $-CF_2CO_2H$ strong acids was supplied. Nevertheless, such a fluorinated group enabled the synthesis of a highly crosslinked reprocessable materials which did not need any metallic or organic catalyst. After reaction, the insoluble content was higher than 95%. Such an original vitrimer displayed reprocessing abilities and underwent ten reshaping cycles in a role, keeping its transparency without losing any mechanical properties, thus gathering durability and recyclability.

Additionally, the same group[67] used an alpha CF_3-substituted tetracid ester in polycondensation to achieve catalyst-free epoxy vitrimers (Scheme 5). Two diepoxy monomers (bisphenol A diglycidyl ether, DGEBA and BDGE) were involved in such a reaction. Curing was monitored by rheology, DSC, and FTIR leading to a high gel content (> 70%). The accelerating effect of the alpha-CF_3 group on transesterification reactions was evidenced by stress-relaxation studies and analysed computationally on a model system. Reshaping tests showed that both the mechanical and thermal properties of the reprocessed materials were similar to those of the initial ones.



Scheme 5 Synthesis of vitrimers achieved from a tetra-acid bearing CF_3 groups in the α-Positions (TTA) and bisphenol A diglycidyl ether (DGEBA) or 1,4-butanediol diglycidyl ether (BDGE) [67] (reproduced with permission from American Chemical Society).

In conclusion, though that third family of polymers containing a few Fluorine atoms that makes the link between the historically opposed 3D networks (thermosets) and linear polymers (thermoplastics), is still at its infancy, these studies highlight the high potential of electron-withdrawing fluorinated groups as powerful internal activators for transesterification achieved without catalyst. These vitrimers in which associative exchange reactions take place under specific conditions combine durability, reprocessability and recyclability and are of great interest for recycling fluoropolymers.

To complete this sub-section on polymers containing low fluorine amounts, Sathe et al.[68] reported that semi-fluorinated polymers could undergo a chemical recycling to generate the corresponding monomers at room temperature. First, these semi-FPs were prepared by ring-opening metathesis polymerization of functionalized trans-cyclobutane fused cyclooctene (tCBCO) monomers and displayed very good thermal stability (with decomposition onset temperatures higher than 280 °C) and were hydrophobic. Indeed, that simple preparation, functionalization, and recycling, along with the diverse thermomechanical properties and demonstrated hydrophobicity make the tCBCO-based depolymerisable semi-fluorinated polymers promising candidates for sustainable functional materials. These polymers could be depolymerized to over 90% conversion in presence of ruthenium complexes at room temperature while the modular nature of the tCBCO scaffold was used to insert diverse thermomechanical features. Among them, depolymerisable amphiphilic polymers could find applications in antifouling materials and controlled small-molecule release.[68]

4. Thermal degradation of FPs

4.1. Introduction on the methods of decomposition

Usually, several methods are investigated to safely dispose of various PFAS waste, particularly end-of-life FPs in materials.[69-75] These methods encompass open burning (OB), open air detonation (OD), incineration, smoldering and pyrolysis. FPs are specialty polymers of quite a low health concern during their life span when involved in many applications. [57] Once they end their normal lifecycle and are disposed of, the degradation of FPs have been studied by several research groups to evidence potential degradation products.

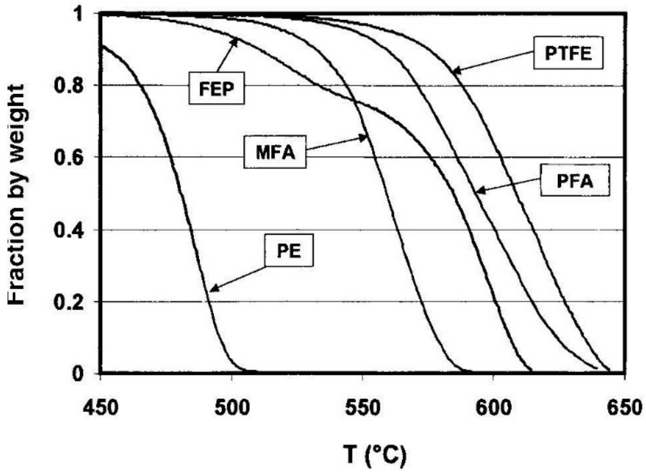
OB is defined as an open-air combustion process by which excess, unserviceable, or obsolete munitions are destroyed to eliminate their inherent explosive dangers. Open air detonation (OD) is used for the disposal of excess, unserviceable, or obsolete munitions whereby an explosive donor charge initiates the munitions being treated.[76] OB and OD are primary methods of disposal of munitions components including those containing PFAS components. While OB and OD are used mainly for munitions components, other techniques exist to degrade FP waste in more common materials such as coatings for non-stick cookware, water proofing of fabrics, and stain repellents for carpets.

Incineration is a high-temperature flaming process occurring in open air space, whereas smoldering is regarded as a flameless combustion process that happens on the surface of a condensed fuel. While both methods can be used to destroy fluorinated waste, the main difference between both is that smoldering is self-sustaining and, therefore, more energy efficient compared to incineration which requires continuous energy input.

Lastly, pyrolysis is similar to incineration related to a high-temperature process used for thermal decomposition, except it takes place in an inert atmosphere [77].

Moreover, techniques of thermal degradation and waste treatment of polymers containing PFAS can be greatly expanded to favor environmentally safe and conscientious processes.

Comparison of the thermal stabilities of various FPs are supplied in Fig. 11.[78]



Polymer	5% weight loss T (°C)
PTFE	561
PFA	547
MFA	540
FEP	520
ETFE	466
PVDF	438
PE	434
ECTFE	420
PCTFE	407
PVF	383

Fig. 11 Thermogravimetric analyses (left) and 5% weight loss temperature (T*)*, (right) of commercially available FPs[78] (reproduced with permission from Wiley).

4.2. Thermolysis

Various articles on the thermolysis of FPs have been reported. The temperature has a great influence of both the decomposition (partial or complete) and the nature and amounts of the released products. [77] Tough the decomposition of PTFE begins slowly at 260 °C, temperatures above 400 °C are needed to observe a significant decomposition.[79]

The first study was achieved by Lewis and Naylor[80] as soon as 1947 who highlighted that TFE was almost the unique compound generated in the pyrolysis of PTFE under vacuum at 600 °C. But, its yield dropped drastically at atmospheric pressure, whereas HFP and octafluorocyclobutane (c-C_4F_8, OFCB) contents were increased. In 1956, Wall and Michaelsen reported the thermal decomposition of PTFE in various gaseous atmospheres at ca. 450-510 °C (Fig. 12).[81] Thermal ageing of PTFE in the molten state was also reported.[82]

Daikin industries, Ltd. patented a continuous thermolysis by using kiln.[83] claiming that TFE, HFP and OFCB are released at 600 ~ 650 °C with steam.

Further, non-exhaustive articles are supplied hereafter. In 1977, Arito and Soda characterised the pyrolysis products of PTFE and FEP and the influence of pyrolysis conditions on such generated compounds to evaluate their inhalation toxicity.[84] Both (co)polymers were pyrolysed at various temperatures in a flow of nitrogen and air, either dry or humid and the pyrolysis products were analysed by infrared spectrometry combined with gas chromatography/mass spectrometry. In pyrolysis of both polymers in a nitrogen stream, octafluoroisobutylene (OFIB) was identified in addition to the main products such as TFE, HFP and OFCB. The main pyrolysis products of both polymers in an air stream were carbonyl fluoride and trifluoroacetyl fluoride. TFE and HFP were far less in quantity but OFIB was found only from the pyrolysis of FEP. Furthermore, perfluoroalkanes were produced by oxidative pyrolysis of PTFE at high temperatures. Influence of the water vapor in the gas flow on the product formation was significant only under oxidative pyrolysis. In the presence of water vapor, carbonyl fluoride was chemically changed into HF and CO_2, while trifluoroacetyl fluoride led to trifluoroacetic acid (TFA) and HF.

Furthermore, in 2001, Ellis, Mabury et al. comprehensively studied the thermal decomposition of PTFE,[36] that was further revisited two years later (on PTFE, PCTFE, ECTFE and PFA) from complimentary analytical techniques as ^{19}F NMR spectroscopy coupled with GC/MS.[85] As in previous studies, the most abundant volatiles produced from the thermolysis of PTFE were TFE, HFP and fluoroformaldehyde.[79,84,86,87] These authors identified TFA as the major acid product and a related homologous perfluoroacids of longer chain length (ranging in perfluoroalkyl length from 2 to 13, was confirmed using authentic standards and the mass spectra of PFOA).

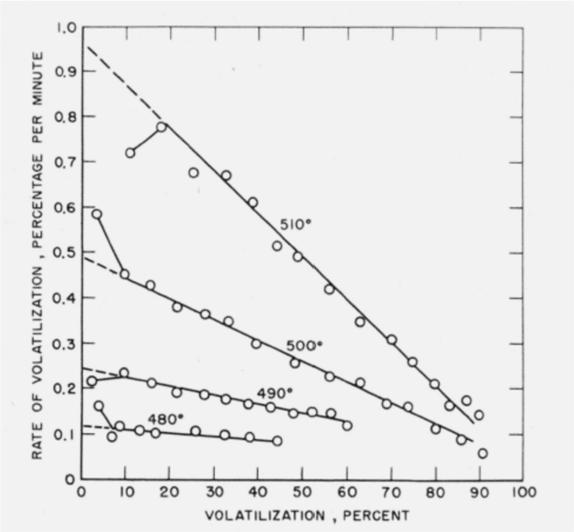


Fig. 12 Rate of thermal degradation of PTFE *versus* the % volatisation at different temperatures[81] (released from the U.S. Government).

At 400 °C, under air atmosphere, COF_2 is the principal gas evolved, which, reacting with traces of water yielded HF[87] and carbonyl fluoride ion, detected in high amount in the combustion process of PTFE.[88] The toxicity of pyrolysis products from PTFE was evaluated by exposure to different animals.[89] COF_2 was identified as the principal toxic component, estimating that at 550 °C, 20–25 g of PTFE would be the dose necessary to kill half the animals exposed for 1 h, being classified as ''moderately toxic''. Tsai et al. indicated that, by heating at 260 °C, PTFE generates ''polymer fumes''.[90] Among other products, TFA may be partially responsible for pulmonary edema noted in workers at a PTFE plant.

In 1995, Jun et al. pyrolysed PTFE in the 510–600 °C range.[92] TFE, HFP and OFCB were produced and, in most conditions, TFE was the major product. OFCB was regarded as the secondary product formed from the thermolysis of TFE because its formation strongly depended upon the degradation rate.

In 1998, Simon and Kaminsky pyrolysed PTFE at 500–600 °C in a fluidised bed reactor using steam.[79] They noted that the primary decomposition products were TFE and $^{\bullet}CF_2^{\bullet}$ diradicals. Further products were formed by secondary reactions. Actually, C_2F_4 is inflammable in O_2 atmosphere, releasing CF_4 and CO_2. As reported above, TFE reacted to generate HFP and OFCB above 600 °C.

Mabury's group studied the thermolysis of PTFE and noted the formation longer chain polyfluoro- and/or polychlorofluoro- (C3-C14) carboxylic acids which may be equally persistent.[36,85] Furthermore, among other thermal degradation products, these authors detected chlorofluorocarbons (CFCs) and fluorocarbons known to attack ozone and to act as greenhouse gases, respectively. They proposed a mechanism for the thermal degradation of PTFE[36], involving primarily the reaction of a $^{\bullet}CF_2^{\bullet}$ carbene diradical, for the production of the main fluorinated compounds observed (Fig. 13). These authors also confirm and completed previous findings[79,84,92-94] as well as additional products observed in their investigation (Fig. 13). They also reported that PCTFE and other polyfluorinated polymers have not been deeply studied in the same comprehensive methodology, though Zulfiqar et al.[95] previously tackled that approach (*vide infra*). However, these authors suggested that the mechanism for their degradation is similar, based upon the distribution of related products observed.

Ellis et al.[36] detected TFE, HFP as well as fluoroformaldehyde as the most abundant products obtained in the thermolysis of PTFE. However, they also noted many other fluorinated species, such as perfluoroalkene acids, fluoroether acids, perfluoroacids and branched perfluoroacids (Fig. 13), including TFA as the major identified acid product.

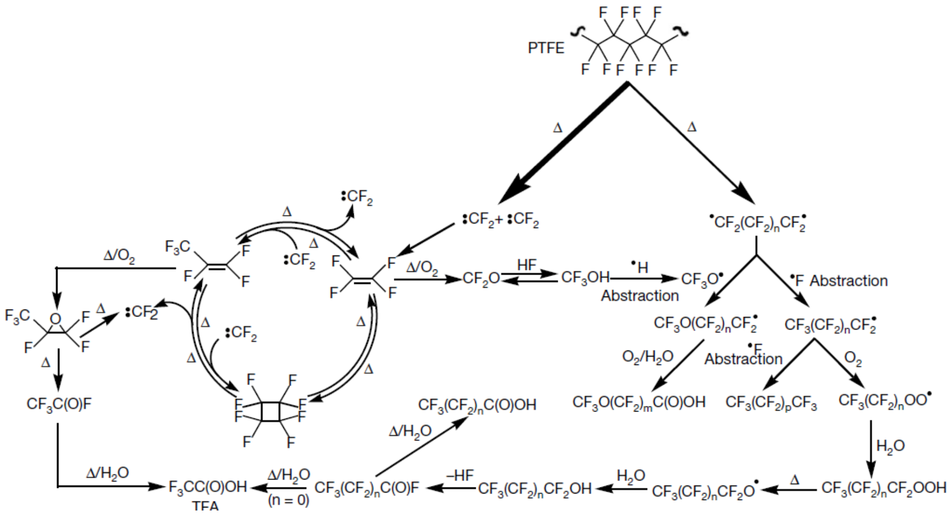


Fig. 13 Proposed significant pathways in the thermal decomposition of FPs; Δ stands for heat[36] (reproduced with permission from Nature Publishing Group).

As indicated by the bold arrow, the most significant step in the thermal decomposition is the formation of $^{\bullet}CF_2^{\bullet}$ carbene radicals recombining into TFE. Longer-chain diradicals are also formed, which can undergo fluorine abstraction or reaction with carbonyl fluoride to produce fluoroalkyl (p = 0±4) or fluoroalkoxy radicals. These radicals then react with constituents present in the air, oxygen and traces of water to form perfluorinated acids (n = 0-12, m = 1-7) including TFA, the yield being inversely proportional to the number of carbon atoms in the chain. The distribution of product yield depends on the temperature and the composition of the atmosphere. These mechanisms were supported by ^{19}F NMR spectroscopy combined with GC/MS analyses.[85]

From an environmental-fate perspective, the thermal degradation of FPs produces monomer units that degrade in the troposphere into CO_2,[96] or halogenated propenes[92,97] (Fig. 14). These latter further decompose generating long-lived haloacetic acids[98] such as TFA which are expected to be terrestrially deposited via wet (e.g. rain) and dry depositions.[99] In addition, various perhalogenated acids and perfluorodecanoic acid, have been evidenced to act as peroxisome proliferators and as inhibitors of gap junctional intercellular communication.[100] As known, CFCs were produced through the decomposition of chlorofluorinated (co)polymers and may migrate to the stratosphere causing a negative effect on the ozone layer.

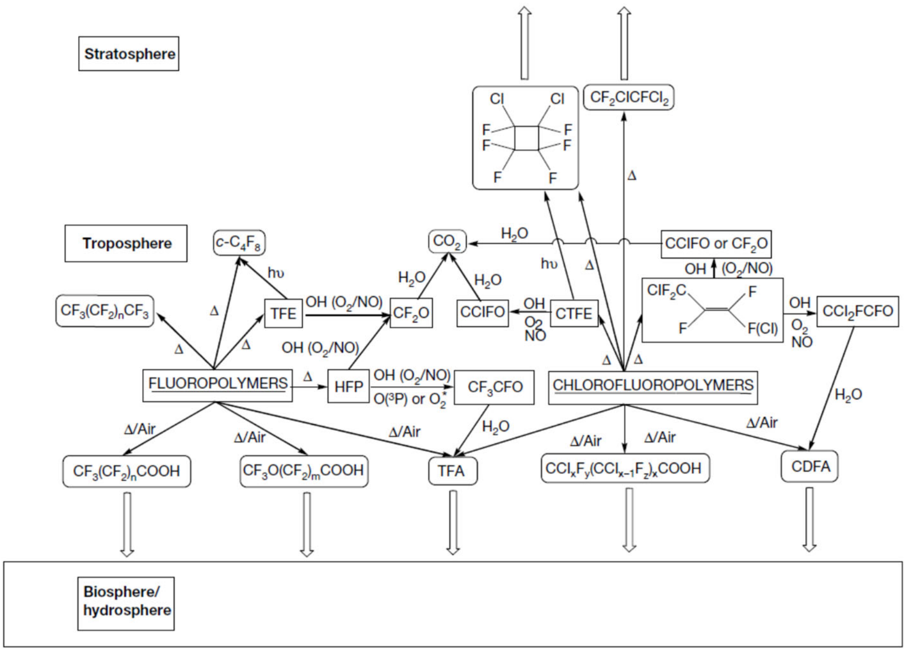


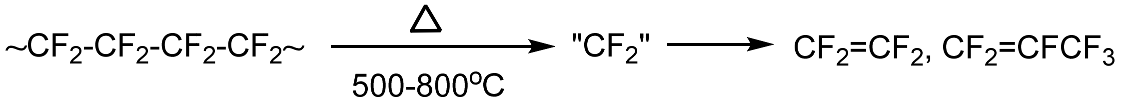
Fig. 14 Suggested environmental reaction pathways for the thermal degradation of fluoro- and chlorofluorinated polymers. Rectangular boxes represent environmentally transient species (t1/2 < 10 years) and important environmental impacts. Reaction processes are either proposed on the basis of this study, or are based on refs 67 and 81). Significant perhaloacid concentrations (x = 0±2, y = 1±3, z = 1±2, n = 1± 12, m = 1±7) are produced, primarily TFA and chlorodifluoroacetic acid (CDFA) (1-10 wt%). Tropospheric oxidation of the perhalopropenes also predominantly leads to, or is expected to lead to, the formation of TFA and CDFA. The thermal decomposition of the chlorinated FPs leads to the production of saturated CFCs[36] (reproduced with permission from Nature Group Publishing).

In 2007, Garcia et al.[101] suggested that PTFE decomposition involves random chain cleavage followed by depolymerisation and termination by disproportionation.[102] Most investigations on PTFE degradation products have been performed at slow heating rates and temperatures below 700 °C, to characterise the polymer fumes produced from PTFE manufacture process as well as the degradation products obtained from PTFE under harsh chemical and thermal conditions. This study completed that reported by Baker and Kasprzak[87] on the isothermal thermogravimetric measurements under air at different temperatures, in the range 150–525 °C, analysing the gases released by infrared spectroscopy. Dynamic thermogravimetry curves, up to 700 °C, under air and N_2 atmospheres, were carried out by Conesa and Font[88] characterising the evolved gases by mass spectrometry. PTFE was pyrolysed inside an electric furnace at 550 °C in an air stream to evaluate the toxicity of decomposition products measuring the carbonyl fluoride (COF_2) concentration.[89] Slow thermolysis of PTFE up to 500 °C in a laboratory scale tube reactor was carried out in air to especially collect and analysing by ^{19}F NMR and mass spectrometry, the fluoroacids formed while TFE, HFP and fluoroformaldehyde were the most abundant products.[85] However, as mentioned above, these authors detected many other fluorinated species, such as linear and branched perfluoroacids, fluoroether acids, and TFA as the major acid.

Actually, although perfluorocarbons (PFCs) and hydrochlorofluorocarbons (HCFCs) have been proposed as replacements for CFCs, in some applications, as they do not deplete the ozone layer, they are potent greenhouse gases, with global warning potentials (approximately 6500 and 9200 times that of CO_2 for CF_4 and C_2F_6, respectively) and have lifetimes that exceed

10,000 years.[103-104] TFA is a compound with no known loss mechanisms in the environment, and higher concentrations in natural waters have been shown to be mildly phytotoxic.[36] Furthermore, Meissner et al.[105] studied the influence of experimental parameters (temperature in the 600–800 °C range), pressure (100–760 mmHg), PTFE feeding rate (250–1000 g/h) and nitrogen flow (0–200 L/h)) on PTFE pyrolysis, using statistical methods of experimental design.

Additionally, a pyrolysis temperature of 555 °C, led to 76 wt% TFE, 7.1 wt% HFP and 5.2 wt% OFCB, from the PTFE input as observed by Simon and Kaminsky.[79] Early results were reported on the pyrolysis of PTFE at 600 °C and under vacuum (7×10^2 Pa) releasing 97 % of TFE.[106-107] Under an atmospheric pressure of 1.103×10^5 Pa, this yield dropped down to only 16 %, whereas those of HFP and c-C_4F_8 increased. More recently, Kaminsky[108] carried out that pyrolysis in a fluidised bed, under normal pressure with nitrogen as a fluidising gas at various temperatures. The high heat transfer is one of the advantages for using a fluidized bed reactor. An increase of temperatures from 605, 650 to 700 °C decreased the TFE release from 79 to 60% but increased the OFCB from 4 to 16, while the HFP content was steady (5 to 6%). Other fluorocarbons and carbon oxides were detected only as traces. SiF_4 and soot were also formed by reactions of fluorocarbons with sand, used as fluidizing medium. The SiF_4 amount increased with increasing temperatures. It is possible to use also filled PTFE material for the pyrolysis. For a bronze filled PTFE at 600 °C, the TFE yield is significantly reduced to 60 wt% by a catalytic effect. Other fillers did not show any effect. At 500-800 °C, PTFE is known to release TFE and HFP (Scheme 6).[109]



$$\sim CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\sim \xrightarrow[500\text{-}800^{\circ}C]{\Delta} \text{"}CF_2\text{"} \longrightarrow CF_2{=}CF_2,\ CF_2{=}CFCF_3$$

Scheme 6 Decomposition of PTFE to generate TFE and HFP[109] .

At higher temperatures (750–1050 °C) and in a horizontal tubular reactor, Garcia et al.[101] identified various compounds generated from the thermal degradation of PTFE, studying the influence of the atmosphere, from pyrolysis to nearly total combustion. Evolutions with the temperature and oxygen/mass ratio, of the major PFCs (CF_4, C_2F_6, C_3F_6 and C_2F_4) as well as traces of semi-volatiles detected, have been monitored. At 1000 K, the half-life of PFOS is reported to be 0.2 s;[110] decreasing sharply as the temperature increases further. These results show that the acid end-group in PFOS can efficiently spoil the incinerators. Understanding the exact decomposition mechanism and kinetics of PFOS will help to improve remediation technologies actively under development.

Ellis et al reported that TFE, HFP and OFCB were the main gases produced upon thermolysis of the pure fluorinated polymers and of the tested commercially available products (Table 1).[36] Actually, HFP has the potential to react with $^{\bullet}$OH radicals in the troposphere to produce TFA (in 100% conversion).[98] Analogously, PCTFE yielded CTFE, chloropentafluoropropene (CPFP) and 1,2-dichlorohexafluorocyclobutane (DCHCB), as well as DFA and TFA.[85] The reaction kinetics of CPFP with $^{\bullet}$OH radicals[85] is expected to be similar to that of HFP, based upon its reactivity onto other radicals[111] and the behaviour of similar molecules[98] producing CDFA in the troposphere. As well as PTFE and PCTFE, ECTFE and PFA copolymers were also tested in similar conditions by Ellis et al. (Table 2).[36] A large, previously unidentified class of thermolysis compounds, perhalogenated acids, was also detected (Table 2). TFA and CDFA were the main acids to be observed in the thermolysis of the fluoro- and chlorofluoropolymers, while other longer-chain perhalogenated acids were also identified.

Table 2: Positively identified species produced in the thermal decomposition of various fluoropolymers[36] (reproduced with permission from Nature Group Publishing)

Polymer	Thermal product identified [a]	Yield (%)
PTFE	TFE	-
	HFP	10.8
	TFA	7.8
	o-OFB	-
	$CF_3(CF_2)_nCOOH$	>0.01
	$CF_3O(CF_2)_mCOOH$	-
	DFA	>0.01
	MFA	>0.01
PCTFE	CTFE	-
	CPFP	13.1
	CDFA	9.5
	TFA	>0.1
	DCHB	-
	DCHFCB	-
	TCTFE	-
	1,3-DCTEP	-
	1,1,3-TCTFP	-
	$CCl_xF_y(CCl_{x-1}F)_zCOOH$	-
ECTFE	TFA	6.3
	CDFA	7.2
	HFP	-
	CPFP	-
PFA	TFA	2.5
	HFP	-

[a] MFA: monofluoroacetic acid; DFA: difluoroacetic acid; FDCA: fluorodichloroacetic acid; DCFP: dichloroperfluoropentanoic acid; DCFB: dichloroperfluorobutanoic acid; DCHFCB: 1,2-dichlorohexafluorocyclobutane; TCTFE: 1,1,2-trichloro-1,2,2- trifluoroethane; 1,3-DCTFP: 1,3-dichlorotetrafluoropropene; 1,1,3-TCTFP: 1,1,3-trichlorotrifluoropropene; ECTFE: poly(ethylene-*co*-chlorotrifluoroethylene) copolymer;
PFA: poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether) copolymer.
For the long-chain acids, $n = 1\text{-}12$, $m = 1\text{-}7$, $x = 0\text{-}2$, $y = 1\text{-}3$, $z = 1\text{-}2$.

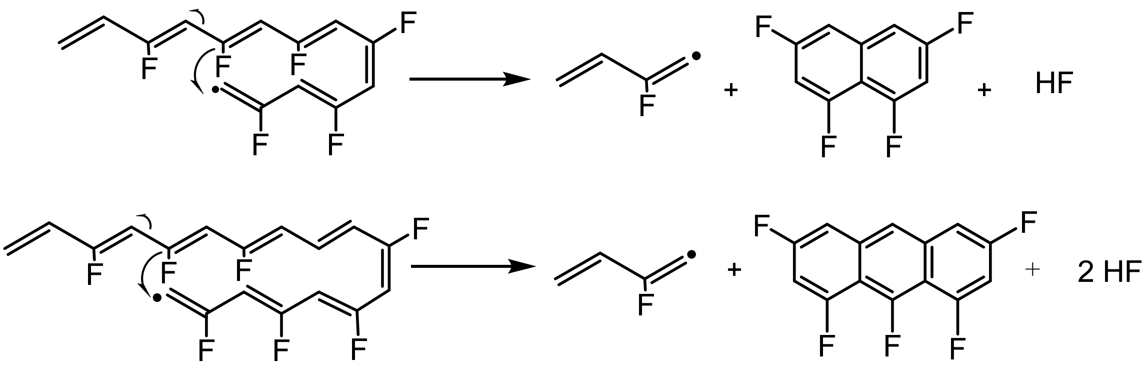
Montaudo et al.[112] extensively analysed the decomposition of PVDF by mass spectrometry and detected a characteristic peak of low intensity at ***m/z*** value of 20, assigned to HF, while the spectrum was dominated by three abundant peaks at ***m/z*** values of 132 (corresponding to trifluorobenzene), 200 (assigned to tetrafluoronaphthalene) and 268 (for pentafluoroanthracene) (Table 3).[112] Hexafluoronaphthacene was also observed with a reduced intensity at ***m/z*** 336 as well as several fluoro-containing aliphatic ions (Table 2 for peak assignments), including a small VDF amount *(m/z* 64).

Table 3 Fluoro-containing EI Fragments of Compounds Formed in the Pyrolysis of PVDF[112] (reproduced with permission from Wiley)

Fragment	*m/z*
HF	20
CH_2=CF_2	64
$C_6H_3F_3$ (trifluorobenzene)	132
$C_{10}H_{10}F_4$ (tetrafluoronaphtalene)	200
$C_{14}H_4F_5$ (pentafluoroantracene)	268
$C_{18}H_6F_6$ (hexafluoronaphtacene)	336
CH_2=CF-CH=CHF	90
CH_3-CF-CH=CHF	91
CH_2=CF-CH_2-CHF_2	110
CHF=CH-CF_2-CH=CHF	140
CH_3-(CF_2-CH_2)$_n$-CF_2	65(0), 129(1), 193(2), 257(3), 321(4)
CF_2=CH-(CF_2-CH_2)$_n$-CF_2	113(0), 177(1), 241(2), 305(3), 369(4)
CHF_2-(CH_2-CF_2)$_n$-CH_2-CF_2	115(0), 179(1), 243(2), 307(3), 371(4)
CH_2=CF-(CH_2-CF_2)$_n$-CH_2CF_2	109(0), 173(1), 237(2), 301(3), 365(4)
CHF=CH-(CF_2-CH_2)$_n$-CF_2	95(0), 159(1), 223(2), 287(3), 351(4)

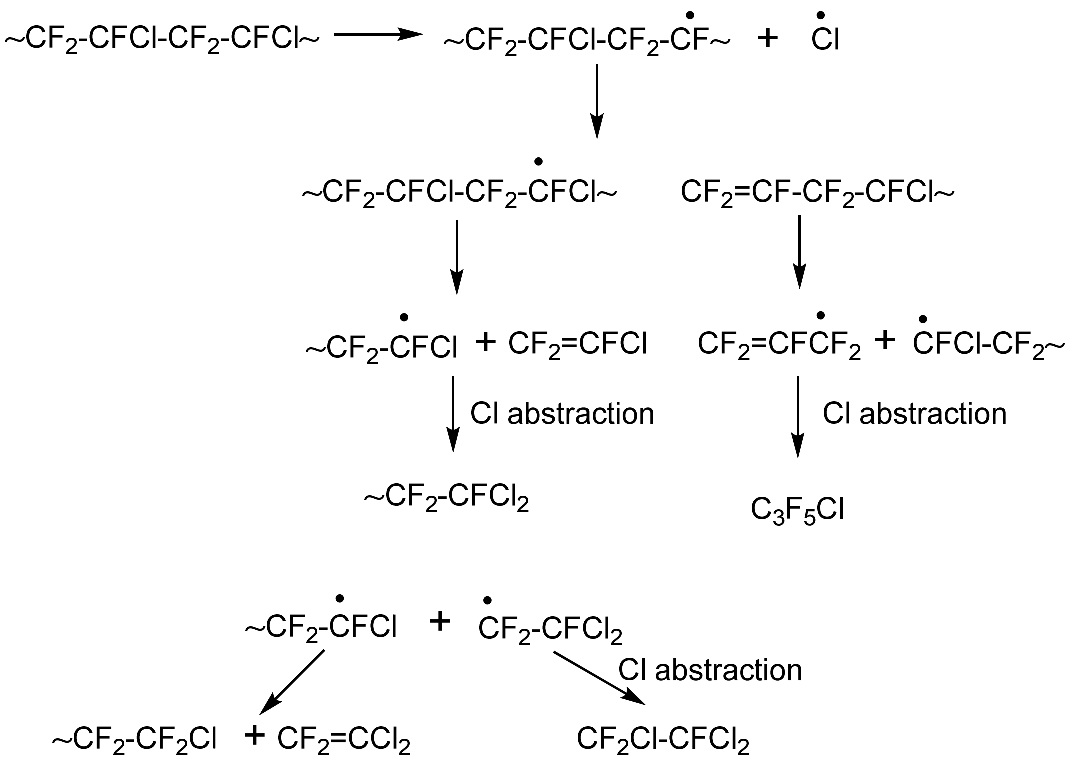
As known, PCTFE or poly(VDF-*co*-CTFE) copolymer display a different thermal stability than that of PTFE, due to the facility of dehydrochlorination compared to dehydrofluorination.[113] The former rearranges and decomposes intramolecularly to produce chloroaromatic compounds. Basically, two competitive thermal degradation processes are operating in these (co)polymers: (1) HX generation, with production of polyene sequences, and (2) main chain cleavage. This process occurs in parallel with a straightforward crosslinking reaction which yields char.[112]

Dehydrofluorination occurs at about 500 °C in PVDF and produces the formation of fluoroaromatic compounds, as described in Scheme 7.[112] However, at these high temperatures, main chain cleavage becomes competitive with dehydrofluorination, and fluoroaliphatic compounds are also formed.



Scheme 7 Mechanism of decomposition of PVDF[112] (readapted with permission from Wiley).

As it has already been noted, the products from the poly(VDF-*co*-CTFE) copolymers are the same as those deriving from the homopolymers corresponding to the monomer units except for the presence of some HCl. The types of reaction in Scheme 8 might be assumed to occur, the relative importance of the individual reactions being influenced by the proportions of the monomer units. HCl is likely to result from elimination involving adjacent ----CF_2CFCl- (Scheme 8), either following an initial C-Cl homolysis or by molecular elimination (Scheme 9).



Scheme 8 Thermal degradation of PCTFE[95] (readapted with permission from Elsevier).

The degradation kinetics of PTFE and poly(ethylene-*alt*-TFE) copolymer (ETFE) was reported by Hondred et al. by TGA.[114] These authors developed kinetic models describing the degradation of such (co)polymers from the activation energy, represented as a function of the extent of degradation. In the onset of degradation, these (co)polymers may fail in their desired function. It is found that an *n*th-order, a single-step autocatalytic reaction model enabled to best describe the degradation of PTFE, while a consecutive three-step autocatalytic reaction model was more appropriated in the degradation of ETFE.

Scheme 9 Thermal degradation of poly(CTFE-*co*-VDF) copolymer[95] (reproduced with permission from Elsevier).

From a more fundamental approach via a multi-step degradation model, Teyssedre et al.[115] compared the degradation of PTFE, polyimide (PI) and poly(TFE-*co*-perfluoroalkylvinyl ether) copolymer (PFA) for aeronautic cable insulation. PFA is a semicrystalline polymer with typical crystallinity of 60%[97] Commercial grades of PFA melt in the 300-315 °C temperature range with a high thermostability (Fig. 15). These authors noted that PFA displays a higher activation energy than those of PTFE and PI as well as a higher equivalent mass loss at 333 °C compared to PTFE (at 250 °C), hence making an excellent candidate for high performance cables with extruded insulation.

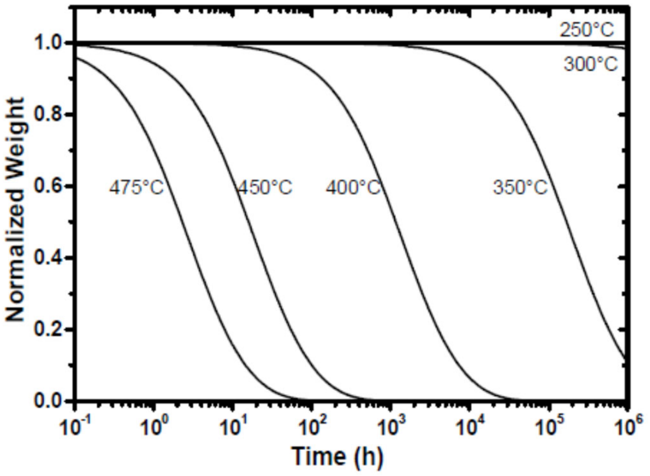


Fig. 15 Isothermal mass loss kinetics of PFA obtained by simulation following[115].

As a matter of fact, the thermolysis of ECTFE and PFA copolymers led to the acids also identified in the case of PTFE and PCTFE. No major differences in the fluorinated acetic acid products or acid precursors (*e.g.* TFA, CDFA, HFP and CPFP) were observed, suggesting that all classes of FPs, when subjected to thermal degradation will result, to differing degrees, in the production of fluorinated acids and also to environmental precursors to C3 haloacetic acids.

TFA has been well-identified in acid rains and reported in many studies that we cannot detail exhaustively. Its formation has been a controversial issue. Cui et al.[117] studied the thermolysis of three FPs, including PTFE, poly(VDF-*co*-HFP) and poly(VDF-*co*-CTFE) *via* a specific procedure sketched in Fig. 16 where the FP was burnt is a quartz vessel (boat) at 400-650 °C followed by detection and identification of the released products, including TFA.

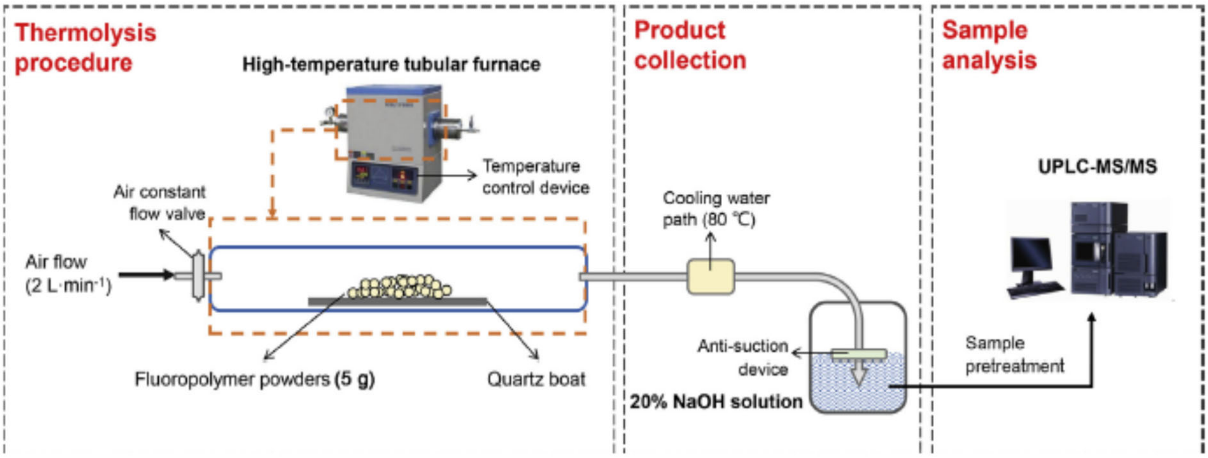


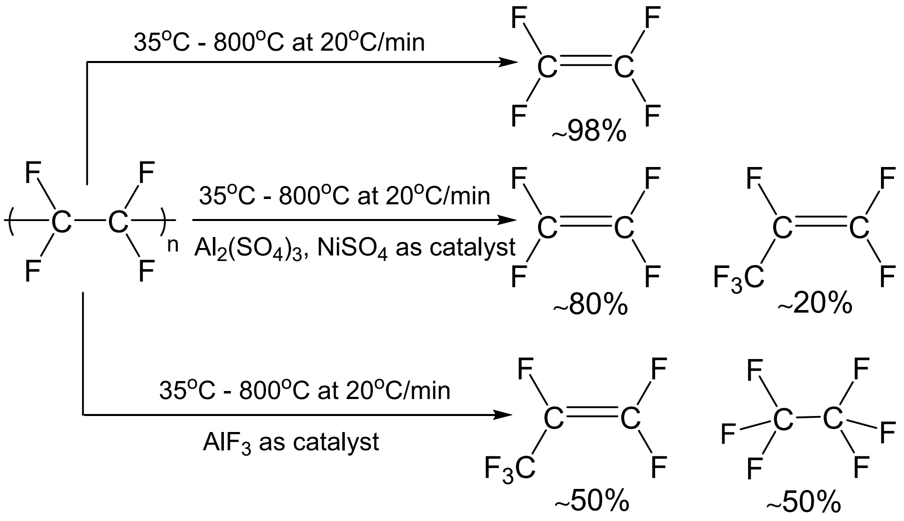
Fig. 16 Schematic diagram of the thermolysis experiment for various fluoropolymers[117] (reproduced with permission from Elsevier).

Hence, the authors set up a laboratory simulation experiment to analyse the TFA amounts.[117] Thermolysis of these FPs occurred from 400 °C to 650 °C, with the peak weight loss rate at ca. 550-600 °C. TFA could be produced through FP thermolysis when being heated to 500 °C and above. Average TFA yields from PTFE, poly(VDF-*co*-HFP) and poly(VDF-*co*-CTFE) copolymers were 1.2%, 0.9% and 0.3%, respectively. Furthermore, the same authors[117] evaluated the contribution of FP thermolysis and CFC alternatives to rainwater TFA in Beijing, China by using a Two-Box model. They estimated that the degradation of FPs and HCFCs/HFCs could explain 37.9-43.4 ng L^{-1} rainwater TFA in Beijing in 2014 (Table 4). The thermolysis of FPs contributed to 0.6-6.1 ng L^{-1} of rainwater TFA, accounting for 1.6-14.0% of the TFA burden from all the precursors which were considered.

Table 4: Gaseous TFA concentration in the fluoropolymer thermolysis products[117] (reproduced with permission from Elsevier)

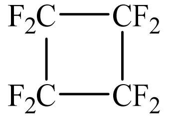
Compounds	TFA concentration (pg m^{-3})					TFA yield (%)
	300 °C	400 °C	500 °C	600 °C	700 °C	
PTFE	514 ± 26	518 ± 39	626 ± 35	879 ± 73	893 ± 21	1.2
PVDF-CTFE	499 ± 57	503 ± 48	744 ± 57	726 ± 39	739 ± 19	0.3
PVDF-HFP	502 ± 38	514 ± 35	761 ± 58	794 ± 4	753 ± 86	0.9
bank sample	521 ± 13	517 ± 29	525 ± 43	537 ± 21	520 ± 54	-

In 2014, we reviewed the thermal degradation and pyrolysis of PTFE in a book chapter,[118] and then, Puts and Crouse[109,119] highlighted the generated fluorinated compounds from pyrolysis of PTFE by heating from 35 °C to 800 °C at 20 °C/min in absence or presence of various metals or salts (Scheme 10). These South African authors found that in absence of salts, TFE was produced in 98% while the nature of the salt may induce other released gases (Scheme 10 and Table5) with the influence of inorganic materials as common oxides of Al, Ga, In, Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Zr and La.[119]



Scheme 10: Thermal decomposition of PTFE in absence or presence of various metals or salts (adapted from [109]).

Table 5: Various compounds released from the thermal decomposition of PTFE from 35 to 800 °C[109] (the abbreviations are defined at the end of the review) (adapted from [109])

Chemical name	Abbreviation	Molecular structure	CAS No.
Tetrafluoroethylene	TFE	$F_2C{=}CF_2$	116-14-3
Hexafluoroethane	PFE	$F_3C\text{-}CF_3$	76-16-4
Hexafluoropropylene	HFP	$F_3C\text{-}CF{=}CF_2$	116-15-4
Octafluoropropane	PFP	$F_3C\text{-}CF_2\text{-}CF_3$	76-19-7
Octafluorocyclobutane	OFCB		115-25-3
Octafluoroisobutene	PFIB	$F_2C{=}C(CF_3)_2$	382-21-8
Octafluoro-1-butene	PF1B	$F_3C\text{-}CF_2\text{-}CF{=}CF_2$	357-26-6
Octafluoro-2-butene	PF2B	tr-$F_3C\text{-}CF{=}CF\text{-}CF_3$	360-89-4

Bhadury et al.[120] studied the flash pyrolysis of PTFE in a quartz assembly while Hiltz[121] characterised two different TFE terpolymers (including FKM elastomers) by pyrolysis (Py) GC/MS, FTIR, DSC, and TGA. The Py-GC/MS method identified the polymers positively based on the variations in the pyrolytic degradation by-products. The different analysed copolymers were FR17/75 fluoroelastomer, a terpolymer based on TFE, HFP, and VDF, and LR6316/75 and FR25/80 fluoroelastomers bearing TFE, VDF, and PMVE units. The TFE, HFP, and VDF based-elastomers could be utilised within a temperature window from -12 and 210 °C, while the temperature to use LR6316/15 and FR25/80 were ranging between -29 and 205 °C and -41 and 200 °C, respectively. As expected, PMVE lowered down the T_g of the fluoroelastomer to -31 °C for FR25/80 (while that of FR17/75 was -13 °C).

The TGA displayed similar weight loss (ca. 60%) for LR6316/15 and FR25/80 elastomers, whereas FR17/75 elastomer had approximately 70% weight loss at the primary step. FR17/75 had greater residual mass than those of LR6316/75 and FR25/80 fluoroelastomers, and this could be explained by the presence of fillers in FR17/75. The fingerprint of the pyrogram of each fluoroelastomer was different. Figure 17 sums up the possible ways for the generation of some of the ions in the mass spectra of FR17/75.

FR17/75 fluoroelastomer degradation products contained unique ions differing in mass spectrometry by 20, 50, 64, and 100 units, and corresponding to the losses of HF, CF_2, $C_2H_2F_2$, and C_2F_4 ions, respectively.

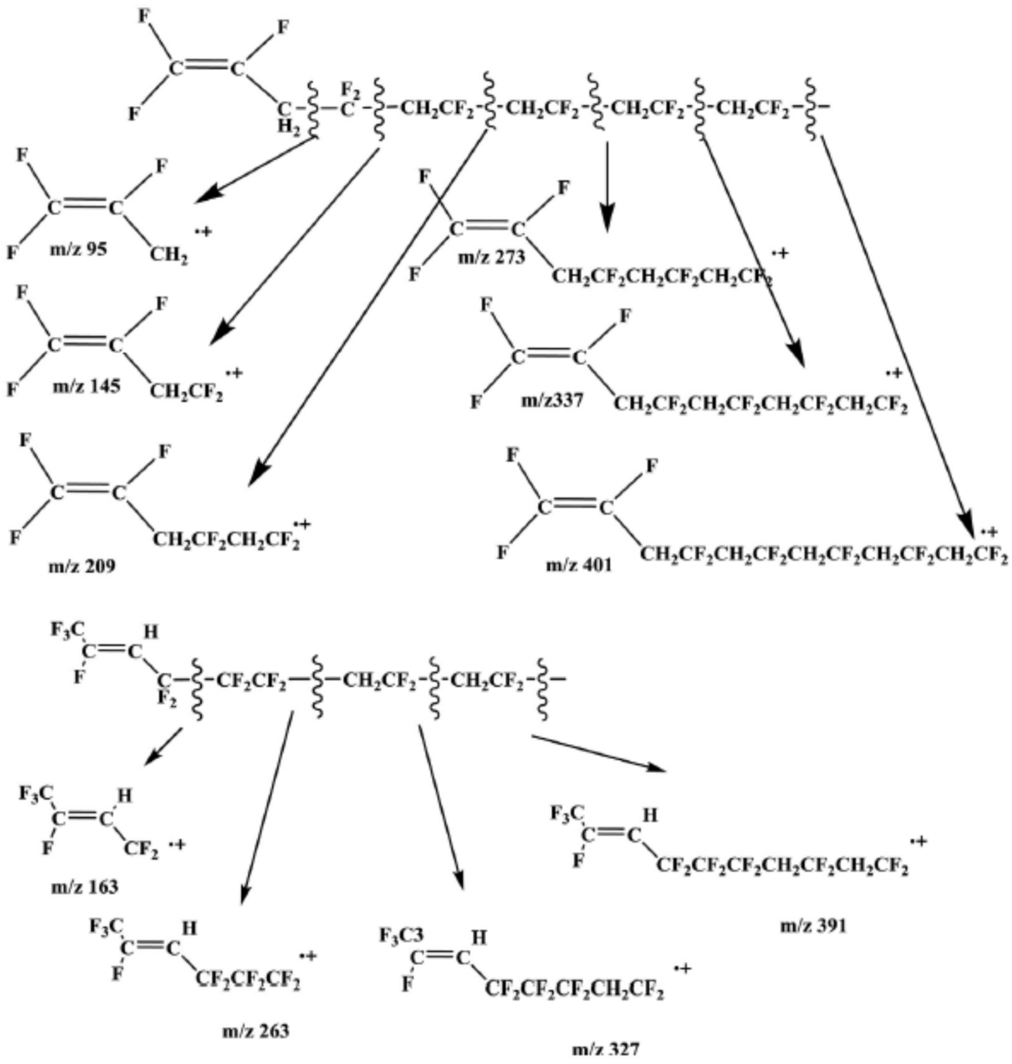


Fig. 17 Possible paths for the generation of some of the ions in the mass spectra of the major degradation by products of poly(VDF-*ter*-HFP-*ter*-TFE) terpolymer FR17/75[121] (reproduced with permission from Elsevier).

Degradation of another type of functional FPs was also reported. Feng et al.[122] studied the thermal decomposition of Nafion® N117 membrane, an innovative ionomer processed from a copolymer based on TFE and a perfluorovinyl ether bearing a perfluorinated ether side chain bearing a SO_3H end function. This typical perfluorosulfonic acid membrane (PFSA) electrolyte is quite involved in various chemical technologies including electrolysers and proton exchange membranes for fuel cells, PEMFC [e.g. for Mirai (Toyota),[123] Nexo (Hyundai), Clarity (Honda), Focus (Ford), X-trail (Nissan), Chevy electrovan (General Motors) vehicles,[124] FCVs]. Fuel cells are energy converters which transform the chemical energy of an oxidation-reduction into clean electricity, water and heat. They have the high potential to deliver environmental and economic benefits across various domains, including transportation, power generation, industrial equipment, consumer electronics and military power. However, the PFSA proton conducting polymer (or ionomer) as the heart of the membrane electrode assembly of a PEMFC undergoes chemical degradation, such as the attack on the polymer chains by reactive oxygen species electrochemically generated. These authors could identify at least 20 thermolysis products in methanol and water (m/z fragments ranging between ca. 100 and 600) by means of liquid chromatography-electrospray ionization-tandem mass spectrometry (LC/ESI-MS/MS).

The fluorinated released products (perfluorinated compounds, including PFCAs) were detected by an ion-chromatography system, while the membrane thermal stability was characterised by TGA. Hence, based on these data, they proposed a thermolysis mechanism involving the cleavage of both the polymer backbone and its side chains by the attack of radicals. This is the first report on the thermolysis products of Nafion® by simulating its high-temperature operation and disposal process *via* incineration. Additionally, this study provides an analytical evidence of the LC/ESI-MS/MS method for characterising the degradation products of polymer electrolyte membranes.

Moreover, the degradation of such PFSA was reported and four graphical degradation mechanisms are proposed in Figure 18.[125] The "unzipping" mechanism in the chemical decomposition of PFSA ionomers changed with the evolution in the ionomer post-fluorination process. A new generation of chemically post-treated PFSA membranes with reduced number of COOH groups show considerably improved durability. Furthermore, this improvement significantly increased with release of $–OCF_2CF(CF_3)$ group from the polymer dangling fragment.[126] This behaviour indicates the contribution of radical attack onto the side chain to overall membrane decomposition (Fig. 18).[125]

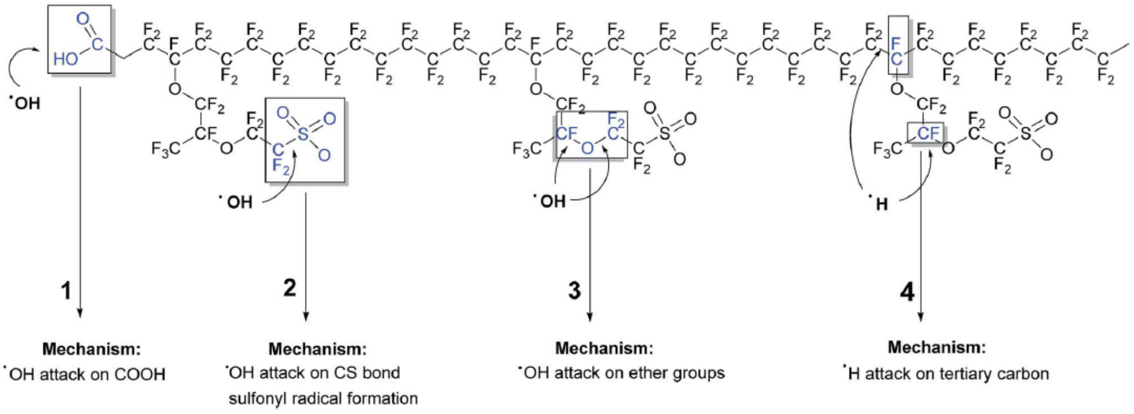
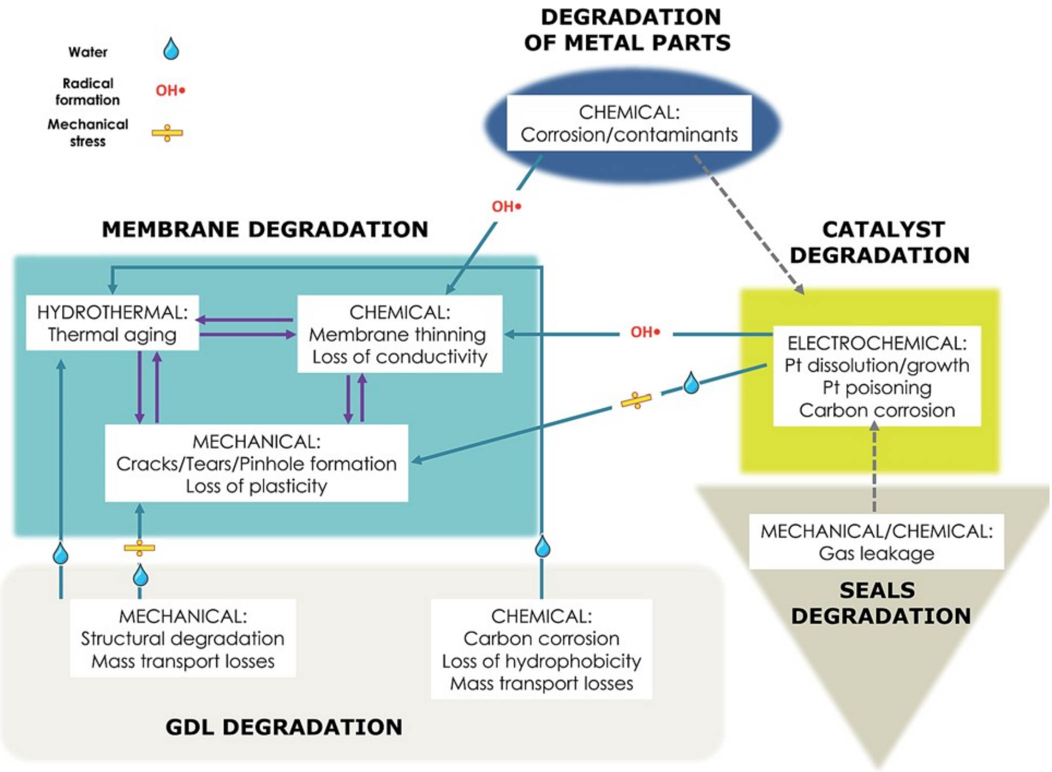


Fig. 18 Various mechanisms of HO• radical attack onto the Nafion® membranes[125] (reproduced with permission from The Royal Society of Chemistry).

In real operation, the performance loss may come from the pinhole formation[127] inducing mechanical and chemical membrane degradation cycling, concomitantly to changes of the relative humidity, temperature and loading cycling and start-up, shut-down which also enhance some membrane dimensional failures leading to polymer deformation and presence of cracks and pinhole. Then, high hydrogen crossover induces a fast radical release and favors the PFSA degradation. The decomposition profile proceeds until the thin membrane, weakened by such a radical attack, can no longer bear mechanical stress yielding a poor quality of the membrane electrode assembly (Scheme 11).[125]



Scheme 11: Parameters influencing the degradation of perfluorosulfonic acid (PFSA) fuel cell membrane[125] (reproduced with permission from Royal Society of Chemistry).

In 2005, Grot and Grot[128] pioneered the recovery of Nafion® membranes from a dissolution of used PFSA membranes in water and various solvents and then heating the mixture under pressure followed by the separation of components.
Recently, the Chemours Company [129] has announced three main goals to ensure a sustainable Hydrogen economy involving PEMFCs: i) to reach 60% absolute reduction of CO_2 emissions by 2030; ii) to align with Climate goal (with the Paris 1.5 °C rule by process emission reductions, energy efficiency, renewable energy) and iii) to commit achieving net-zero CO_2 emission from operations by 2050. To do so, that company plans four main actions: i) to recycle and reuse PFSA ionomers (recaptured at end of device lifetime and /or to convert into new ionomers with no loss in performance and durability), ii) to "repair" them (any damaged ionomer regions "healed" by chemical treatment at end of life), iii) to repurpose (ionomer is recaptured, but "*wear and tear*" or conversion challenges restrict the use to secondary) alternative markets for ionomers, and finally iv) to restart (ionomer broken down into elemental constituents and used as recycled fluorine in manufacturing of Nafion®).

4.3. Thermal Processing

Under normal conditions of use, FPs are rarely decomposed because they are heated (or processed) at a temperature slightly above their melting point of the FP. [57] However, outside of normal, foreseeable use conditions, when FPs are extruded, injected, sintered or calendared at temperatures much above their appropriate processing temperatures, they might decompose. Upon degradation, FPs generate volatile products of decomposition.[130] At 450 °C, the decomposition of PTFE only proceeds at a slow rate on the order of 1% per hour. It is not until considerably above the polymer first-order transition temperature (329 °C) that a significant degradation is observed.[131] When the temperatures increase above suitable processing temperatures, the rate of generation rises and may sufficiently degrade the polymer to release dangerous gaseous by-products and polymer fume fever.[130] Temperature, presence of O_2, the morphology of the polymer item, and the residence time at elevated temperature are valuable parameters influencing the decomposition and the nature of the degradation products,[130] mainly fluoroalkenes, hydrogen fluoride, oxides of carbon, and lower molar mass FP particles. As in studies mentioned above, from PTFE, TFE is the main gaseous product observed at temperatures near 330 °C.

4.4. Incineration of FPs

As for all plastics, [1,2,48,132-133] incineration is the major way of elimination of FPs (it represents 83.5% in 2020, ca. 20.4 kt *versus* landfill, 13.1% , 3.1 kt and recycling, 3.4%, 0.8 kt[9,37]) regarded as the destruction of chemicals in presence of heat and is a mature technology used for various solid and liquid waste. FP are (co-)incinerated in municipal solid waste incineration (MSWI) plants or devoted to hazardous waste incineration plants (e.g. treating various waste from chemical waste manufacturers).

The total penetration of FP waste by mass is in mixed or commingled waste streams typically very low (<0.01%). Heat is directly applied to the FPs eventually contaminated (by soil, sediment, spent adsorbents, or waste) or liquids (water, wastewater, leachate, chemicals). Vaporised combustion products can be trapped (by precipitation or wet scrubbing) and/or further oxidised at high temperature.

FP waste from industrial and commercial waste producers can be used for energy recovery. Some fractions of pre-sorted waste are sent to recycling, either to domestic recyclers or exported for recycling in intra- and extra-EU countries.[9]

Incineration is one of only a few technologies that can potentially decompose FPs and PFAS totally. In December 2020, USEPA released a draft interim guidance on destruction and disposal of PFAS.[134] Nowadays, this is an active area of research 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.

Regarding design and operating considerations, waste incinerators are fixed facilities. US federal and state permits dictate the materials processed, core incinerator operations [135] (e.g., temperature, time and turbulence), and control of process air, liquid, and solid waste. Permit and design/construction similarities reduce the operational and performance differences between individual incinerators.

When regarding waste disposal options, energy costs, transportation costs, regulatory approvals, and final disposition of process, waste residues should be evaluated as these differ among incineration facilities.

As for sustainability, the environmental footprint for incineration includes transportation and supplemental fuel for the incineration process. Incineration of contaminated soils, liquid waste, and investigation derived waste (IDW) is energy-intensive and PFAS emissions, including potential PFAS combustion byproducts, from incinerators are currently not well-understood.[134] Truck hauling traffic affects the local community by creating additional traffic congestion, noise, and particulate matter emissions. The cost for this approach is high, but the solution may be cost-competitive for smaller treatment volumes.

This is an active area of research in evaluating effective destruction temperatures and treatment time, the potential to generate products of incomplete combustion, stack gas analyses, deposition onto land, and other risk factors.

As mentioned above, incineration is a high-temperature flaming process that occurs in open air space, whereas smoldering is a flameless combustion process that happens on the surface of a condensed fuel. While both methods can be used to destroy fluorinated waste, the main difference between them is that smoldering is self-sustaining and, therefore, more energy efficient compared to incineration which requires continuous energy input. The incineration, or combustion, differs from thermolysis in that a source of fuel is used in order to purposefully induce a complete decomposition of FPs (as a source of TFA and CDFA).[36] Furthermore, it is unlikely to yield environmentally significant levels of TFA or TFA precursors, due to the high temperatures and oxidizing conditions used, which would result in the cleavage of most Carbon-Fluorine bonds. 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 great source of fluorinated acids.

Several countries are currently using incineration. One example, achieved in Norway,[136] though the municipal waste incineration is performed at ca. 850 °C, the emissions of FP degradation products from household waste incineration have not been studied yet. However, on the laboratory scale, severe degradation of FPs, mainly PTFE, were investigated in the 700-1050 °C temperature range, leading to CF_4, CHF_3, C_2F_6, TFE and HFP as main released products (Table 6).

Table 6 FPs and their main decomposition products at various temperatures from in the literature. In parenthesis: PFC-code[136] (reproduced with permission from Norwegian Institute of Air Research (the acronyms are defined at the end of the review).

Polymer	*T* (°C)	Main products	References
PTFE	450	COF_2. HF	130
	400~500	TFE, HFP, PFIB	137
	500	HFP, TFA	36
	530	CF_4 (PFC-14), C_2F_6 (PFC-116), TFE, HFP, *c*-C_4F_8 (*c*-OFB) (PFC-318)	138
	550	CF_2O, C_2F_6, CF_3CFO, C_5F_4, CF_3CF_2CFO, $(CF_2)_3O_2$	139
	600-700	TFE, OFCB) (PFC-318)	120
	750-800	HFP	120
	850-900	PFIB	120
	800°C	CF_4 (PFC-14)	130
	>900 °C	C_2F_6 (PFC-116)	130
	850	HFP, TFE	101
	750-1050	C_2F_6 (PFC-116), CF_4 (PFC-14)	101
ETFE	350	COF_2, PFBE, TFE, CO	130
ECTFE	500	TFA, CDFA	130
FEP	400	COF_2, CHF_3 (HFC-23), HFP, TFE, PFIB	130
PFA	400	COF_2	130
PEEPE	500	TFA	36
CPTFE/ PCTFE	500	CPFP, CDFA	130
PTFE/PFA + PTFE/FEP	800	CH_4, CHF_3 (HFC-23), C_2F_6 (PFC-116)	140

As expected and mentioned in pyrolysis section, these generated products are strongly dependent on the incineration conditions such as temperature, moisture, oxygen content, use of catalysts, etc. A few surveys have been reported on the incineration degradation products of FPs other than PTFE.[136]

Myers et al.[141] analysed and evidenced many products from the thermal decomposition of PCTFE including 29 perhalogenated carboxylic acid groups and 21 chlorofluorinated-yclic aromatic hydrocarbon groups, such as mixed halogenated benzenes and naphthalenes.

Wang et al. reported that PFAS can be created from the waste handling of FPs at the end of useful life, specifically as a result of the municipal incineration of PTFE.[142] While PTFE is inert in the environment due to its high chemical and thermal stability, Taylor et al.[143] found that municipal waste incinerators operating with a mean gas temperature of 1000 °C over the effective length of the reactor can be used to decompose PTFE. Recently in 2019, Aleksandrov et al.[72] built upon this prior investigation and evaluated the potential formation of 31 PFAS compounds from the waste incineration of PTFE. The 31 selected compounds were cited in previous literature, occurrence in the environment, and availability of validated methods from commercial laboratories. A constant mass flow of wood pellets was utilised while these authors added PTFE into the reactor to maintain a consistent thermal profile, as shown in Fig. 19.

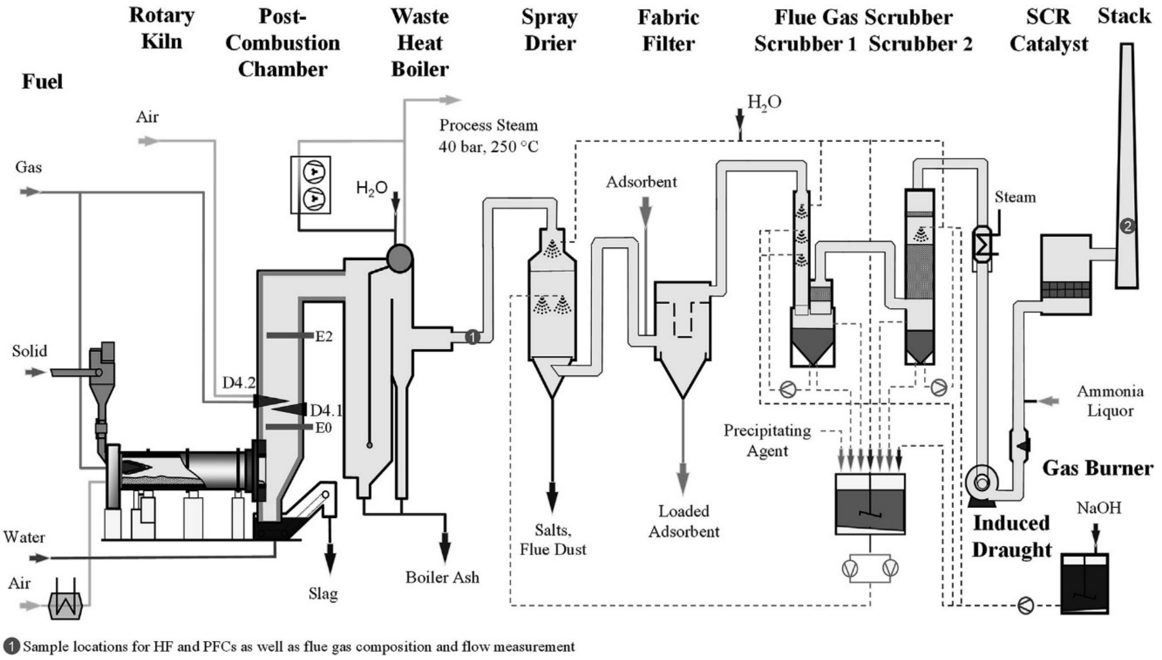


Fig. 19 Schematic of the German acronym for "*Brennkammer mit Dampfkessel*" (BRENDA) pilot combustion facility at Karlsruhe Institute of Technology.[72] (Reproduced with permission from Elsevier).

This study also attempted 7 of 26 to validate that PTFE almost entirely transforms fluorine into HF and a number of trace PFAS species in concentration ranging from 0.3 to 24 μg/Nm^3 using incineration under MSWI conditions.[72] To reduce the probability of false results by means of tandem liquid chromatography-mass spectrometry (LC-MS/MS) detection methods, the process was scaled up to pilot plant incineration levels, meaning the solid combustion material input was orders of magnitudes higher than in lab-based simulations. To characterise PFAS concentrations, flue gas samples were collected to test the compounds of interest after they cooled from ca. 850 to 1000 °C to below 300 °C, allowing for potential condensation reactions to occur. Using TGA, PTFE decomposition started from ca. 500 °C and was completed at about 650 °C. While the detection limit varied between 0.3 and 24.0 μg/Nm^3

depending on the compound, only 11 out of 31 compounds could be detected as the other 20 derivatives were below the detection limit. By using paired t-testing for significance for these 11 compounds, their results showed no statistically significant evidence that the studied PFAS was noted during the PTFE incineration. Due to these findings, these authors concluded that municipal incineration is an acceptable form of waste treatment and that external environmental contamination, not PTFE incineration, was likely the reason that the 11 PFAS samples were detected[72] and that, within procedural quantitation limits, no statistically significant evidence was found that the studied PFAS were generated during the incineration of PTFE. Therefore, MSWI of PTFE using best available technologies is not a relevant source of PFAS and should be regarded as an acceptable form of waste treatment.

Moreover, Tsang et al. determined the unimolecular reaction rates to highlight that CF_4 molecules require 1440 °C for a little bit more than 1 s to achieve 99.99% destruction.[144] Therefore, CF_4 molecules represent a reference for the destruction removal efficiency testing on the required temperatures, times, and turbulence during incineration. Despite the ease of removing or oxidizing the polar functional groups such as decarboxylation, the resulting products of incomplete combustion (PIC) are not well understood.[145]

A technique to better understand the PIC products of PFAS combustion was utilised during thermal treatment by direct- and indirect-fired thermal oxidation mitigation through a by-passing flame and packed bed reactor with $Ca(OH)_2$ to yield CaF_2.[142] This approach provided a way to manage the HF, CO and CO_2 generated during decomposition in an elevated pH media to investigate and characterise the reaction compounds.

In conclusion, many surveys have been published on the incineration of FPs under normal, foreseeable MSWI conditions targeting specific analyses. Presently, most legislation addresses the HF release as the only critical parameter. Limit values are for stack emissions. Future work should investigate incineration under a range of relevant conditions to more comprehensively determine the released substances and their amounts. Such an incineration study is underway (e.g. from various companies including W.L. Gore Company[146]). In addition, the practice of the open burning of FPs, or for that matter of any polymer, is unacceptable and unsafe. Responsible incineration of FPs, adhering to regulatory guidelines, at the end of their life cycle is appropriate.

4.5. Smoldering

In terms of soil treatment, the Strategic Environmental Research and Development Program (SERDP)—the DoD's Environmental Science and Technology program—looked at the use of a surrogate fuel that can support smoldering and achieve temperatures above 900 °C to remediate PFAS in contaminated soils.[69] While PFAS is commonly removed from water by sorption onto carbon or other sorbents or many other techniques recently well summarised by Interstate Technology and Regulatory Council (ITRC),[147] it is a challenge for soil contamination. The smoldering of other contaminants has been shown to exceed temperatures above 900 °C, which is high enough to treat PFAS waste. However, PFAS cannot support smoldering Major[69] found that granular activated carbon (GAC) could behave efficiently as a fuel and smolder at a required temperature higher than 900 °C, thus enabling *ex situ* and *in situ* treatment of PFAS contaminated materials. Indeed, this study can be improved by conducting more experiments to determine how much fuel is needed for successful smoldering.

4.6. Mineralisation of FPs

In order to avoid the possible formation of oligomers that would bring severe toxic and persistency issues, the total decomposition of FPs trying to minimize greenhouse gases release would be to enable a totally degradation. One possibility consists in the mineralization that yields to fluoride anions. Though the mineralisation of low molar mass-PFASs has been reported,[148] to the best of our knowledge, the only strategy involving that of FPs has been well-established at the Kanagawa University. Hori's team is currently studying the mineralisation process of various FPs by subcritical water[149] (i.e., superheated water) as a high-pressure liquid water, the temperature ranging between 100 ºC and its critical temperature, 374 °C (while supercritical (sc) water is defined as water at temperatures and pressures higher than the critical point: 374 ºC and 22.1 MPa).[149-155] Since, in these conditions, the water displays high diffusivity, low viscosity and ability to hydrolyze many organic compounds including biomass, reactions using subcritical or sc water are considered environmentally benign in chemical engineering with the aim of developing a technique for the recycling of fluorine element.

In 2014, Hori et al.[150] described that PVDF could mineralize (i.e. decomposed into F^- and CO_2) completely in sc water at 380 ºC in the presence of a ca. 5.8-fold molar excess of O_2 relative to the fluorine or carbon atom content in PVDF. Furthermore, PVDF also led to complete mineralisation in subcritical water at 300 ºC in presence of H_2O_2, the amount of which was 31-fold molar excess relative to fluorine and carbon contents in PVDF, respectively.[151]

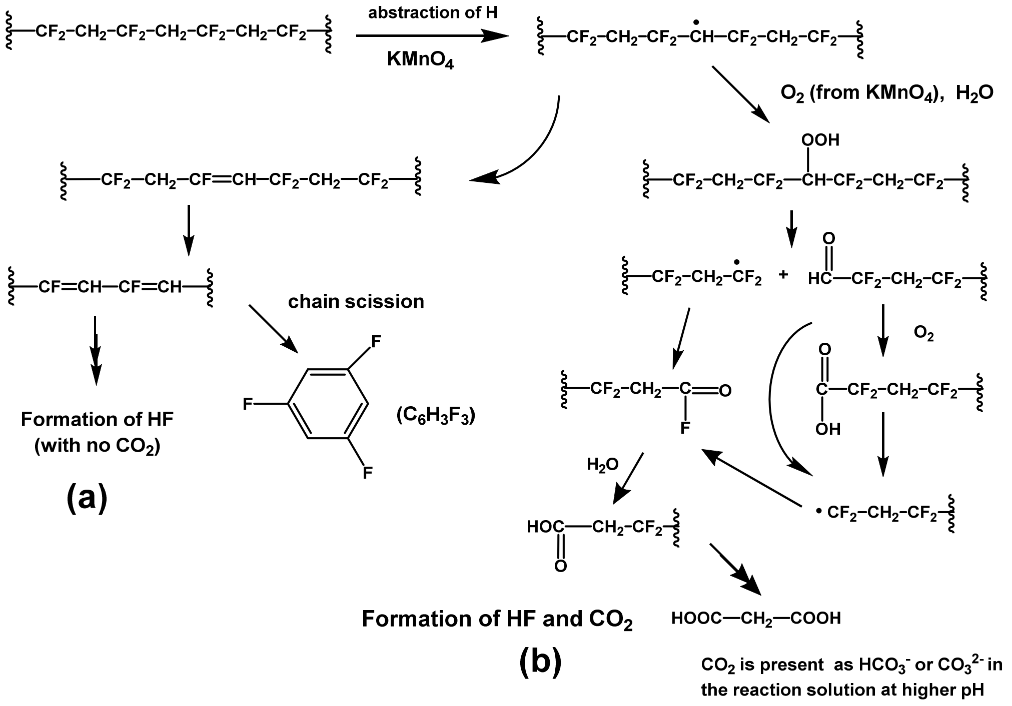
More recently, a stronger treatment in basic medium enabled to favor this mineralisation.[155] For saving energy consumption, lowering temperature that enables complete mineralisation was achieved by the same team, from a similar technology from poly(VDF-*co*-HFP) and poly(VDF-*co*-PMVE) copolymers treated in subcritical water by addition of $KMnO_4$.[153] As known, $KMnO_4$ is a safe oxidizing agent, used at drinking water treatment plants to remove iron component and to control the formation of trihalomethanes and other disinfection byproducts.

Table 7 Decomposition of PVDF and VDF copolymers in subcritical water[153] (Reproduced with permission from American Chemical Society)

Entry	Polymer	Initial [$KMnO_4$] (mM)	*T* (ºC)	*P* (MPa)	F^- (μmol) [yield (%)]	CO_2 (μmol) [yield (%)]	Malonic acid (μmol)	Other minor products (μmol)	TOC (μmol) [ratio (%)]
1	PVDF	0	250	4.5	1.52 [0]	2.1 [0]	0.14	n.d.	3.7 [0]
2	PVDF	158	250	4.6	877 ± 20 [91 ± 2]	354 ± 36 [38 ± 4]	0.42	n.d.	39.3 ± 4.4 [4 ± 1]
3	poly(VDF-*co*-HFP)	0	200	2.0	0.21 [0]	4.8 [1]	0.18	CHF_3 (0.04)	83.3 [9]
4	poly(VDF-*co*-HFP)	158	200	2.1	420 [45]	1.3 [0]	0.39	CHF_3 (0.02)	29.1 [3]
5	poly(VDF-*co*-HFP)	158	250	4.2	898 [96]	213 [24]	0.69	CHF_3 (1.08) $C_6H_3F_3$ (0.03)	50.8 [6]
6	poly(VDF-*co*-PMVE)	0	300	9.0	21.7 [2]	8.6 [1]	0.68	n.d.	n.d.
7	poly(VDF-*co*-PMVE)	158	250	4.1	599 [59]	0.83 [0]	0.71	n.d.	49.1 [7]
8	poly(VDF-*co*-PMVE)	158	300	9.0	1.00×10^3 [99]	299 [43]	1.04	n.d.	16.7 [2]

This led to a *quasi*-complete mineralisation of PVDF performed at 250 ºC as well as for poly(VDF-*co*-HFP) and poly(VDF-*co*-CTFE) copolymers.[153] Table 7 summarizes the features of the mineralisation of such copolymers while Scheme 12 supplies a suggested mechanism. In these reactions, MnO_4^- was chemically modified into MnO_2. Compared to the above method (combination of H_2O_2 and subcritical water), the reaction temperature that allows complete mineralisation was reduced by 50 ºC. Furthermore, these authors examined the CaF_2 formation[153-155] from the reaction solutions to close the loop on the fluorine element, since CaF_2 is the source for all fluorinated compounds.

This strategy was further extended to the mineralisation of various copolymers such as ETFE (efficiently mineralised in sc water at 380 °C in the presence of excess amount of O_2[150] or a lower temperature in presence of H_2O_2),[151]VDF-containing copolymers,[154] poly(VDF-*ter*-HFP-*ter*-TFE) fluoroelastomer[152] as well as perfluorosulfonic acid (PFSA) membranes.[149] (usually involved in ion-exchange polymer membranes, PEMFC, chloro-alkali process to produce chlorine and sodium hydroxide from brine, desalination for drinkable waters, etc).
In addition, several authors have reported that the degradation of PFSA membranes generate analogues of perfluoroalkanoic acids[156] and perfluoroalkane sulfonic acids.[157]

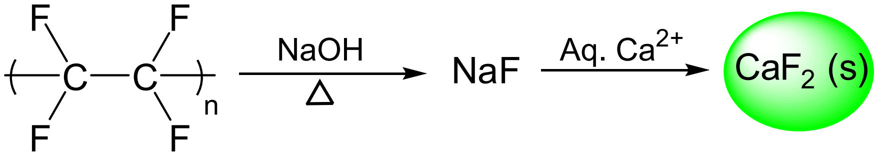


Scheme 12: Proposed reaction scheme for PVDF decomposition in subcritical water in the presence of $KMnO_4$[153] (reproduced with permission from American Chemical Society)

Though these surveys were academic, huger pilot plant reactors (Fig. 20) to treat plastics and other items are also available.

Fig. 20 Industrial supercritical water reactor for organic solvent treatment. This flow reactor can treat 1 metric tonnes waste per day. (The photograph was kindly provided by Organo Corporation (Tokyo). Permission for use was obtained from the company).

More recently, Yanagihara and Katoha[158] used a molten alkaline metal hydroxide (NaOH was shown to be much more efficient than KOH) to mineralize various FPs. This simple, easy, and environmentally benign strategy based on a two-step process enabled the chemical recycling of various FPs in an efficient mineralisation. However, that process seems a bit surprising since it is well-known that liquid sodium is able to etch PTFE. In the first step, these polymers were decomposed to soluble alkaline fluorides *via* degradation in such molten hydroxides at elevated temperatures (500 °C) and atmospheric pressure. In the latter step, CaF_2, which is an essential mineral for all the organofluorine chemistry, was obtained following treatment of the former aqueous solution with $CaCl_2$. PTFE, was mineralised from that strategy, as well as PVDF, PCTFE, and poly(VDF-*co*-HFP) copolymer. When PTFE was heated with a large excess of NaOH at 500 °C for 3 h, 73.8% yield of CaF_2 was obtained (Scheme 13) with respect to the initial PTFE amount.



Scheme 13: Proposed procedure for the mineralisation of PTFE by molten NaOH[158] (readapted from Royal Society of Chemistry).

Actually, these temperatures are not far from those enabling the unzipping depolymerisation of PTFE [36,79,109,119] and it can be assumed that for the other FPs, which are less thermostable than PTFE, the degradation should also occur, even without any base. These authors reported that i) no decomposition was noted in presence of molten NaOH below 400 °C while ii) at 600 °C the CaF_2 yields dropped to 46% (from 67% and 74% at 450 and 500 °C, respectively, Fig. 21).

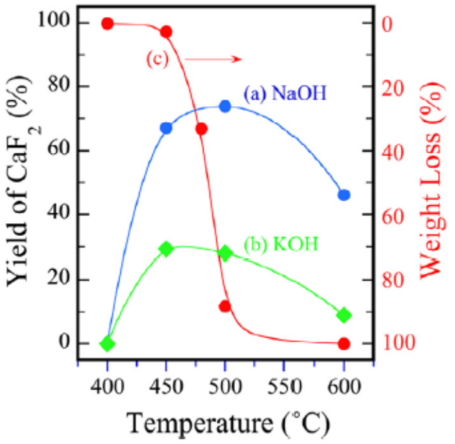


Fig. 21 Temperature dependence of PTFE degradation by molten alkaline hydroxides (curves a and b) and simple isothermal weight loss of PTFE (curve c). In each experiment, approx. 5 mmol of PTFE and an excess of MOH (M = Na, K) were placed in a crucible and reacted for 3 h at each reaction temperature[158] (reproduced with permission from Royal Society of Chemistry).

For the other FPs, under the same experimental conditions, using NaOH, the CaF_2 yields were 83.7% for PVDF, 52.3% for PCTFE, and 84.0% for poly(VDF-*co*-HFP) copolymers (Table 8). When the optimal reaction temperatures were compared, the efficiency of mineralisation of the FPs by molten NaOH decreased according to the following order: PCTFE > poly(VDF-co-HFP) ≈ PVDF ≫ PTFE. Moreover, the optimal temperature for each process was not necessarily proportional to the melting point of the corresponding fluoropolymer. Indeed, it was observed that poly(VDF-*co*-HFP) copolymer, which possessed the lowest melting point of the various tested FPs (i.e., 140–145 °C), decomposed at 400 °C giving the highest CaF_2 yield, despite the fact that the melting point of PCTFE was significantly lower (i.e., 210 °C). A mechanism was suggested based on the interdependence of polymer pyrolysis and nucleophilic attack by O^{2-} generated from the molten NaOH. As well as being effective as a FP mineralisation reaction, this reaction involving molten NaOH also has the potential to treat other general-purpose polymers without any exhaust gas generation.

When the temperature rises to ca. 450 °C, the FP chains exhibit vigorous molecular motion, and chain scission takes place in the PTFE backbone. Subsequently, various small segments are generated *via* an unzipping mechanism.[79] The resulting small segments of the main chain then undergo further scission to form oligomers and/or low molecular compounds. The obtained small molecules (i.e., oligomers and monomers) then react with O^{2-}, which attacks the carbon atom in a nucleophilic manner to generate CO_2 and eliminate F^-.

Table 8 Optimal experimental conditions and yields of CaF_2 for the mineralisation of PTFE and other fluorinated (co)polymers by molten NaOH[158] (Reproduced with permission from The Royal Society of Chemistry)

(Co)polymer	Molar ratio	*T* (°C)	Yield (%)
PTFE	16.3	500	74
PCTFE	18.0	350	52
PVDF	12.4	400	84
Poly(VDF-*co*-HFP)	12.7	400	84

5. Decomposition of FPs by irradiation

FPs can be affected by irradiations.[159-160] Low molar-mass (M_n) PTFE micropowder is added to wax (e.g. for use in automotive equipment, bike chain lubricants[161] and printing machines) and is produced by radiation-initiated degradation. However, PFOA is produced as a by-product in concentrations greater than 25 ppb. Dams and Hintzer[61] reported the degradation of high M_n -FPs by electron beam radiation as a commercial process, even continuously for economic reasons. Then, the resulting material is milled to get the expected particle size.

In addition, combining irradiation and heat treatment in an oxygen-free atmosphere under atmospheric conditions, Oshima et al.[162] evidenced the PFOA-formation and could upscale that manufacturing process for a novel low- M_n PTFE micropowder that contains traces of PFOA (less than 5 ppb). They could extend the PFOA-free PTFE micropowder up to a 11 kg-scale. Figure 22 proposes the presumed PFOA-formation mechanism for PTFE irradiation in an oxygen atmosphere. Irradiation under oxygen-free conditions results in the formation of alkyl radicals by dissociative electron attachment because the fluorine electron acceptor easily accepts electrons and dissociates as F-ions, which is the fastest and most important reaction of PTFE, as previously suggested.[163-164] Main-chain scission, induced by alkyl radicals, occurs via β-scission to produce *Rf*-CF_3, *Rf* -CF = CF_2, and chain-end radicals.

In the case of air exposure immediately after irradiation (see Fig. 22, process A), the trapped alkyl/chain-end radicals were converted into their respective peroxy radicals at a ratio of 10:1,[165] which indicates that the remaining scission-type peroxy radicals react with water in the atmosphere with increasing time, producing around 25 ppb PFOA (*i.e.*, REACH environmental limit[15]).

After irradiation, during long-term storage or heat treatment under oxygen-free conditions (Fig. 22, process B), the chain-end radicals preferentially decay, and the radical yield is reduced to about 60% or less of the initial level. Following exposure to the atmosphere, the scission-type peroxy radicals resulting in the PFOA formation, became a very minor component, and PFOA was formed at levels below the legal limit.

In contrast, when heat treatment is performed in the open atmosphere after irradiation (Fig. 22, process C), the peroxy radicals react with O_2 and water in the atmosphere to provoke thermal oxidative degradation producing scission-type peroxy radicals. As a result, the released PFOA amount exceeds the environmentally regulated limit.[162]

After irradiation, when the sample was exposed to the atmosphere and then heat-treated without O_2 (Fig. 22, process D), both types of peroxy radical were reconverted into alkyl radicals with very small amounts of chain-end radicals, as also reported.[166]

In this case, because the radical yield is 60% or less of the initial value before exposure to air, the scission-type peroxy radicals, which may be related to a PFOA-formation factor, are present as very minor components, and the PFOA amount released is much lower than the REACH limit.

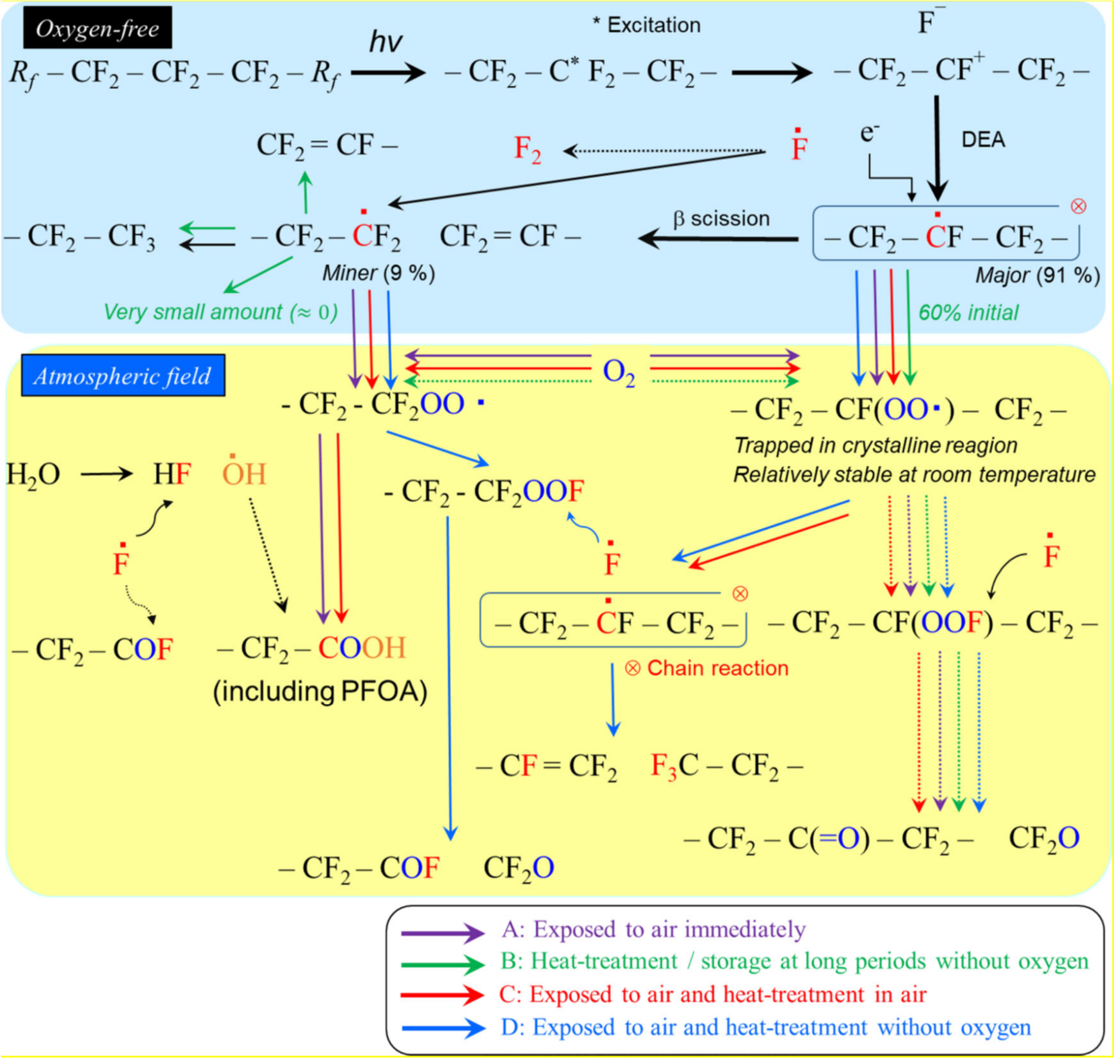


Fig. 22 Reaction mechanism of PTFE irradiated in an oxygen-free atmosphere. Process A: Exposing to air immediately after irradiation. Process B: Heat treatment/storage for long periods in the absence of oxygen after irradiation. Process C: Exposure to air immediately after irradiation and then heat treated in air. Process D: Exposure to air immediately after irradiation and then heat treated without oxygen. Solid line: main reaction, Dotted line: minor reaction (DEA stands for dissociative electron attachment)[162] (reproduced with permission from Nature Group Publisher)

Table 9: Emitted various PFCAs after γ-irradiation 11 kg of PTFE with a 150 kGy-dose in air (reproduced with permission from Nature Group Publishing) [162]

PFCAs*	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
Concentration (ppb)	196	201	480	277	590	265	165	97	71	14	<5

*Acronyms are defined in the list at the end of the review

The authors could extend their technology from Laboratory scale to a small pilot plant scale. Actually, 11 kg of PTFE were placed in tri-layer polymer bag comprising PET/aluminum/polyethylene. The sample was then irradiated at a 400-kGy dose of γ-rays with an oxygen concentration of 100 ppm (Table 9), with subsequent heat treatment carried out at 423 K for 20 h in the same atmosphere. PFOA content in the obtained PTFE micropowder was lower than 5 ppb (Table 10), similar to that noted from the lab-scale experimental result mentioned above. Furthermore, even after a year stored in a closed container under ambient conditions, PFOA content in this sample was still below 5 ppb. [162]

Table 10: Effect of re-heating of PTFE micropowder in air that cleared REACH regulation on PFOA value. The powder obtained by vacuum irradiation of 400 kGy and radical treatment (reproduced with permission from Nature Group Publishing).[162]

Radical decay treatment	Re-heat treatment (K)	Amount of PFOA (ppb)
297 K, 2 days	-	5
	423 K, 18 h	37
423 K, 18 h	-	< 5
	423 K, 18 h	< 5

Specific irradiation tests were also achieved on Teflon® AF, an amorphous copolymer, and McKeen reported[167] the effect of the dose rate onto its tensile strength, showing some progressive failure from 20 to 100 kGy (Fig. 23).

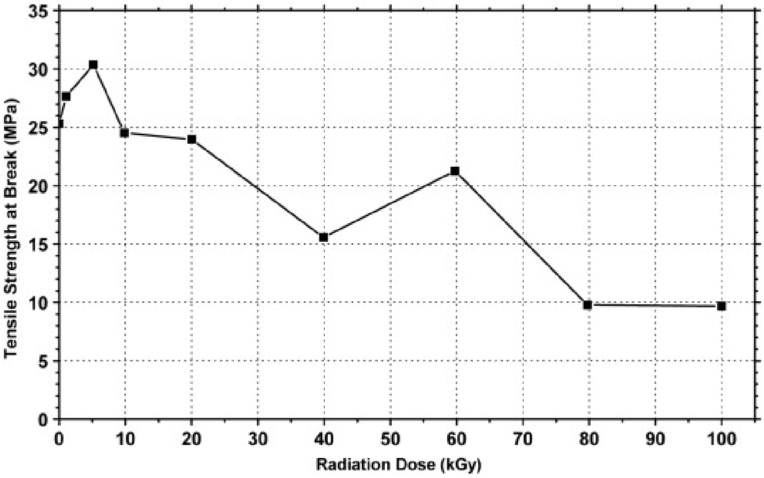


Fig. 23 Tensile strength at break *versus* radiation dose of DuPont PTFE (Teflon®AF1600) irradiated films[167] (reproduced from permission from Elsevier).

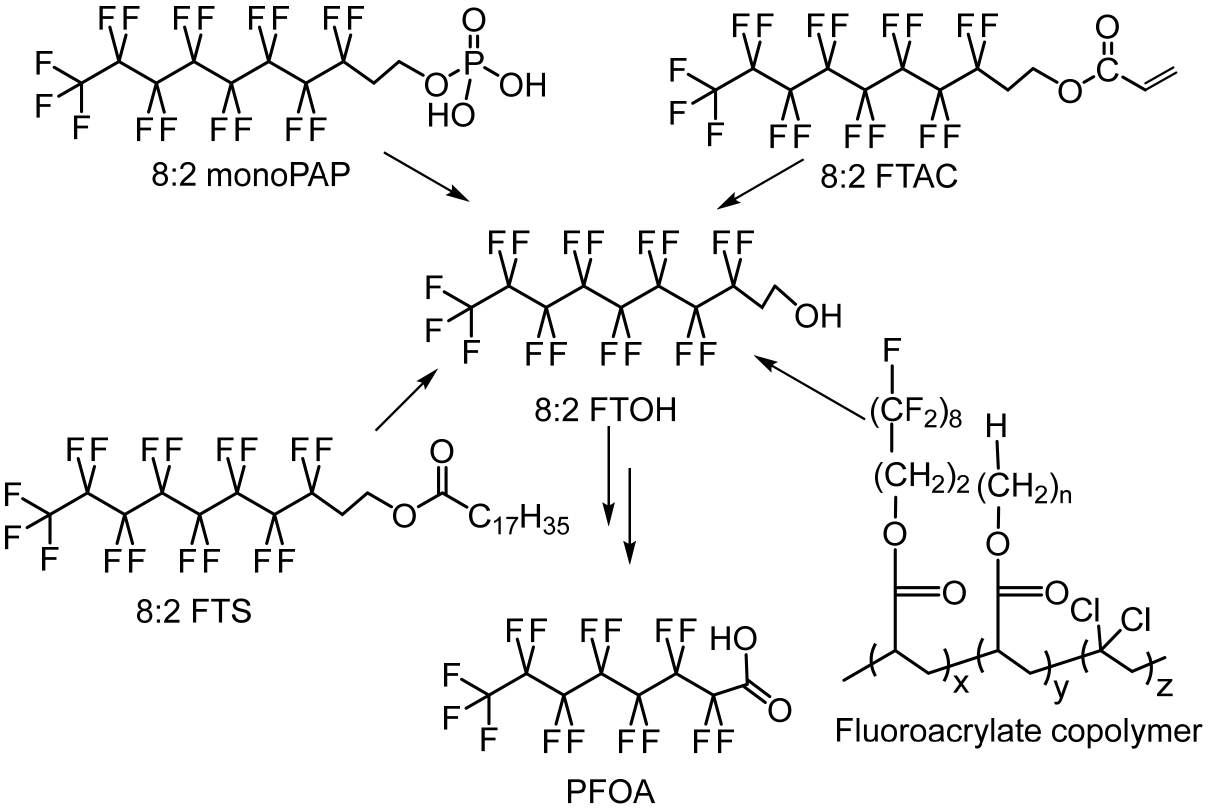
On the other hand, Van der Walt and Bruinsma[106] reported the depolymerisation of waste PTFE inside a reactor heated by a radiofrequency induction generator. PTFE was fed vertically downward from the hopper, with a screw feeder into the vessel where the depolymerisation happened. Such a continuous process enabled to produce TFE, hexafluoroethane, HFP, and OFCB from PTFE waste. The reactor was able to operate at various temperatures (ranging from 600 to 900 °C) as well as various pressure (5-80 kPa). Under certain conditions, high TFE amount (>94%) was obtained concomitantly to a few by-product amounts.

Stefani et al.[168] compared the photo-oxidation degradation (which further favored the amount of contaminants accumulated) of greenhouse films made of ETFE, poly(ethylene-*co*-vinyl acetate) copolymer, EVA, and low density polyethylene (LDPE) and their waste generation at the end of their service life (Table 11). According to the class of duration of the plastic films, waste quantities of plastic covering sheets for 1 ha of multi-span greenhouse were tested in a climatic situation corresponding to Southern Italy (period of time considered: 15 years). The chemical contaminations (assessed from titration of sulfur, iron and chlorine elements) of both films were reported after an exposure in the experimental field for 60 days. The results suggested that the use of ETFE copolymer covering sheets significantly reduced the waste of plastic materials in a 5 to 10 times range, with the further advantage of a significant recovery value for the used sheets.

Table 11: Waste quantity of films for 1 ha of multi-span greenhouse from the class of duration of the plastic films in a climatic simulation corresponding to Southern Italy for a simulated time of 15 years)[168]

Film type	Cumulated film surface area (m^2/ha)	Cumulated waste quantity range (kg/ha)
LDPE or EVA, B Class	195000	22669-27203
LDPE or EVA, C Class	130000	18135-21158
LDPE or EVA, D Class	91000-104000	14810-19344
LDPE or EVA, E Class	65000	12090-13601
ETFE	13000	2210-2431

As a matter of fact, microbial degradation of FPs has scarcely been reported. To the best of our knowledge, no study has been achieved on FPs bearing fluorine atoms in the backbone (probably to the high chemical and ageing stability). One example concerns the case of poly(fluoroacrylate)s studied by Liu and Avendaño.[169] These polymers possessing ω-perfluorinated dangling moieties have led to 8:2 fluorotelomer derivatives (Scheme 14) while several studies have reported the decomposition and releasing of the fluorinated side chain under various conditions.[18,170-173]



Scheme 14: Illustration of microbial degradation of poly(fluoroacrylate)s that generate 8:2 fluorotelomer derivatives.[169] (reproduced with permission from Elsevier).

Moreover, FPs containing oxidizers have also been used in pyrotechnic compositions though fluorinated oxidizers, less explored for metalised propellants and explosives despite a potential advantage of substantial heat release combined with gaseous combustion products. Valluri et al.[174] reviewed various families of fluorinated oxidizers involved in energetic formulations or of potential interest for such systems, including gases, polymers, and inorganic compounds, especially energetic formulations involving metals and FPs (Fig. 24). Characteristic morphologies and reaction sequences were observed in different metal-fluorinated oxidizer composites. Procedures probing ignition and combustion of metal-fluorinated oxidizer composites in laboratory conditions have been also reviewed, underlining flash heating, impact, and shock ignition. Finally, several practical tests for energetic formulations have been described and the authors suggested reaction mechanisms expected to govern ignition and combustion in various metal-fluorinated oxidizer composites.

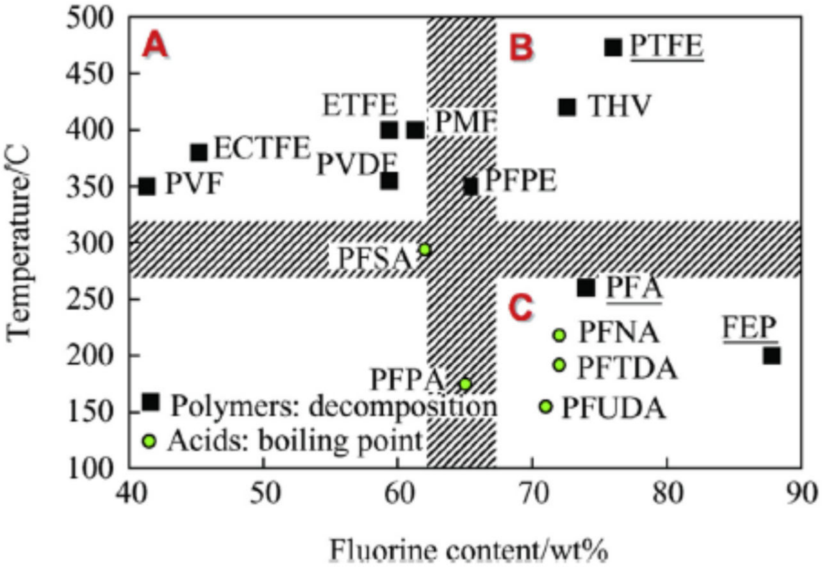


Fig. 24 Fluorinated polymers and acids based on their fluorine content and decomposition temperatures or boiling points[174] (PVF, PFNA, PFSA, PFPA, PFPE, PFTDA and PFUDA stand for poly(vinyl fluoride), perfluorononanoic acid, perfluoro sebacic acid, perfluoropentanoic acid, perfluoropolyether, perfluorotetradecanoic acid and perfluoroundecanoic acid, respectively. (reproduced with permission from Elsevier).

6. End-of-life

Other methods used to destroy various PFAS waste such as end-of-life FPs in various materials include *in situ* chemical oxidation,[175] granular activated carbon,[69] thermal,[176] and photochemical processes, well-reviewed by the Interstate Technology and Regulatory Council.[147] While these methods can be used to treat fluorinated waste, smoldering is a self-sustaining and is, therefore, more energy efficient compared to incineration. Pyrolysis is similar to incineration (i.e. a high-temperature process used for thermal decomposition), except it occurs in an inert atmosphere. Critical to the effectiveness of this process is achieving a temperature greater than 900 °C. The goal of these methods pertaining to PFAS waste is to ensure that these FPs are exposed to a sufficient and sustainable temperature that ensures successful destruction of toxic PFAS compounds, as the FPs thermally degrade while still being efficient and safe. Several studies have tested the efficacy of these methods to determine if they reach temperatures high enough for a sufficient duration to allow for complete degradation.[72-73] Alternative methods to incineration such as mineralisation (see section 4.6) 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.

At end-of-life, when a FP has fulfilled its intended use and will be disposed of, the fate of FPs should be further studied. 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,[177] the downstream, end-of-life process of incineration deserves more investigations. For instance, as mentioned above, at temperatures above 450 °C, PTFE begins to degrade, generating hazardous substances such as HF.

In order to improve the PTFE properties, it is often compounded with glass fibers, carbon fibers, coal/soot, bronze, steel, molybdenum sulphide or polymers like polyimides or poly(phenylene sulphide).[79,178] As also observed in above processes (section 3.2), the primary decomposition products are TFE and difluorocarbenes radicals. Further products are formed by secondary reactions depending on temperature, reaction pressure and reaction atmosphere. The typical main products are TFE, HFP, OFCB and other fluorocarbons. Most of these substances are non-toxic but highly toxic substances like perfluoroisobutylene (PFIB) or fluorophosgene are also formed under some reaction conditions.

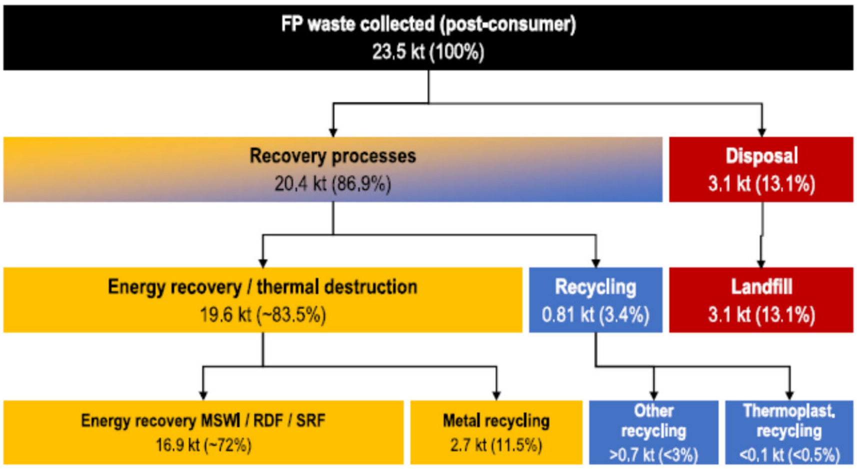


Fig. 25 Fate of collected FP waste and tonnages (percentages) involved in recycling, recovery, reuse and landfill.[9]

The global situation is represented in Fig. 25,[9] showing that, in overall, ca. 23.5 kt of FP waste were collected in 2020 (< 0.01% of the total waste collection). In comparison, about 29,450 kt of plastics were collected in 2020 (<5% of the total waste collection excluding mineral fractions). Moreover, ca. 84% (20.4 kt) of the total FP waste collected 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 proportion was exported for recycling (e.g. to Asian countries).[48]

7. FPs fulfill the PLC Criteria

The criteria of polymers of low concern (PLC) represent the combined experience and knowledge of global regulatory authorities on factors demonstrated to be predictive of health and environmental hazards of polymers.[179-181]Actually, to be eligible as a PLC, a polymer must not have any known hazard classification while basic consensus exist according to the followings criteria:

i) high number average molar mass (M_n) and oligomer content are the most commonly used criteria for PLC assessment. The EU assessment report[180] states that the "*most potential health concern polymers have a number average molecular weight, M_n, < 1000 Da and oligomer content >1%.*" The higher the oligomeric content, the more likely a polymer is to be health or eco-toxicological.[179] In fact, when comparing the potential health concern of polymers with varying the percentage of oligomer, "*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*".[179]

ii) Reactive functional groups (RFG) requirements. RFG categories – low, moderate and high concern. Indeed, RFGs in the moderate concern category have evidence of reactivity in biological and/or aquatic media but the effects are not severe enough to place the functional group in the high concern category. If there is no, insufficient or contradictory information on a RFG it defaults to the high concern category. This category applies until sufficient information becomes available to move it to another class;

iii) solubility in solvents and in water lower than 10 mg/L);

iv) other criteria such as a low cationic density, contain approved elements only; not contain any difluoromethylene or trifluoromethyl groups; be stable under the conditions in which it is used (The primary concern for such fluorinated polymers is degradation in the environment to release potentially persistent, bioaccumulative or toxic degradation products; not be a high molar mass water absorbing polymer (≥10,000 g/mol); not have any known hazard classification.

FPs satisfy the PLC criteria related to RFGs and RFG ratio to M_n.[180-182] PTFE most typically has a terminal $-CF_3$ group[15] that is not an RFG. When this is not the case, the most common terminal group is –COOH, which M_n is an important predictor of biological effect because very large molecules (>1000–10 000 Da) are too big to penetrate cellular membranes[183-185] and thus cannot react with "target organs," such as the reproductive system, and are not bioavailable. Therefore, as the M_n of a polymer increases, a reduced incidence of potential health concern effects might be expected. [179]

In contrast, a polymer does not suit the PLC criteria if it degrades significantly, decomposes or depolymerises during use. This means that it is considerably, meaningfully or to a significantly large extent changed into simpler, lower molar mass-chemicals as the result of, but not limited to: oxidation, hydrolysis, heat, sunlight, attack by solvents or microbial action. Actually, FPs are resistant to such reactions/degradations. [13]

Based on such relevant properties and above PLC criteria, Henry et al.[15] provided some evidences on four main FPs (PTFE, FEP, PFA and ETFE) justifying that these FPs fulfil the 13 criteria of OECD definition of PLC.[15,186] This was highlighted by GC/MS and LC/MS analyses and these authors characterised the extractible fractions from PTFE (and of the three other copolymers) and found only 2 ppm leachable (Table 11). Actually, possible M_n leachables are critically important to the potential for a polymer to affect health and the environment, given that they may migrate out of the polymer and the cross cell membranes to potentially react with biomolecules.

Table 12 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) [15]

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 molecular weight 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[179] 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.[179] According to U.S. EPA's Safer Choice criteria (SCP, 2015), tetrafluoroethylene is a residual of concern, which is not allowed to be present in Safer Choice recognised products at 0.01% or higher. There is no specific limit on residual monomer in the PLC criteria.[179]

#Isopar K, an unavoidable ambient air contaminant adsorbed to the PTFE fine powder, was detected at ≤ 2 ppm.

In a report to the EU,[177] the polymer policies for 10 countries around the world, including the EU REACH handling of polymers, were reviewed. It 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*." But, in the case of high molar mass FPs, such characteristics are not observed (Table 12).

For the PFAS and PFCA as stated by USEPA, the 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*)."[187] 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*."[187] Thus, in a USEPA's review, the presence of –CF_3 group is relevant since it is a structural alert to consider potential degradation products. The USEPA[134] may make a determination whether the potential degradation of the polymer taken into account displays an unreasonable risk to health and the environment under Toxic Substances Control Act (TSCA). As shown in Table 12, these FPs are not subject to degradation.

With respect to applicability, among all FPs and as an example, PTFE is not a substance currently registered under REACH regulations which usually gives the definition for 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*".[188] However, because PTFE, as all FPs, is an identifiable organic substance, the proposed Universal Basic Asset (UBA) framework for assessment using the proposed PMT criteria (persistent, mobile and toxic) would be applicable. Further, PTFE is highly stable in the environment and is resistant to thermal degradation. Being stable for years at temperatures up to 260 °C; [57,130] it is stable to hydrolysis, oxidation, and light, as well as to anaerobic and aerobic degradations.[189] Therefore, PTFE would fulfill the UBA's proposed persistence criterion. 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, the water solubility of PTFE would be classified as insoluble ($1\text{-}10^{-5}$ mg/L or 0.01mg/L) to very slightly soluble (10^{-4} mg/L or 0.1 mg/L).[190] The mobility of PFTE is 1,000 to 10,000 lower than UBA's proposed mobility criterion. Therefore, PTFE does not fulfill UBA's proposed mobility criterion and would not be classified as a PM or PMT substance.

Another advantage of PTFE deals with its non-toxicity. Actually, the average Mn of PTFE is too high (several million) for the polymer to cross a cell membrane, which means it is not bioavailable or toxic. PTFE has been tested extensively in the USA and European Union to assess commercial applications for food contact, global medical device regulations and surgery.[24-28]

FPs contain none or negligible monomer(s) (which are gaseous), oligomer(s), and leachable contents and no reactive functional groups with high toxicity. These comparisons of PLC and various regulatory assessment criteria demonstrate that, in the realm of PFAS, high molar mass-FPs as PTFE exhibit vastly different properties than do other PFAS. Therefore, they are truly a separate class of materials that must be determined on their own merits.

More recently, the American Chemical Council led the Fluoropolymer industry Group (Fluoropolymergroup) to investigate a similar study on 14 additional fluorinated (co)polymers.[182] 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.

Following PLC criteria, circular economy of FPs has not quite been studied except one peculiar report from Wahlström et al.[4] including several flows (Fig. 26) ranging from the manufacture of FPs to their use and their recycling (case of PTFE that depolymerises back into TFE as explained above).

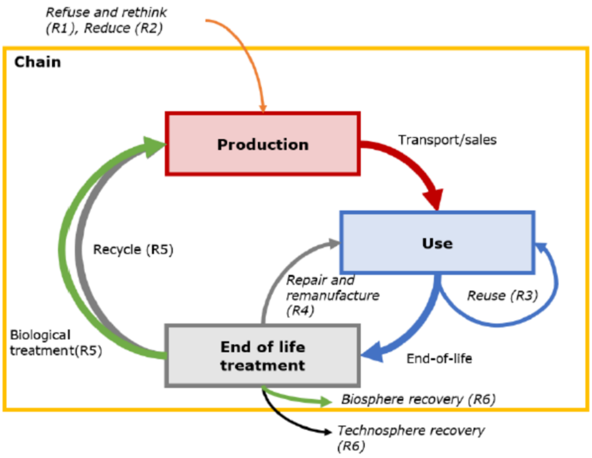
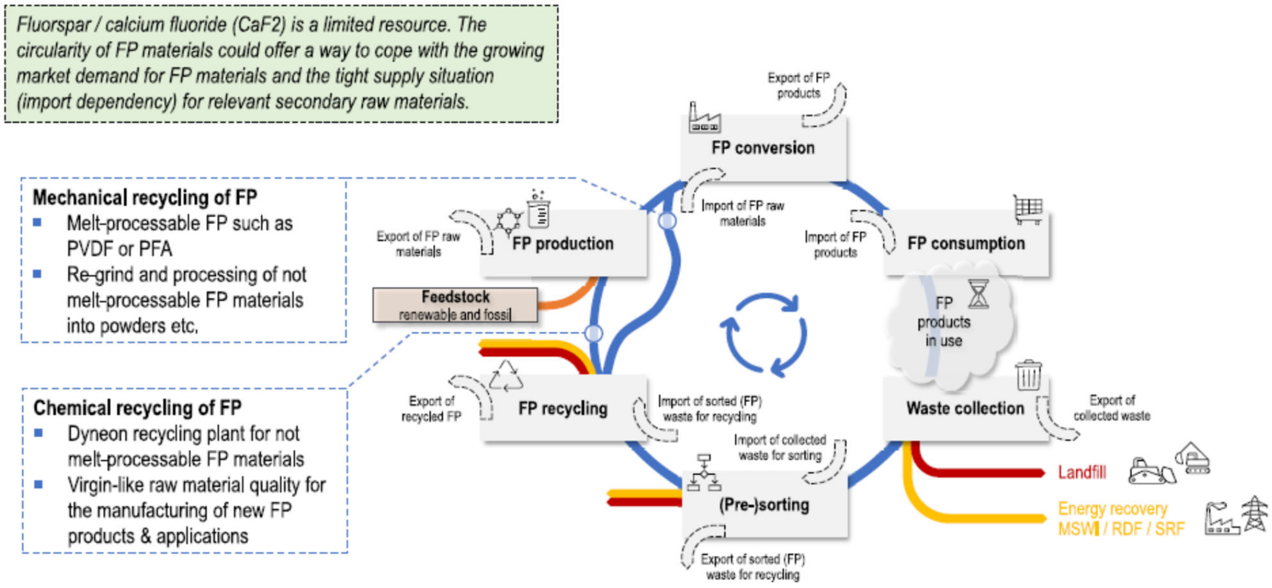


Fig. 26 Schematic view of possible flows of materials in a circular economy[4] (reproduced with permission from the European Topic Centre Waste and Materials in a Green Economy).

The Conversio report[9] lists the treatment of FP waste by industry segments (automotive, aerospace, and chemical industries, electronics and semiconductors[191]) in the EU in 2020 regarding collected waste, energy recovery, landfill and recycling as well as co-treatment of FP and associated waste streams (Fig. 27).


Fluorspar / calcium fluoride (CaF2) is a limited resource. The circularity of FP materials could offer a way to cope with the growing market demand for FP materials and the tight supply situation (import dependency) for relevant secondary raw materials.

Mechanical recycling of FP
- Melt-processable FP such as PVDF or PFA
- Re-grind and processing of not melt-processable FP materials into powders etc.

Chemical recycling of FP
- Dyneon recycling plant for not melt-processable FP materials
- Virgin-like raw material quality for the manufacturing of new FP products & applications

Fig. 27 Circular economy situation of FPs: lifecycle of FPs from feedstocks extraction to end of life[9]

Lohmann et al.[30] identified and reported issues for environmental and human health resulting from possible emissions during the FP the life cycle (i.e. production, processing and disposal). These authors reviewed the link between some types of FPs and PFAS emissions but, in the last

10-15 years, many efforts have been developed by at least five manufacturers of FPs by modifying their production, using non-fluorinated surfactants and reducing the gas and liquid emissions significantly.[192-199]

8. Concluding remarks

FPs are bioninert, non-bioaccumulative, non-mobile, non-toxic niche technical polymers endowed with outstanding properties. Because of their exceptional properties (including their high performance in aggressive media), stability to hydrolysis, UV, aging, oxidation and biodegradation, and high molar masses, they fulfil the PLC criteria and are irreplaceable. So far, no alternative has been found.[200] For examples, 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. In addition, since the Challenger disaster in 1986, all shuttle packing and gaskets have been made of fluoroelastomers. Moreover, FPs involved in electronics[191] also are able to resist to aggressive media where all over materials fail. Actually, most of the FPs are safe in use and are currently involved many High-Tech applications used in extreme conditions. More recently, various manufacturers have announced stringent modifications in both using non-fluorinated polymerization aids and modifications to drastically reduce the gaseous and liquid PFAS emissions.[197] The present review has brought together recycling (including PTFE micropowders and FP recycled materials), reuse, closed loop systems, decomposition and end of life of FP.

Many studies have shown, on a small and pilot scale, the ability to convert FPs back to their monomers (*via* CRM). This approach to a closed loop economy for FPs deserves additional work and discussion, as does the recycling and reuse of FPs. Considering their annual plastic production of more than 460 million tons,[1] only 9 % has been recycled[46,48] while that percentage fell into 3.4% for FPs (yearly production of 320,300 tons in 2018).[9,199] 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[52], at Karlsruhe Institute of Technology[72] or by Arkema company[53,54]), 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. Moreover, quite a slow decomposition of PTFE occurs above the application temperature of 260 °C for months. However, to favor a significant degradation to occur, temperatures above 400 °C are needed. Thus, incineration is one of only a few technologies that can potentially destroy FPs (e.g., PTFE) and from 850 °C, a total decomposition is observed without generating any PFAS. In December 2020, USEPA[134] released a draft interim guidance on the degradation and disposal of PFAS. 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. In addition, on melt processible polymers, reactive extrusion has been reported to be a versatile technology to recycle such materials[201] and could be adapted to FPs.

To overcome possible issues of incineration, recent alternative processes regarding the thermal treatment (mineralisation to release fluoride anions, precursor of CaF_2 as the starting point of the Fluorine Chemistry) of FPs either under subcritical water or with molten sodium are quite relevant to close the loop and deserves to be scaled up.

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, they have quite tiny oligomer content or organic or inorganic leachables. Hence, the data presented demonstrate that the FP class of PFAS is well-defined, safe and an essential subset of PFAS. Thus, it should be considered as distinctly different from other classes of PFAS.[198] Though the dossier is still under evaluation,[202] the restriction of FPs under REACH regulations may hamper the EU strategic sustainability ambition.[203]

Nevertheless, data show that FPs (especially PTFE) has been extensively tested to satisfy US, Japanese[48] 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, and also are exempted from REACH legislation. FPs meet the persistence criterion only, but not the bioaccumulative, toxic, or mobile criteria.

Actually, thanks to the inertness, thermal, chemical, photochemical, hydrolytic, and biological stability of FPs (especially PTFE), FPs satisfy the requirement for fulfilling regulatory assessment criteria to be considered as PLCs. Many studies have been conducted to investigate the PLC criteria of FPs of interest to most FPs manufacturers and, so far, 96 % of FPs fulfill the 13 criteria.

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.

The following reflections are supplied on how these features may be explored in future work. Research is needed, to determine if emissions from thermal disposal of FPs, at temperatures consistent with OB, OD, or incineration contain PFAS. Furthermore, methods of the thermal degradation and waste treatment of polymers containing PFAS can be greatly expanded on to enable environmentally safe and conscientious processes. 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 process of incineration deserves future actions.

FP manufacture includes fluoromonomers and a wide range of initiators, catalysts, salts, activators, etc… including polymer production aids, some of which are fluorinated surfactants. Perfluorocarboxylic acids such as PFOA and perfluorononanoic acid (PFNA) were used as polymerisation aids in the manufacture of FPs. Presently, they are no longer used by the leading global FP manufacturers, who have been using non-fluorinated alternative substances such as functional oligo(ethylene oxide), alkyltrimethyl-ammonium bromide, SDS, cetyltrimethylammonium bromide, or biosourced derivatives for a couple of years. [200] The toxicological and environmental properties (e.g., persistence, bioavailability, and mobility) of these alternatives merit further studies.

Though the demand of FPs is still increasing,[204] future work should deal with FP manufacture highlighting the safety, health, and environmental management practices, under applicable regulations. It also should assess substances used in FP manufactures, their human health and environmental attributes.

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10. List of Acronyms and Abbreviations

APFO	ammonium perfluorooctanoate
CDFA	chlorodifluoroacetic acid
CPFP	chloropentafluoropropene

CRM	chemical recycling to monomers
CTA	chain transfer agent
CTFE	chlorotrifluoroethylene
DCFB	dichloroperfluorobutanoic acid
DCFP	dichloroperfluoropentanoic acid
DCHFCB	1,2-dichlorohexafluorocyclobutane
DCTFP	1,3-dichlorotetrafluoropropene
DFA	difluoroacetic acid
DMA	dimethyl acetamide
DPn	degree of polymerisation
DSC	differential scanning calorimeter
EB	electron beam
ECTFE	poly(ethylene-alt-chlorotrifluoroethylene) copolymer
FDCA	fluorodichloroacetic acid
FEP	poly(tetrafluoroethylene-*co*-hexafluoropropylene) poly(TFE-*co*-HFP)
FP	fluoropolymer
HFP	hexafluoropropylene
ITRC	Interstate Technology and Regulatory Council
LCA	life cycle assessment
MFA	monofluoroacetic acid
MSWI	municipal solid waste incineration
M_n	average molar mass in number
NMR	nuclear magnetic resonance
OECD	Organisation of Economic Co-operation and Development

OFCB	Octofluorocyclobutane
PCTFE	poly(chlorotrifluoroethylene)
PEG	poly(ethylene glycol)
PEMFC	proton exchange membranes for fuel cells
PFA	poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether) poly(TFE-*co*-PPVE)
PFCA	perfluorocarboxylic acid
PFDA	perfluorodecanoic acid
PFDoDA	perfluorododecanoic acid
PFHpA	perfluoroheptanoic acid
PFHxA	perfluorohexanoic acid
PFIB	perfluoroisobutylene
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFPeA	perfluoropentanoic acid
PFPEs	perfluoropolyethers
PFTeDA	perfluorotetradecanoic acid
PFTrDA	perfluorotridecanoic acid
PFUnDA	perfluoroundecanoic acid
PLC	polymer of low concern
PMT	persistant, mobile and toxic
PMVE	perfluoromethyl vinyl ether
POP	persistent organic pollutants
PPRA	processing and recycling aid
PTFE	poly(tetrafluoroethylene)

PVDF	poly(vinylidene fluoride)
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RT	room temperature
SVHC	Substances of Very High Concern
TCTFE	1,1,2-trichloro-1,2,2-trifluoroethane
1,1,3-TCTFP	1,1,3-trichlorotrifluoropropene
TFE	tetrafluoroethylene
TFA	Trifluoroacetic acid
TPE	thermoplastic elastomers
TSCA	Toxic Substances Control Act
VDF	vinylidene fluoride
VF	vinyl fluoride