

Recycling and the end of life assessment of fluoropolymers: recent developments, challenges and future trends†

 Bruno Améduri *^a and Hisao Hori^b

Herein, we present the state of the art technology on the recycling, reuse, thermal decomposition (by thermolysis, thermal processing, flash pyrolysis, smoldering, open burning, open-air detonation, and incineration), and the life cycle assessment of fluoropolymers (FPs, ranging from poly(tetrafluoroethylene), PTFE, poly(vinylidene fluoride), and PVDF to various fluorinated copolymers based on VDF and TFE). FPs are niche specialty polymers endowed with exceptional properties and have found many applications in high-tech industries. However, compared to other polymers, the reuse of FPs is still not well-established and is in its infancy. Accordingly, their recycling has attracted increasing interest, even reaching the pilot stage. In addition, recently, several studies have been reported on vitrimers, which are regarded as polymers ranking between thermosets and thermoplastics. In this case, although many articles have reported to date on the thermal degradation of these technical polymers, intensive efforts have been devoted to avoiding the release of 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 reports demonstrated the complete decomposition of PTFE, leading to the formation of TFE (and hexafluoropropylene or octafluorocyclobutane to a lesser extent). Incineration is one of only a few technologies that can potentially degrade FPs and completely degrade PTFE and other PFAS from 850 °C. Recent studies on the mineralisation of FPs under subcritical water represent an interesting approach to close the loop of the fluorine chemistry cycle. Because of the high molar masses (several million for PTFE) and thermal, chemical, photochemical, and hydrolytic inertness and biological stability of FPs, it has been clearly evidenced that they satisfy the 13 accepted regulatory assessment criteria to be considered as polymers of low concern.

Received 22nd December 2022

DOI: 10.1039/d2cs00763k

rsc.li/chem-soc-rev

1. Introduction

Nowadays, plastics play an indispensable role in daily life. Population growth and higher incomes have driven an increase in global plastic production, which doubled between 2000 and 2019, reaching 460 million tonnes in 2021,¹ and is predicted to reach 1.12 billion tonnes annually by 2050² and up to 1231 Mt by 2060. This situation is both appealing and worrying considering the immense plastic waste, which is forming the “8th Continent”.² In the period of 2000–2019, the growth of plastics outpaced that of economic growth by almost 40%. Recently, MacLeod *et al.*³ highlighted the global threat induced by plastic

pollution. Their concerns were based on the high environmental persistence of plastics. Among them, and in contrast to commodity polymers, the consumption of fluorinated polymers (FPs) as niche materials was estimated to be 320 300 tonnes in 2018,⁴ representing only 0.1% of all polymers. Their global consumption in 2015 was 270 kt, showing an 18.6% increase over this period. However, the recycling of plastics is challenging^{1,3,5–8} given that only *ca.* 9% of polymers is recycled, while in the case of FPs, recycling accounts for only 3.4%.⁹

Due to the electronegativity and small radius of the fluorine atom, which make the C–F bond short and exceptionally strong, FPs are specialty polymers endowed with outstanding properties. They bring safety and performances where other materials fail, are essential in daily life and involved in many high-tech areas.^{10–14} Because of the growing need for higher performance-materials possessing specific properties for high-tech applications, fluoropolymers have undergone rapid development. Specifically, FPs are used in core and cladding for optical fibers, specific UV- and aging-resistant coatings, wires

^a ICGM, University of Montpellier, CNRS, ENSCM, 34095 Montpellier, France.

 E-mail: bruno.ameduri@enscm.fr
^b Kanagawa University, Faculty of Science, 2946 Tsuchiya, Hiratsuka 259-1293, Japan. E-mail: h-hori@kanagawa-u.ac.jp

 † Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2cs00763k>

1 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 applications
[proton exchange fuel cell membranes, backsheets of photo-
voltaic panels, cathode binders in lithium ion batteries, and
electroactive (piezoelectric) devices], plastic/polymer-bonded
explosives and 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 copolymers
based on tetrafluoroethylene (TFE) and vinylidene fluoride
(VDF) (which can be either thermoplastics or elastomers).¹³
Usually, under the conditions that FPs are used, they are non-
toxic, non-bioaccumulative, non-mobile, insoluble in water,
thermally, chemically and biologically stable, durable, hydro-
lytically stable, and are not degraded by hydrolysis, catalysis or
metabolism. Thus, due to these features, they are not consid-
ered as substances of very high concern (SVHC).

Although FPs are also regarded as per- and poly-fluoroalkyl
substances (PFAS),^{15,16} they represent a special family in the
polymeric PFAS, which are composed of: (i) polymers bearing
fluorinated side chains such as poly[fluoro(meth)acrylate]s,^{18–}
²¹ poly[fluoro(oxetane)]s³ and 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 photo-
polymerisation of TFE and hexafluoropropylene (HFP) in the
presence of oxygen²² and (iii) polymers bearing carbon and
fluorine atoms in their backbones (Fig. 1 and 2).

More than 200 use categories and sub-categories have been
identified for more than 4,730 individual PFAS, while they
account for more than 9000 compounds according to the US
Environment Protection Agency.²³ The regulatory agencies (as
Registration, Evaluation, Authorisation and Restriction of Che-
micals, REACH, or Toxic Substances Control Act, TSCA) support
initiatives aimed at regulating the substances of greatest con-
cern and will endeavor to contribute to the broad and complex
scientific, technical, and also economic forthcoming debate on
the substances that may be of concern.

Regarding their biotic stability (aerobic, anaerobic and
in vivo), FPs such as PTFE are biologically inert and are not
degraded by microorganisms under oxygenated (aerobic) or
anoxic (anaerobic) conditions. Furthermore, *in vitro* and
in vivo studies on PTFE demonstrate the absence of acute or
subchronic systemic toxicity, irritation, sensitization, and 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
by bacteria, enzymes and oxidants. For example, PTFE hernia
patches explanted from patients and examined by scanning
electron microscopy, attenuated total reflectance Fourier trans-
form infrared spectroscopy, modulated differential scanning
calorimetry, and optical microscopy showed no degradation
in vivo.²⁹ In addition to these properties, FPs exhibit excellent
thermal stability, and therefore high temperatures are require
for their decomposition.¹⁴

In 1997, less than 1% of all polymers were used in areas of
elevated temperatures, a group composed primarily of FPs. The
sub-category of plastics known as engineering plastics, in



Bruno Améduri

Bruno Améduri is a CNRS Research Director at the Institute Charles Gerhardt, Montpellier, France. After obtaining his MSc in Quebec, Canada and a 6 month-internship at IBM in the USA, he came back to France to obtain his PhD (1988) from the University of Montpellier. He became an internationally well-known expert on fluoropolymer (FP) synthesis and characterization, contributing significantly to this

field for 30 years. He has co-authored more than 400 peer-reviewed publications, ca. 50 book chapters or reviews (including 5 Chemical Review and 12 Progress in Polymer Science), (co)edited 7 books, and is the co-inventor of 80 patents. In the last two decades, his team has made giant strides in developing the field of FPs and applications therefrom (collaborating with companies as 3M/Dyneon, Arkema, DuPont Performance Elastomers, Daikin, Great Lakes/Chemtura, Honeywell, Pall, Peugeot PSA and many academic labs around the world).



Hisao Hori

Hisao Hori received his PhD degree in 1990 from Keio University (Yokohama, Japan). He worked as a Researcher at Toshiba Corporation for three years, after which he became a Senior Researcher at the National Institute for Resources and Environment (later National Institute of Advanced Industrial Science and Technology, AIST, Tsukuba). He was also a Visiting Researcher at Max-Planck-Institut für Kohlenforschung

(Mülheim an der Ruhr, Germany, 1997–1998). In 2004, he was appointed as a Group Leader at the Research Institute for Environmental Management Technology, AIST. Since 2010, he has been a Full Professor at Kanagawa University. His current research interests include environmental remediation, resource recovery, and green production related to critical raw materials and functional materials.

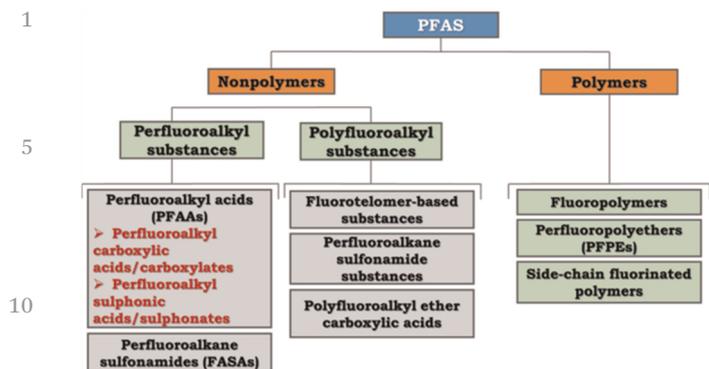


Fig. 1 Per- or poly-fluoroalkyl substances (PFAS) are gathered in various distinct families¹⁵ (reproduced with permission from Wiley).

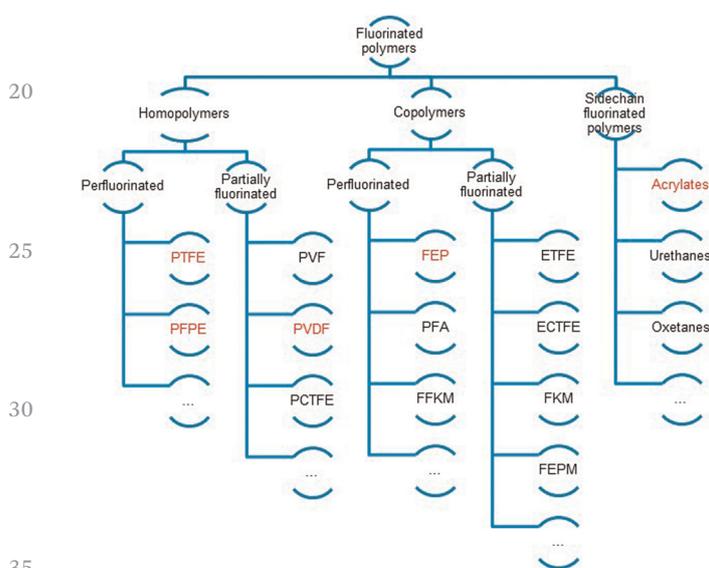


Fig. 2 Classification of FPs from the type of monomer base units³ (reproduced with permission from European Topic Centre Waste and Materials in a Green Economy), where most acronyms are described at the end of this review.

particular FPs, operate at extreme temperatures. PTFE, for instance, will endure 260 °C for several months,^{10–13} and even years until failure due to degradation. Generally, FPs are either recycled or degrade *in situ*, making research on the toxicity of their decomposition products necessary. The onset of the thermal degradation of FPs is known to initiate cleavage of their backbone and subsequent rearrangement to produce significant amounts of trifluoromethylated species.

The traditional method for the disposal of plastics involves burying them in landfills.^{1–3} However, landfilling of FPs has led to the contamination of leachates with PFAS and contributed to the release of plastics and microplastics.³⁰ Wahlstrom *et al.*⁴ published an intensive report on a toxic free economy and global scan of fluorinated compounds (including fluoropolymers), ranging from the extraction of fluorspar (and related

environment health and impact) to the synthesis and applications of fluoropolymers, including municipal waste and landfills in European countries (Fig. 3).

Despite their exceptional chemical and thermal stability, FP particles decompose into microplastics upon exposure to physical stress, resulting in their further dispersion and increased bioavailability.³¹ In this case, their 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 aim of this review is to present the state-of-the-art on the recycling, reuse, thermal decomposition, and life cycle assessment of FPs, as well as reprocessable new fluorinated vitrimers. The first part deals with the reuse of FPs (although little information is available), while the second part presents the recycling of these technical polymers (even produced on the pilot scale), including definitions of several recycling stages. Current efforts in recycling FPs focus on mechanical recycling, which requires extensive sorting and the addition of harsh chemicals; however, mechanical processing of the refined material typically leads to a reduction in its molar mass and degradation of its mechanical properties. In the third part, we summarize the thermal degradation of these FPs, which is classified into several sub-categories (thermolysis, thermal processing, flash pyrolysis, smoldering, open burning, open-air detonation, and incineration, with last one being one of a few technologies that can potentially decompose FPs (PTFE and PFAS)).^{32,33} Among the thermal techniques, the mineralisation of FPs under subcritical water has shown promise to close the loop, releasing CaF₂ as the starting point of fluorine chemistry. Finally, the concept of polymers of low concern (PLC), which FPs satisfy, will also be discussed.

2. Reuse

Reuse, recycling, and closed loop systems are alternative options to deal with FPs at the end of their 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 achieve a closed loop economy for FPs merits additional work and discussion, together with the recycling and reuse of melt-processible FPs, such as FEP, PFA or PVDF.

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

Recovery can also be achieved and there are several ways for the recovery of fully fluorinated thermoplastics (Fig. 4).³⁷

To the best of our knowledge, because of their inertness, FPs are difficult to be reused. One case study investigated the coating of FEP waste, where 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} due to the fluorine-fluorine

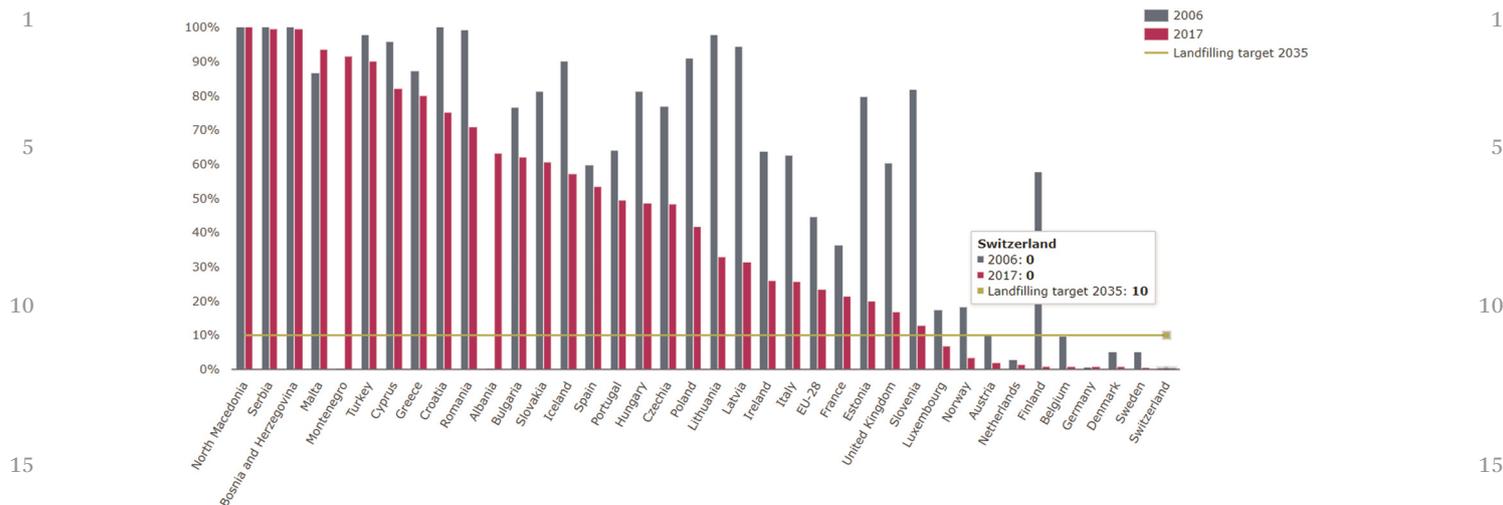


Fig. 3 Landfill rates in member and cooperating countries of the European Environment Agency, 2006 and 2017, %. Cluster column chart shows development in landfill rate in European countries in 2006 (blue) and 2017 (red). Data is presented in descending order according to 2017 values. Line chart represents 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).

interactions.^{40–43} The choice of these three monomers was based on the hydrophilicity of PEGMA, enabling water-soluble nutrients to reach plants, (ii) NBMA as a sensor to observe the growing roots of plants in transparent soil and (iii) adhesion of FATRIFE on FEP *via* F–F interactions. In this case, although the

kinetics of terpolymerisation was not studied, it was assumed that the α -fluoroacrylate was the most reactive monomer. The morphology of the resulting materials was a core-shell, in which the core was made of FEP while the terpolymer

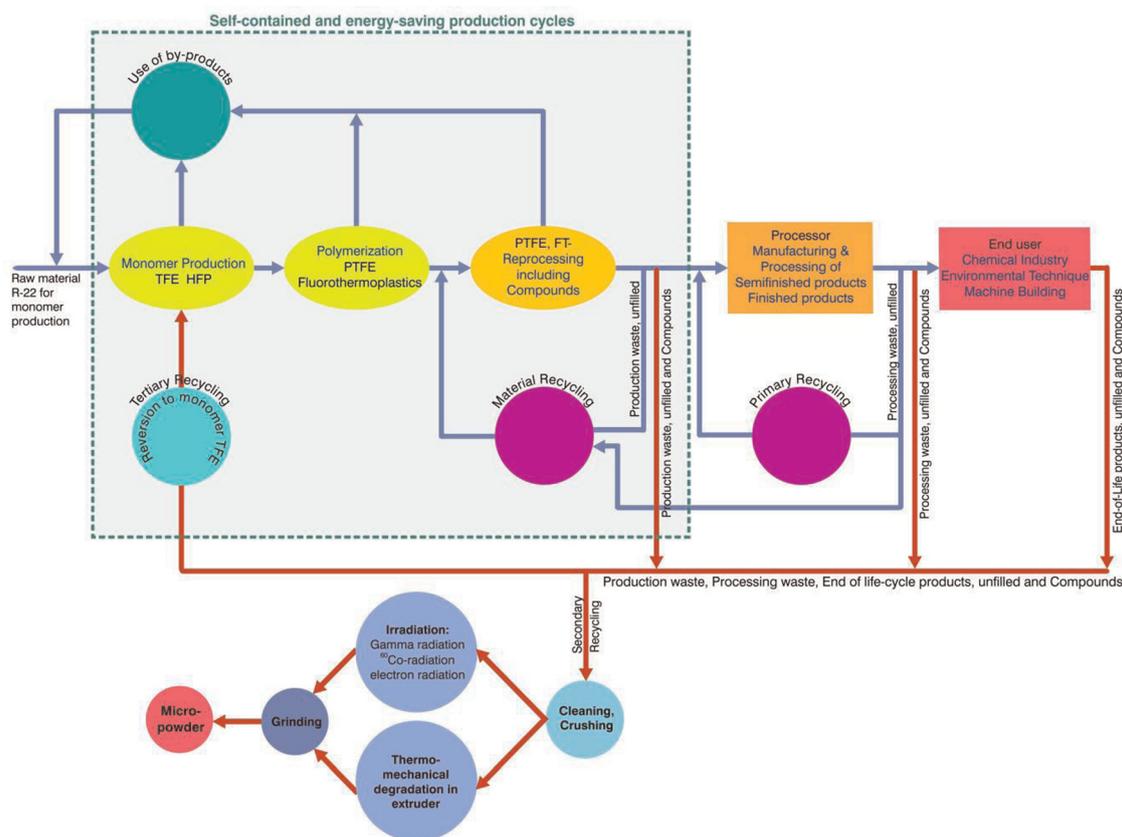


Fig. 4 Recovery cycle of PTFE and fluorinated thermoplastics^{9,37} (reproduced with permission from Recycling of fluoropolymers, FPGROUP).

contributed to the shell, with the objective to prepare transparent soils to assist and observe growing roots of lettuce plants.

3. Recycling

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

3.1. How to manage FP waste and disposal?

A peculiar example was 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 Sections 6–8 KrWG (dating from 2012), five stages in waste-management have been suggested.

3.1.1. Stage 1: prevention of waste. (Qualitative and quantitative prevention of waste, repeated use or longevity applications). For example, 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, they can be re-used in other applications, while export restrictions must be considered.

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

Examples – grouping of processing machines and exhaust systems according to FP categories.

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 and PTFE micro-powder.

Collected PTFE waste can be separated into standard and modified PTFE. In addition, processing for use as pre-sintered pellets for ram extrusion⁴⁴ or after radiation-induced degradation for the manufacturing of PTFE micro-powder.

However, it is difficult to use recycled PTFE as a molding powder because is not easily deformed by compression. Daikin Industries, Ltd.⁴⁵ claims that the mechanical recycling of PTFE can produce 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 the recycled PTFE, and it was found that modified PTFE was more suitable for this method in terms of development of mechanical properties.

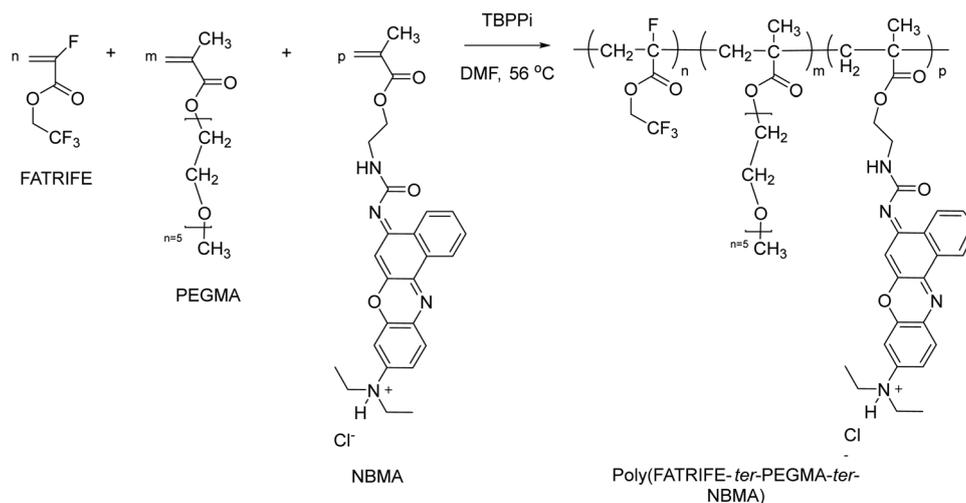
Fully fluorinated thermoplastics can be disposed of by cleaning, pelletising and re-use either as pure regrind or blended regrind material for thermoplastic processing.

Up-cycling (thermo-chemical) of end of life products made of PTFE, PFA or FEP.

3.1.4. Stage 4: other uses. Other material recycling: PTFE and other perfluorinated polymers cannot be used as substitute fuel for thermal incineration if their caloric value is below 11 000 kJ kg⁻¹ (required according to Section 8 KrWG). For example, sintered FP waste can possibly be used as flux in the cement or steel industry;

For un-sintered lathe chips, they can possibly be re-used as molding powder provided that the waste can be milled to a 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, the disposal of waste from PTFE-compounds is very expensive. Thus, to promote their re-utilization, Section 9 KrWG additionally requires the collection of specific waste (such as metals and polymers) separately. If the fluoropolymer waste is contaminated, it may fall in the class of dangerous substances. In this case, providing supporting documents about the disposal chain (Section 50



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 peroxy pivalate (TBPPi), resulting terpolymers coated onto FEP to produce transparent soils.^{38,39}

KrWG) is required, as follows: “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 their caloric value is less than 6.000 kJ kg⁻¹. This is mainly the case with PTFE waste given that its caloric value amounts to ca. 5.500 kJ kg⁻¹. If the caloric value exceeds 6.000 kJ kg⁻¹, 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 that 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 metal 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 companies³⁷ (e.g., Invertec³⁵). Typical products are micro-powder 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 this case, a separate pre-treatment is necessary to prepare them for recycling.

Given that PTFE also contain fillers, the techniques for their recycling are limited.

3.2. Different techniques for 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 materials or energy sources. Recycling should help preserve resources and avoid 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 for FPs was only 3.4% (yearly production of 320 300 tons in 2018).⁹

FP waste from commercial and industrial waste producers or obtained directly from dismantling operations is either pre-sorted 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 techniques for the recycling of FP materials include re-grinding and sintering as well as chemical recycling. Table 1 lists the four main ways for their recycling.

3.2.1. Primary (or mechanical) recycling. Primary recycling involves extruding pre-consumer polymer or other “mechanical” processes (Fig. 5) or pure polymer streams. As an example, sintered PTFE waste is 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 extrusion⁴⁹). The mechanical properties (e.g., tensile strength, elongation and cold flow) of the

Table 1 Various ways for recycling plastic^{1,46}

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

^a Also including chemical recycling to monomer, CRM.

resulting PTFE differ from that of virgin PTFE. The appropriate recycling companies (and their addresses) are listed in the ESI.†

3.2.2. Secondary recycling. In contrast to primary recycling, secondary size requires sorting of the polymer waste streams and reduction of the polymer waste size, followed by processing (extrusion, sintering or others). With suitable control of the processing conditions, many polymers can undergo several cycles of primary and secondary mechanical recycling without the limitation of performance loss. For example, the recycling of FPs enables the degradation of high molar mass-PTFE into PTFE-micro-powder. This can be achieved either by thermo-mechanical degradation or degradation using irradiation with high-energy radiation (Fig. 6 and Section 5). Typically, the radiation sources implemented in medical technology are either gamma-radiation from a ⁶⁰Co-source or β-radiation (or electron-beam).

The irradiation process (Fig. 6) is supplemented by a grinding step to obtain the desired particle size. This process strongly reduces the molecular chain to around 1% of the original chain length, and thus 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 these 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;

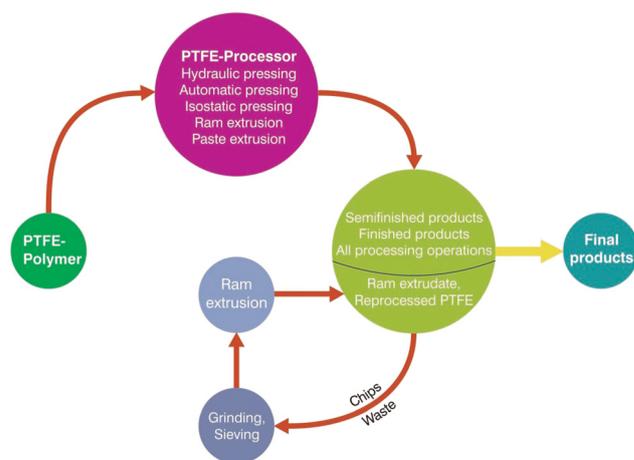


Fig. 5 Primary recovery circuit³⁷ (reproduced with permission from Recycling of fluoropolymers, pro-K Fluoropolymergroup).

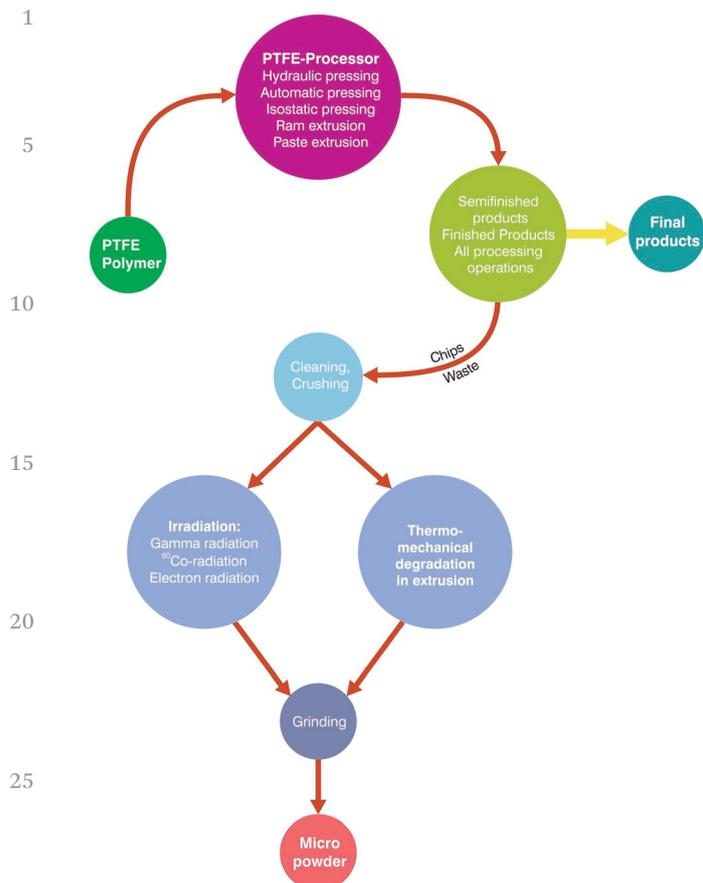


Fig. 6 Secondary recovery circuit³⁷ (reproduced with permission from Recycling of fluoropolymers, pro-K Fluoropolymergroup).

- 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 surfaces; and

Coatings and paints to enhance the processing and non-stick properties.

3.2.3. Tertiary recycling. Tertiary recycling is applied to polymers that are no longer suitable for straightforward mechanical recycling methods.^{2,46} This chemical recycling is often complementary to conventional recycling techniques, and can retain significant value if the 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). This thermo-chemical process is also called “Up-Cycling”^{49,50} (often achieved by pyrolysis), which splits the polymer back into its corresponding monomers (*e.g.*, the pyrolysis of PTFE under an inert atmosphere produces monomers such as TFE and HFP in a high amount (Fig. 7),⁴⁹ which when cleaned, can be re-used for polymerisation). The advantage of this process is that not only homogenous PTFE but also perfluorinated thermoplastics such as FEP or PFA can be processed (Section 3.3). Advantageously, FPs containing mineral fillers can also be recycled in this way.

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

3.2.4. Quaternary recycling. Quaternary recycling is applied to polymers that are unsuitable for all other methods of recycling and are utilised for energy recovery *via* pyrolysis,^{2,46} as 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 Chakraborty⁵¹ reviewed the recycling of PTFE, while two years later, Dams and Hintzer⁴⁹ further reported the recycling of FPs in a book chapter. According to EU-Legislation, fluorinated thermoplastics should be recovered thermally if mechanical recycling is not possible.³⁷ Accordingly, 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 a single fraction, cleaned pelletised and directly used in the thermoplastic processing but may not be suitable for all applications. Meanwhile, these products have found some applications such as tubes and clamping systems in architecture and power plant construction.

Alternatively, if for technical or other reasons, the primary recycling of fluorinated thermoplastics (PTFE, PVDF and copolymers of VDF or TFE such as FEP and PFA) is not possible, they may be used in 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 employed in many applications ranging from aerospace and biomedical to corroding environments in the chemical industry. However, despite its low share in end-of-life products, PFA processing can lead to the generation of up to 30% waste. Thus, understanding how recycled FPs affects the performance of products 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. They studied the

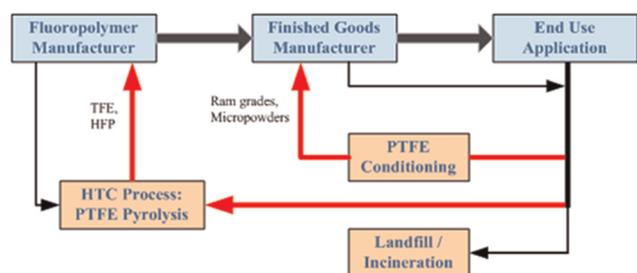


Fig. 7 Upcycling-closing the loop⁴⁹ (reproduced with permission from The Royal Society of Chemistry).

1 effect of PFAR loading (5–100 wt%) in virgin PFA on the thermal, mechanical, and rheological properties, color and chemical resistance, with the latter two showing no significant changes in the range of PFAR content tested. The addition of higher
5 loads of PFAR (≥ 50 wt%) led to a reduction in mechanical properties, particularly stress-strength analysis and elongation at break. However, the elastic modulus and hardness improved with an increase in the degree of crystallinity. Romoaldo *et al.*⁵² noted a decrease in viscosity and yellowing of the samples,
10 which are probably linked to the polymer chain degradation. Nevertheless, the addition of up to 10 wt% of PFAR proved to be an effective alternative to reuse PFA residues based on mechanical recycling.

In addition, due to its performance and wide range of
15 processing methods, PVDF is also an outstanding polymer for durable and sustainable solutions in a circular economy. Due to its ability to be processed and reused for up to five times, PVDF does not lose any appreciable mechanical or physical properties.^{53,54} During processing, it is common to use up to
20 20% reprocessed material in the manufacture of injection molded and extruded products. Moreover, the 3D printing of park bridges using reprocessed PVDF material was reported.⁵³ Furthermore, it is claimed that exposed PVDF materials are safe to reuse in their current form.⁵⁴ PVDF copolymers have been
25 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 different requirements, but using a PPRA can improve the surface finish, increase the output, reduce the extruder pressure and die build
30 up, improve the flow, steady the gauge control and allow processing at lower temperatures. FPs and fluorinated elastomers have been used for years to impart all the above-mentioned features to polyethylene and polypropylene, but with more insight into their recycling, the same benefits given
35 to virgin resins are found to be more advantageous for recycling. The Arkema Company claims that processes involving the use of recycled materials up to only 20–30% before losing some performance can now be reprocessed using up to 90% or even 100% recycled materials to make items such as films,
40 cables, pipes and injection molded parts.⁵³ This company has also reported that materials containing recycled PPRA behave almost the same as the virgin material in which a polymer processing aid (PPA) was added as a master batch in the extruder.⁵⁴ PVDF and VDF copolymers assist in the reprocessing of high-volume polyolefins as 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
50 been reported on this topic, as well summarized by Schuster *et al.*⁵⁵ However, these authors forgot to cite the tertiary recycling of commercially available poly(VDF-co-HFP) fluoroelastomers (average molar mass in number, $M_n = 134\,000$, dispersity, PDI = 3.7 and VDF:HFP = 3:1 mol:mol) into co-oligomers, the M_n of which was in the range of 3300 to 10 400 g
55 mol⁻¹.⁵⁶ This reaction occurred at -10 °C in the presence of

sodium hydroxide, hydrogen peroxide and triethyl ammonium chloride. Then, these transparent telechelic dicarboxyl-terminated co-oligomers were chemically transformed into diacrylates, which were further photo-crosslinked without the use of high pressure, toxic solvent and high temperature. The
5 resulting materials displayed satisfactory hydrophobic and mechanical properties.

Actually, the recycling methods employed in the field of conventional rubber cannot be systematically adapted for fluorinated elastomers. According to the review by Schuster
10 *et al.*,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, as follows: (i) the milling of FKM into a fine powder to be mixed with virgin FKM and (ii) the mechanical devulcanisation of FKM, followed
15 by successive compounding with virgin rubber. Both techniques provide satisfactory thermal stability by maintaining the mechanical properties of the original FKM. Indeed, in this review, for FKM, only patents were supplied. Besides, the cited articles often only referred to degradation and not devulcanization. These authors concluded that recycling FKM is possible and leads to products with competitive properties to that obtained with virgin material. However, as known from engineering on disassembling, Schuster *et al.*⁵⁵ concluded that elastomers, and therefore fluorinated elastomers should be
20 vulcanized for the goal of further facilitating devulcanization.

3.5. Which companies recycle FPs?

Companies involved in the recycling of PTFE and those operating based on the up-cycling of PTFE and selected TFE-based
30 thermoplastics are listed in the ESI.†

On March 2015, the Dyneon Company started the 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
35 production. By regaining resources, this pilot plant not only makes 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, resulting in a positive impact on the environment.

On the industrial scale, the recycling of “clean” PTFE waste or scraps generated in production has already been achieved
40 (*e.g.*, by Dyneon⁵⁰ or on 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 which were also used to reduce wear rate and friction.⁵⁷ This has the unintended consequence of extending
45 the use of FPs, complicating efforts to control and reduce their losses from the technosphere. Alternatively, the recycling of fluoropolymers in consumer articles is not well established, given that these FPs are typically contaminated by other substances and fillers, which makes their recycling difficult.^{34,37} Fluoropolymers applied to metal articles (*e.g.*, non-stick frying
50 pans) may end up in metal recycling streams, leading to their

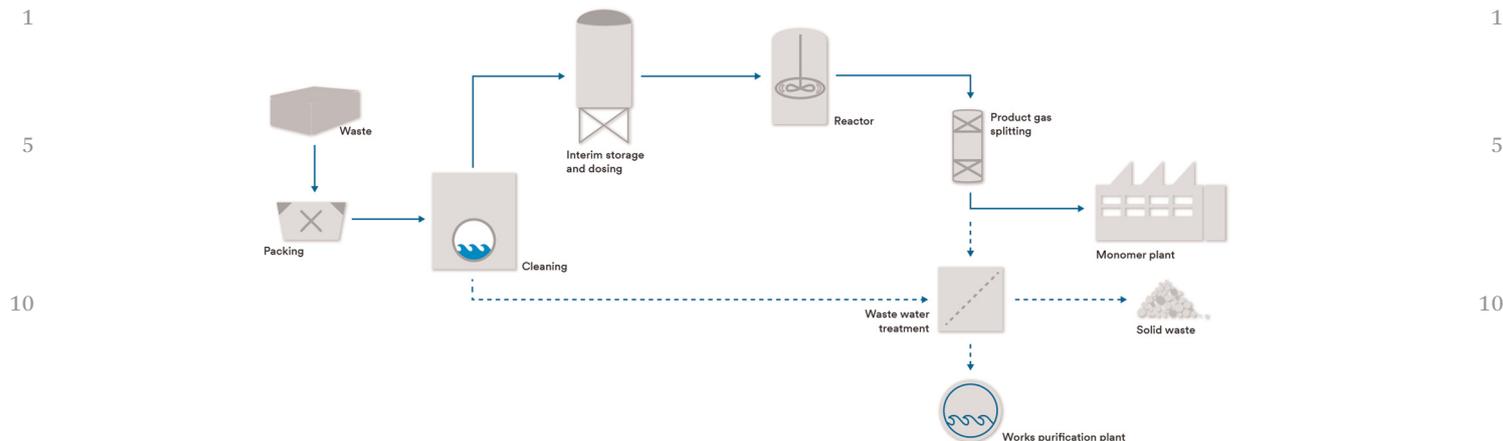


Fig. 8 Sketch of the world's first pilot plant for recycling perfluorinated polymers in Germany (Gendorf)⁵⁰ (reproduced with permission from 3M Dyneon and image courtesy of 3M Company).

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 m². 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, and it is unclear whether the emissions are controlled.^{15,58,59}

3.6. Caloric values of FPs

The caloric value of PTFE is 5400 kJ kg⁻¹, which is 5020 kJ kg⁻¹ for PTFE glass compounds.

Furthermore, Dams and Hintzer⁴⁹ reported the environmental/raw material savings per 1000 tonnes TFE produced by high-temperature conversion processes (Fig. 9).

3.7. Vitrimers

The previous sections summarized the situation of recycling, reuse, and end of life of thermoplastics and elastomers. Alternatively, a third class of polymers called *vitrimers*, which was invented by Leibler *et al.*,⁶⁰ has attracted growing interest. They mainly combine three features, as follows: (i) the mechanical properties and (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 are as follows: (i) an insoluble 3D-network that can flow, (ii) chemical resistance, (iii) unique rheological behaviour and (iv) reshaping ability, making them promising materials for innovative industrial applications. They behave according to two profiles including 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

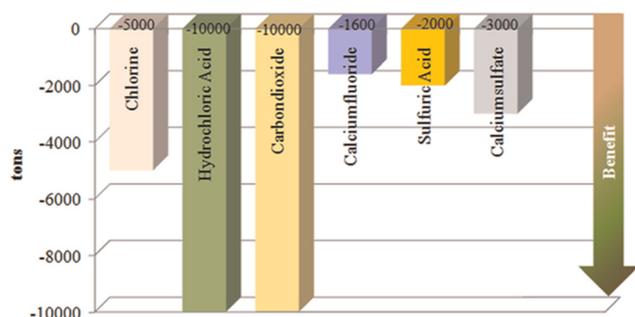
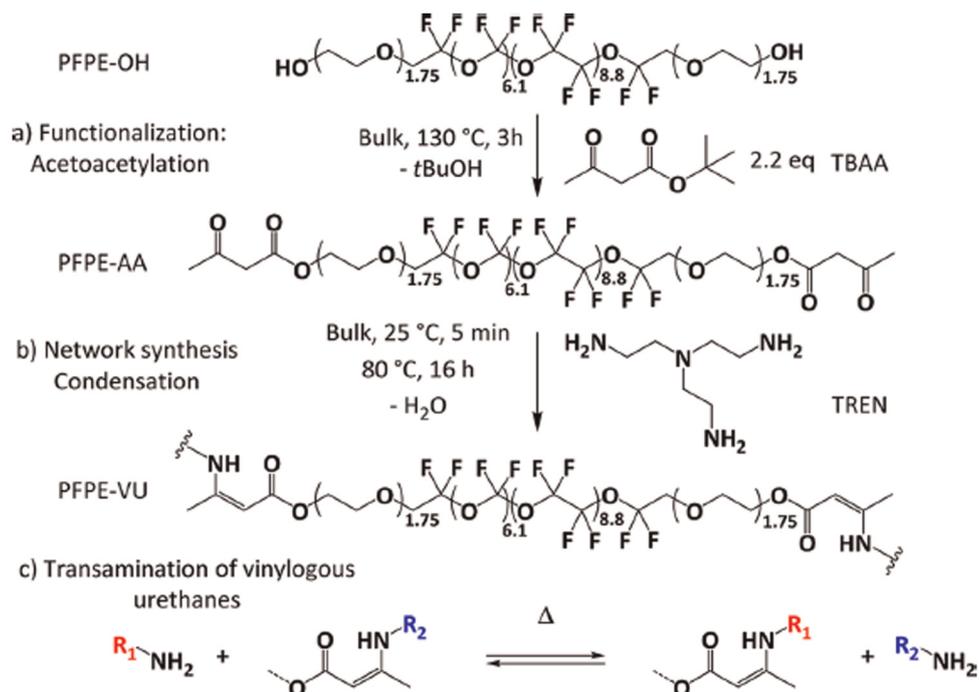


Fig. 9 Environmental benefit (environment/raw material saving per 1000 ton- TFE) from depolymerising perfluoropolymer back to TFE produced by high-temperature process⁴⁹ (reproduced with permission from The Royal Society of Chemistry).

circular economy. This unique behaviour is due to the triggering of certain covalent exchange reactions, which allow the network to rearrange upon the application of a stimulus. They represent a novel family of permanently crosslinked polymers, which exhibit a liquid feature upon heating, while their macroscopic deformation is controlled by the rate of the internal chemical bond exchange reactions.

Du Prez's group⁶² reviewed the recent developments to understand and control covalent adaptable networks and dynamic crosslinking reactions in vitrimers, and how tuning this chemical reactivity can be utilised to favor the properties of materials.

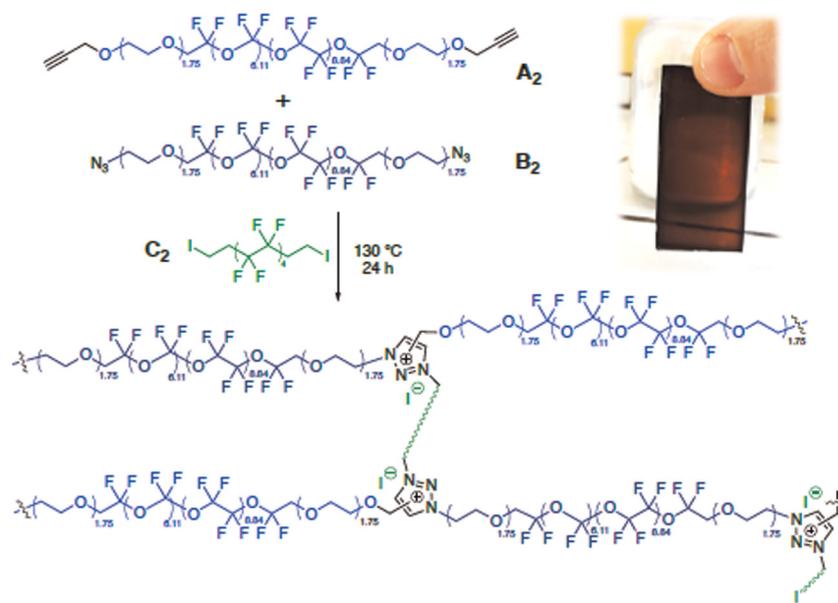
Actually, to the best of our knowledge, vitrimers based on FP (including PTFE, PVDF and copolymers of TFE, CTFE and VDF) have not been reported to date, although a few ones containing either perfluorooligoether (PFPE) or CF₂ and CF₃ moieties are exemplified hereafter. Guerre *et al.*⁶³ studied a catalyst-free fluorinated vitrimer elastomer, which was prepared *via* the polycondensation of a telechelic bis(acetoacetate) PFPE (obtained from PFPE diol, Scheme 2a) and tris(2-aminoethyl)amine (TREN) (Scheme 2b), wherein two competing



Scheme 2 (a) Functionalization of a telechelic PFPE diol into a bis(acetate)-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 urethanes⁶⁵ (reproduced with permission from the American Chemical Society).

bond exchange mechanisms co-exist, each of them showing a strikingly different temperature dependence. This contributes to a highly unusual dual viscosity profile for this new class of vitrimer materials, *i.e.*, a gradual decrease in viscosity at lower temperatures, intercepted by a much sharper drop in viscosity at higher temperatures.

Another strategy also involving low glass-transition temperature (T_g) PFPE led to the production of electrolytes for lithium ion batteries.⁶⁴ Ion-conducting vitrimers were prepared *via* the concomitant thermal initiated-Huisgen polyaddition of telechelic PFPE-diyne (A2) and bis(azido)-PFPE (B2) and *in situ* N-alkylation in the presence of a fluorinated telechelic 1,12-



Scheme 3 Synthesis of a fluorinated network via the 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 the American Chemical Society).

1 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
5 basic environments and could recover its mechanical properties
after two recycling steps. Three PFPE-based vitrimers were
obtained by varying the diiodo-crosslinker content and the
most stable displayed suitable thermal stability (5% weight
loss and $T_d^{5\%} = ca. 300\text{ °C}$), a water contact angle of 136°,
10 and ionic conductivities (as non-doped materials) ranging from
0.5 to $1.0 \times 10^{-6}\text{ S cm}^{-1}$ at 27 °C.

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

15 Cuminet *et al.*⁶⁵ reviewed various strategies to overcome the
issue of high catalyst loading in conventional vitrimers. They
suggested internal catalysis, with the neighboring group parti-
cipation favoring the reshaping ability of these materials. These
authors summarised the influence of the activating groups and
the different types of exchangeable bonds on the exchange
20 reactions in vitrimers.

A peculiar example from the same group⁶⁶ is catalyst-free
transesterification by inserting a difluoromethylene activating
group adjacent to the ester functions. Firstly, they modified
1,1,1-tris(4-hydroxyphenyl)ethane with bromodifluoroethyl
acetate (Scheme 4). After saponification, the resulting aromatic
25 trifunctional $\text{CF}_2\text{CO}_2\text{H}$ reacted with telechelic 1,4- butanediol

bis(glycidyl) ether (DBGE) without any catalyst due to the high
electron-withdrawing CF_2 groups, hence favoring the epoxy-
acid polymerisation, and remarkably transesterification on
the adjacent esters (with a gel time of 1 h 20 min).

Surprisingly, no information on the possible cationic ring-
opening polymerisation of the epoxides initiated by $-\text{CF}_2\text{CO}_2\text{H}$
strong acid was supplied. Nevertheless, this fluorinated group
enabled the synthesis of highly crosslinked reprocessable
materials, which did not require any metallic or organic
catalyst. After the 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 group⁶⁷ used an alpha CF_3 -
substituted tetracid ester to achieve catalyst-free epoxy vitri-
mers *via* polycondensation (Scheme 5). Two diepoxy monomers
(bisphenol A diglycidyl ether, DGEBA and BDGE) were
employed in this reaction. Curing was monitored by rheology,
DSC, and FTIR, leading to a high gel content (>70%). The
20 accelerating effect of the alpha- CF_3 group on transesterifica-
tion reactions was evidenced by stress-relaxation studies and an-
alysed computationally on a model system. Reshaping tests
showed that both the mechanical and thermal properties of
the reprocessed materials were similar to that of the initial
25 materials.

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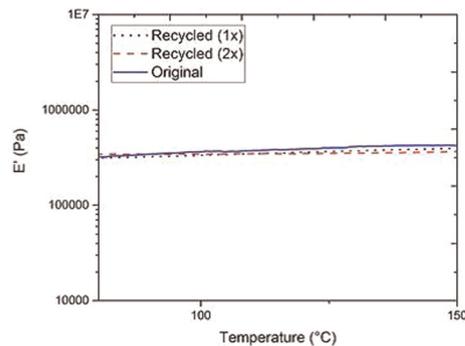
170 °C
200 bar
18 h

35

40

45

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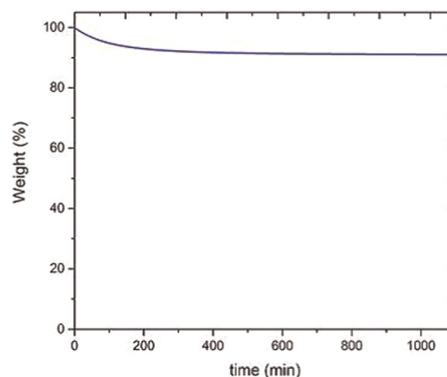
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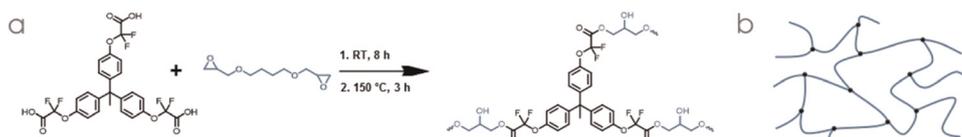
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Fig. 10 Sample made from A2 + B2 + C2 (1 : 1 : 1 mol : mol : mol) cut into small pieces and remolded (left). Storage modulus E' of original and recycled samples (right) (where A2, B2 and C2 stand for telechelic diyne-PFPE, bisazido-PFPE and 1,12-diiodo-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane,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



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 network⁶⁶ (reproduced with permission from The Royal Society of Chemistry).

In conclusion, although the research on this third family of polymers containing a few fluorine atoms, which forms a link between the historically opposed 3D networks (thermosets) and linear polymers (thermoplastics), is still in its infancy, these studies highlight the high potential of electron-withdrawing fluorinated groups as powerful internal activators for achieving transesterification without a 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 can undergo chemical recycling to generate the corresponding monomers at room temperature. Firstly, semi-FPs were prepared by ring-opening metathesis polymerization of functionalized *trans*-cyclobutane-fused cyclooctene (*t*CBCO) monomers and displayed very good thermal stability (with decomposition onset temperatures higher than 280 °C) and were hydrophobic. Indeed, the simple preparation, functionalization, and recycling, together with diverse thermomechanical properties and demonstrated hydrophobicity of *t*CBCO-based depolymerisable semi-fluorinated polymers make them promising candidates as sustainable functional materials. These polymers could be depolymerized to over 90% conversion in the presence of ruthenium complexes at room temperature, while the modular nature of the *t*CBCO scaffold was used to insert diverse thermomechanical features. Among them, depolymerisable amphiphilic polymers can find applications in antifouling materials and controlled small-molecule release.⁶⁸

4. Thermal degradation of FPs

4.1. Introduction of 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 include 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 After their normal lifecycle ends, and they are disposed of, the degradation of FPs has been studied by several research groups to evidence potential degradation products.

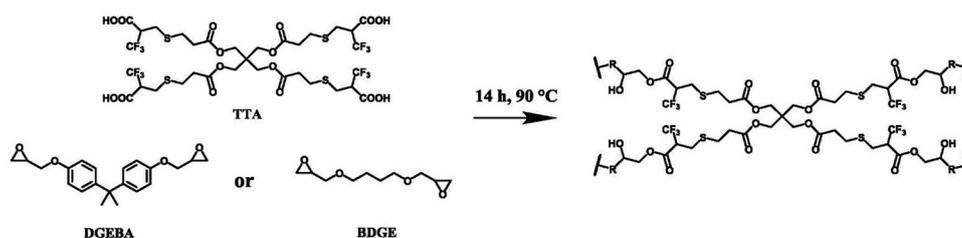
OB is defined as an open-air combustion process by which excess, unserviceable, or obsolete munitions are destroyed to eliminate their inherent explosive dangers. Alternatively, open-air detonation (OD) is used for the disposal of excess, unserviceable, or obsolete munitions, whereby an explosive donor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

Incineration is a high-temperature flaming process that is performed in open air space, whereas smoldering is regarded as a flameless combustion process that is performed on the surface of a condensed fuel. Although 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 a continuous energy input.

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

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

A comparison of the thermal stabilities of various FPs is presented in Fig. 11.⁷⁸



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 the American Chemical Society).

4.2. Thermolysis

There are various reports on the thermolysis of FPs in the literature. The temperature has a great influence on both the decomposition (partial or complete) and the nature and amount of the released products.⁷⁷ For example, although the decomposition of PTFE begins slowly at 260 °C, temperatures of above 400 °C are needed to achieve significant decomposition.⁷⁹

The first study was achieved by Lewis and Naylor⁸⁰ as recent as 1947, who highlighted that TFE was the most unique compound generated in the pyrolysis of PTFE under vacuum at 600 °C. However, its yield dropped drastically at atmospheric pressure, whereas the contents of HFP and octafluorocyclobutane (*c*-C₄F₈, OFCB) 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 process using a kiln,⁸³ claiming that TFE, HFP and OFCB are released at 600–650 °C with steam.

Further, a few articles are supplied hereafter. In 1977, Arto and Soda characterised the pyrolysis products of PTFE and FEP and the influence of the pyrolysis conditions on the 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. During the 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 much less in quantity but OFIB was obtained only from the pyrolysis of FEP. Furthermore, perfluoroalkanes were produced *via* the oxidative pyrolysis of PTFE at high temperatures. The 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 CO₂,

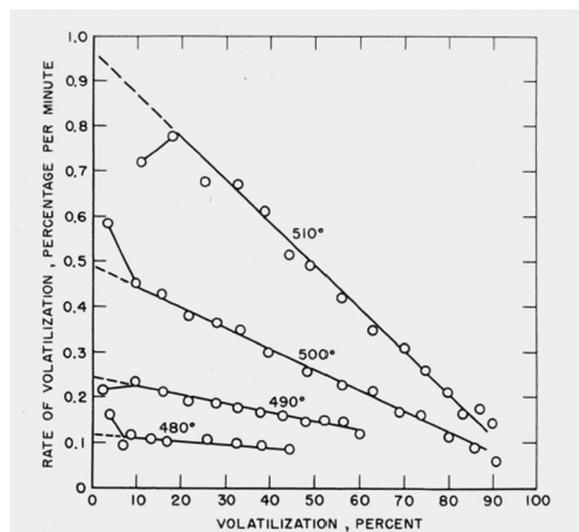


Fig. 12 Rate of thermal degradation of PTFE versus % volatilisation at different temperatures⁸¹ (released from the U.S. Government).

while trifluoroacetyl fluoride led to the formation of trifluoroacetic acid (TFA) and HF.

Furthermore, in 2001, Ellis, Mabury *et al.* comprehensively studied the thermal decomposition of PTFE,³⁶ which was further revisited two years later (on PTFE, PCTFE, ECTFE and PFA) employing complimentary analytical techniques such as ¹⁹F NMR spectroscopy coupled with GC/MS.⁸⁵ Similar to 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 related homologous perfluoroacids of longer chain length (ranging in perfluoroalkyl length from 2 to 13, which was confirmed using authentic standards and the mass spectrum of PFOA).

At 400 °C, under an air atmosphere, COF₂ was the principal gas evolved, and upon reacting with traces of water, yielded HF⁸⁷ and carbonyl fluoride ion, which were detected in a large amount in the combustion process of PTFE.⁸⁸ The toxicity of the pyrolysis products from PTFE was evaluated by exposure to

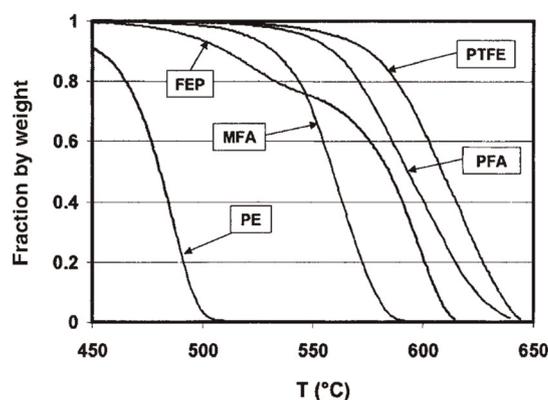


Fig. 11 Thermogravimetric analysis (left) and 5% weight loss temperature (*T*), (right) of commercially available FPs⁷⁸ (reproduced with permission from Wiley).

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

1 different animals.⁸⁹ COF₂ 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,
 which is classified as “moderately toxic”. Tsai *et al.* indicated
 5 that by heating at 260 °C, PTFE generates “polymer fumes”.⁹⁰
 Among the products, TFA may be partially responsible for the
 pulmonary edema noted in workers at a PTFE plant.

In 1995, Jun *et al.* pyrolysed PTFE in the temperature range
 of 510–600 °C.⁹² TFE, HFP and OFCB were produced, and under
 10 most conditions, TFE was the major product. OFCB was
 regarded as the secondary product formed from the thermo-
 lysis of TFE because its formation strongly depended on the
 degradation rate.

In 1998, Simon and Kaminsky pyrolysed PTFE at 500–600 °C
 15 in a fluidised bed reactor using steam.⁷⁹ They noted that the
 primary decomposition products were TFE and •CF₂• diradicals.
 Further products were formed by secondary reactions. Actually,
 C₂F₄ is inflammable in an O₂ atmosphere, releasing CF₄ and
 CO₂. As reported above, TFE reacted to generate HFP and
 20 OFCB above 600 °C.

Mabury's group studied the thermolysis of PTFE and noted
 the formation longer-chain polyfluoro- and/or polychloro-
 fluoro-(C3–C14) carboxylic acids, which may be equally
 persistent.^{36,85} Furthermore, among the thermal degradation
 25 products, these authors detected chlorofluorocarbons (CFCs)
 and fluorocarbons, which are known to attack ozone and act as
 greenhouse gases, respectively. They proposed a mechanism for
 the thermal degradation of PTFE,³⁶ involving primarily the
 reaction of a •CF₂• carbene diradical, for the production of
 30 the main fluorinated compounds observed (Fig. 13). These
 authors also confirmed and complemented 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

using the same comprehensive methodology, although Zulfiqar
*et al.*⁹⁵ previously addressed this approach (*vide infra*). How-
 ever, 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 and fluoroformaldehyde as
 the most abundant products obtained from 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
 10 major identified acid product.

As indicated by the bold arrow, the most significant step in
 the thermal decomposition is the formation of •CF₂• carbene
 radicals, which recombine to form TFE. Longer-chain diradicals
 are also formed, which can undergo fluorine abstraction or
 15 reaction with carbonyl fluoride to produce fluoroalkyl (*p* = 0 ±
 4) or fluoroalkoxy radicals. These radicals then react with the
 constituents present in the air, oxygen and traces of water to
 form perfluorinated acids (*n* = 0–12, *m* = 1–7) including TFA,
 with their yield being inversely proportional to the number of
 20 carbon atoms in the chain. The distribution of the product
 yield depends on the temperature and the composition of the
 atmosphere. These mechanisms were supported by ¹⁹F NMR
 spectroscopy combined with GC/MS analysis.⁸⁵

From an environmental-fate perspective, the thermal degra-
 25 dation of FPs produces monomer units that degrade in the
 troposphere into CO₂,⁹⁶ or halogenated propenes^{92,97} (Fig. 14).
 The latter materials further decompose, generating long-lived
 haloacetic acids⁹⁸ such as TFA, which are expected to be
 terrestrially deposited *via* wet (*e.g.*, rain) and dry
 30 depositions.⁹⁹ In addition, various perhalogenated acids and
 perfluorodecanoic acid, have been evidenced to act as peroxi-
 some proliferators and inhibitors of gap junctional intercellular
 communication.¹⁰⁰ As is known, CFCs are produced through

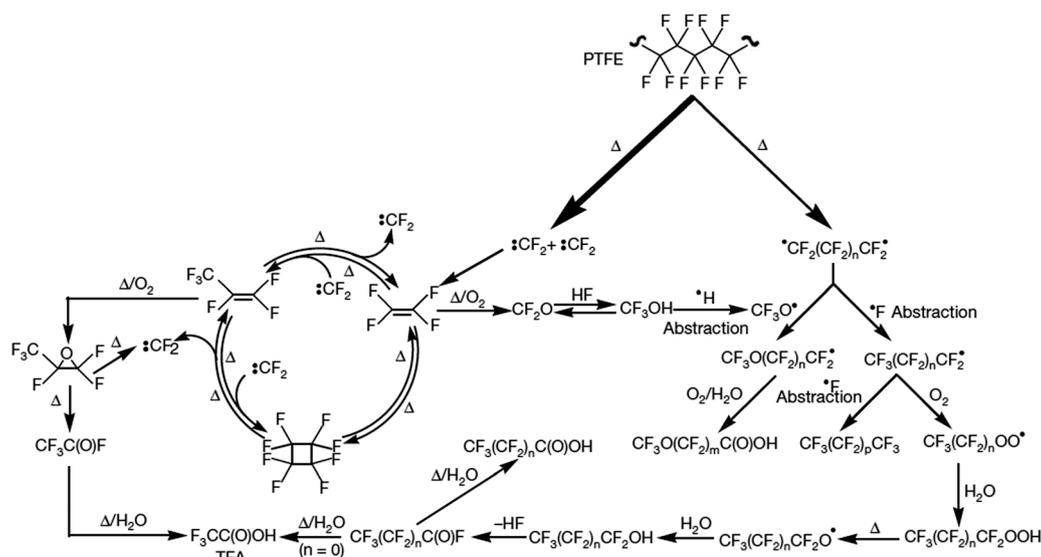


Fig. 13 Proposed significant pathways in the thermal decomposition of FPs, where Δ stands for heat³⁶ (reproduced with permission from Nature Publishing Group).

the decomposition of chlorofluorinated (co)polymers and may migrate to the stratosphere, causing a negative effect on the ozone layer.

In 2007, Garcia *et al.*¹⁰¹ suggested that the decomposition of PTFE 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 the PTFE manufacture process as well as the degradation products obtained from PTFE under harsh chemical and thermal conditions. This study complemented that reported by Baker and Kasprzak⁸⁷ on the isothermal thermogravimetric measurements under air at different temperatures, in the range of 150–525 °C, analysing the gases released by infrared spectroscopy. Dynamic thermogravimetry curves, up to 700 °C, under air and N₂ atmospheres, were measured by Conesa and Font⁸⁸ and the evolved gases characterised by mass spectrometry. PTFE was pyrolysed inside an electric furnace at 550 °C in an air stream to evaluate the toxicity of decomposition products and the concentration of carbonyl fluoride (COF₂) measured.⁸⁹ Slow thermolysis of PTFE up to 500 °C in a laboratory-scale tube reactor was carried out in air to collect the fluoroacids formed and analyse them by ¹⁹F NMR and mass spectrometry, 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, given that they do not deplete the ozone layer, they are potent greenhouse gases, with global warming potential (approximately 6500- and 9200-times that of CO₂ for CF₄ and C₂F₆, respectively) and have lifetimes that exceed 10 000 years.^{103,104} TFA is a compound with no known loss mechanisms in the environment, whereas at higher concentrations in natural waters, it has been shown to be mildly phytotoxic.³⁶

Furthermore, Meissner *et al.*¹⁰⁵ studied the influence of the experimental parameters (temperature in the range of 600–800 °C), pressure (100–760 mmHg), PTFE feeding rate (250–1000 g h⁻¹) and nitrogen flow (0–200 L h⁻¹) 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 × 10² Pa), releasing 97% of TFE.^{106,107} Under an atmospheric pressure of 1.103 × 10⁵ Pa, this yield dropped to only 16%, whereas that of HFP and c-C₄F₈ increased. More recently, Kaminsky¹⁰⁸ carried out the pyrolysis in a fluidised bed, under normal pressure with nitrogen as the fluidising gas at various temperatures. The high heat transfer is one of the advantages of using a

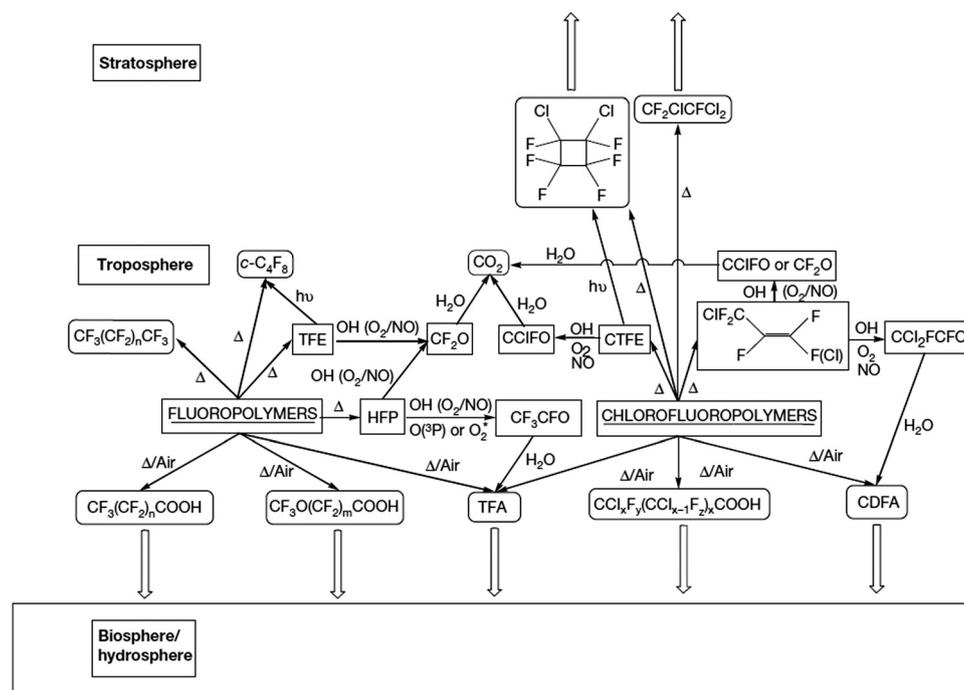


Fig. 14 Suggested environmental reaction pathways for the thermal degradation of fluoro- and chlorofluorinated polymers. Rectangular boxes represent environmentally transient species ($t_{1/2} < 10$ years) and important environmental impacts. Reaction processes are either proposed based on this study or ref. 67 and 81). Significant perhaloacid concentrations ($x = 0 \pm 2$, $y = 1 \pm 3$, $z = 1 \pm 2$, $n = 1 \pm 12$, $m = 1 \pm 7$) are produced, primarily TFA and chlorodifluoroacetic acid (CDFA) (1–10 wt%). Tropospheric oxidation of perhaloalkenes also predominantly leads to or expected to lead to the formation of TFA and CDFA. The thermal decomposition of chlorinated FPs leads to the production of saturated CFCs³⁶ (reproduced with permission from Nature Group Publishing).

fluidized bed reactor. An increase in temperature from 605 °C and 650 °C 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. SiF₄ and soot were also formed by the reaction of fluorocarbons with sand, which was used as the fluidizing medium. The SiF₄ content increased with an increase in temperature. It is also possible to use filled PTFE material for the pyrolysis. For bronze-filled PTFE at 600 °C, the TFE yield was significantly reduced to 60 wt% due to the catalytic effect. Other fillers did not show any effect. At 500–800 °C, PTFE is known to release TFE and HFP (Scheme 6).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. The evolution of the major PFCs (CF₄, C₂F₆, C₃F₈ and C₂F₄) and traces of semi-volatiles with the temperature and oxygen/mass ratio was monitored. At 1000 K, the half-life of PFOS was reported to be 0.2 s,¹¹⁰ decreasing sharply with a further increase in the temperature. 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 pure fluorinated polymers and the tested commercially available products (Table 1).³⁶ Actually, HFP has the potential to react with •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 •OH radicals⁸⁵ is expected to be similar to that of HFP based on its reactivity with other radicals¹¹¹ and the behaviour of similar molecules,⁹⁸ producing CDFA in the troposphere. Besides PTFE and PCTFE, ECTFE and PFA copolymers were also tested under 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 observed in the thermolysis of the fluoro- and chloro-fluoropolymers, while other longer-chain perhalogenated acids were also identified.

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, which was 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 Hexafluoronaphthalene 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).

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

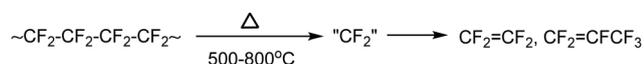
Dehydrofluorination occurs at about 500 °C in PVDF and produces the formation of fluoroaromatic compounds, as described in Scheme 7.¹¹² However, at these high temperatures, main chain cleavage becomes competitive with dehydrofluorination, and fluoroaliphatic compounds are also formed.

As has already been noted, the products from the poly(VDF-*co*-CTFE) copolymers are the same as that derived from the homopolymers corresponding to the monomer units except for the presence of some HCl. The types of reactions shown in Scheme 8 can be assumed to occur, where the relative

Table 2 Positively identified species produced in the thermal decomposition of various fluoropolymers³⁶ (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) _n COOH	> 0.01
	CF ₃ O(CF ₂) _m COOH	—
	DFA	> 0.01
	MFA	> 0.01
PCTFE	CTFE	—
	CPFP	13.1
	CDFA	9.5
	TFA	> 0.1
	DCHB	—
	DCHFBC	—
	TCTFE	—
	1,3-DCTEP	—
	1,1,3-TCTFP	—
	CCl _x F _y (CCl _{x-1} F) _z COOH	—
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; DCHFBC: 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; and PFA: poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether)copolymer. For the long-chain acids, *n* = 1–12, *m* = 1–7, *x* = 0–2, *y* = 1–3, *z* = 1–2.



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

1 **Table 3** Fluoro-containing EI fragments of compounds formed in the
 5 pyrolysis of PVDF¹¹² (reproduced with permission from Wiley)

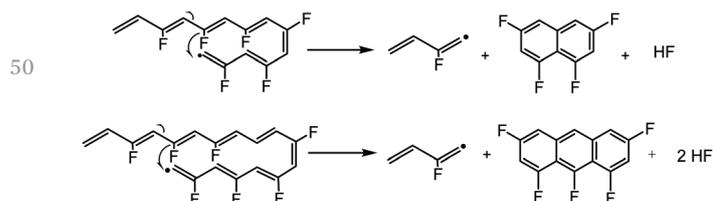
Fragment	<i>m/z</i>
HF	20
CH ₂ =CF ₂	64
C ₆ H ₃ F ₃ (trifluorobenzene)	132
C ₁₀ H ₁₀ F ₄ (tetrafluoronaphthalene)	200
C ₁₄ H ₄ F ₅ (pentafluoroanthracene)	268
C ₁₈ H ₆ F ₆ (hexafluoronaphthalene)	336
CH ₂ =CF-CH=CHF	90
CH ₃ -CF-CH=CHF	91
CH ₂ =CF-CH ₂ -CHF ₂	110
CHF=CH-CF ₂ -CH=CHF	140
CH ₃ -(CF ₂ -CH ₂) _{<i>n</i>} -CF ₂	65(0), 129(1), 193(2), 257(3), 321(4)
CF ₂ =CH-(CF ₂ -CH ₂) _{<i>n</i>} -CF ₂	113(0), 177(1), 241(2), 305(3), 369(4)
CHF ₂ -(CH ₂ -CF ₂) _{<i>n</i>} -CH ₂ -CF ₂	115(0), 179(1), 243(2), 307(3), 371(4)
CH ₂ =CF-(CH ₂ -CF ₂) _{<i>n</i>} -CH ₂ CF ₂	109(0), 173(1), 237(2), 301(3), 365(4)
15 CHF=CH-(CF ₂ -CH ₂) _{<i>n</i>} -CF ₂	95(0), 159(1), 223(2), 287(3), 351(4)

importance of the individual reactions is influenced by the proportions of the monomer units. Specifically, HCl is likely to result from elimination involving adjacent -CF₂CFCl- (Scheme 8) either following initial C-Cl homolysis or by molecular elimination (Scheme 9).

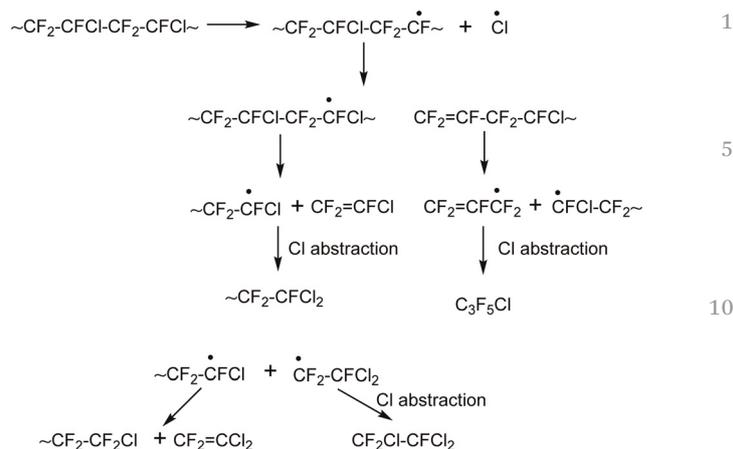
The degradation kinetics of PTFE and poly(ethylene-*alt*-TFE) copolymer (ETFE) was reported by Hondred *et al.* by TGA.¹¹⁴ They developed kinetic models describing the degradation of these (co)polymers from the activation energy, represented as a function of the extent of degradation. In the onset of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

Employing 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 a typical crystallinity of 60%.⁹⁷ Commercial grades of PFA possess high thermostability and melt in the temperature range of 300–315 °C (Fig. 15). These authors noted that PFA displays a higher activation energy than that of PTFE and PI as well as a higher equivalent mass loss at 333 °C compared to PTFE (at 250 °C), making it an excellent candidate for the fabrication of high performance cables with extruded insulation.

Actually, the thermolysis of ECTFE and PFA copolymers led to the formation of acids, which also identified in the case of



55 **Scheme 7** Mechanism of the decomposition of PVDF¹¹² (readapted with permission from Wiley).



Scheme 8 Thermal degradation of PCTFE⁹⁵ (readapted with permission from Elsevier).

PTFE and PCTFE. No major differences in the fluorinated acetic acid products or acid precursors (*e.g.*, TFA, CDFA, HFP and CPPF) were observed, suggesting that when all classes of FPs are subjected to thermal degradation, it will result in the production of fluorinated acids, and also to environmental precursors to C3 haloacetic acids to different degrees.

TFA has been well-identified in acid rain and reported in many studies, which are too many to discuss in detail. However, its formation is still 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, as illustrated in Fig. 16, where FP was burnt in a quartz vessel (boat) at 400–650 °C, followed by the detection and identification of the released products, including TFA.

Hence, the authors set up a laboratory simulation experiment to analyse the TFA content.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 heated to 500 °C and above. The 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 authors¹¹⁷ 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 the presence of 37.9–43.4 ng L⁻¹ TFA in rainwater in Beijing in 2014 (Table 4). The thermolysis of FPs contributed to 0.6–6.1 ng L⁻¹ TFA in rainwater, accounting for 1.6–14.0% of the TFA burden from all the precursors that were considered.

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 fluorinated compounds generated from the pyrolysis of PTFE by heating from 35 °C to 800 °C at 20 °C



Scheme 9 Thermal degradation of poly(CTFE-*co*-VDF) copolymer⁹⁵ (reproduced with permission from Elsevier).

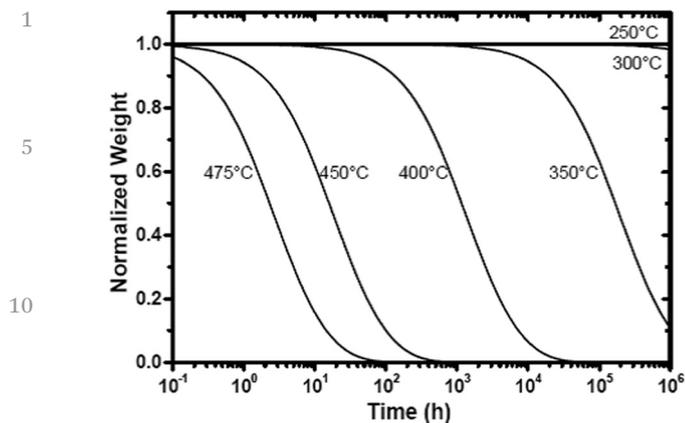


Fig. 15 Isothermal mass loss kinetics of PFA obtained by simulation.¹¹⁵

min⁻¹ in the absence or presence of various metals or salts (Scheme 10). These South African authors found that in the absence of salts, TFE was produced in 98%, while the nature of the salt may induce other released gases (Scheme 10 and Table 5) 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

Bhadury *et al.*¹²⁰ studied the flash pyrolysis of PTFE in a quartz assembly, while Hiltz¹²¹ 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 in a temperature window from -12 °C and 210 °C, while the temperature to use LR6316/15 and FR25/80 was in the range of -29 °C and 205 °C and -41 °C and 200 °C, respectively. As expected, PMVE reduced the *T_g* of the fluoroelastomer to -31 °C for FR25/80 (while that of FR17/75 was -13 °C).

TGA displayed similar weight loss (*ca.* 60%) for the LR6316/15 and FR25/80 elastomers, whereas the FR17/75 elastomer exhibited approximately 70% weight loss in the initial step. FR17/75 had greater residual mass than that of LR6316/75 and

Table 4 Gaseous TFA concentration in the fluoropolymer thermolysis products¹¹⁷ (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
Blank sample	521 ± 13	517 ± 29	525 ± 43	537 ± 21	520 ± 54	—

FR25/80 fluoroelastomers, which could be explained by the presence of fillers in FR17/75. The fingerprint of the thermogram of each fluoroelastomer was different. Fig. 17 presents a summary of the possible ways for the generation of some of the ions in the mass spectra of FR17/75.

The degradation products of the FR17/75 fluoroelastomer contained unique ions, differing in mass spectrometry by 20, 50, 64, and 100 units, corresponding to the loss of HF, CF₂, C₂H₂F₂, and C₂F₄ ions, respectively.

The degradation of another type of functional FP was also reported. Feng *et al.*¹²² studied the thermal decomposition of a Nafion[®] N117 membrane, which is an innovative ionomer processed from a copolymer based on TFE and a perfluorovinyl ether bearing a perfluorinated ether side chain bearing an SO₃H-end function. This typical perfluorosulfonic acid membrane (PFSA) electrolyte is widely employed in various chemical technologies including electrolyzers and proton exchange membranes for fuel cells (PEMFC) [*e.g.*, Mirai (Toyota),¹²³ Nexo (Hyundai), Clarity (Honda), Focus (Ford), X-trail (Nissan), and Chevy Electrovan (General Motors) vehicles,¹²⁴ FCVs]. Fuel cells are energy converters, which transform the chemical energy from an oxidation-reduction into clean electricity, water and heat. They have 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 attack on its polymer

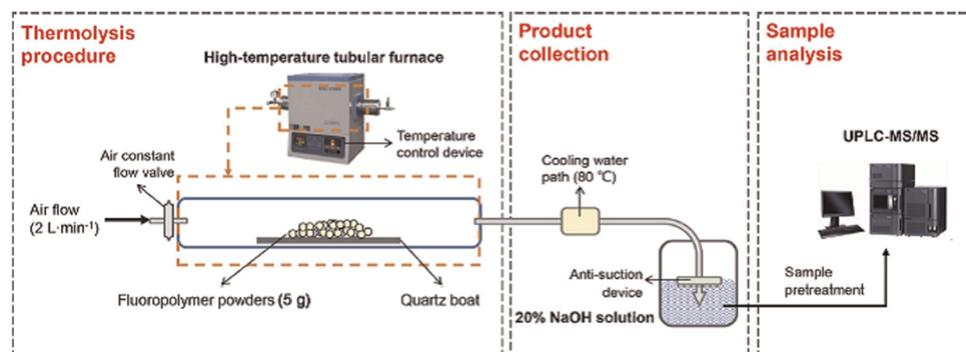
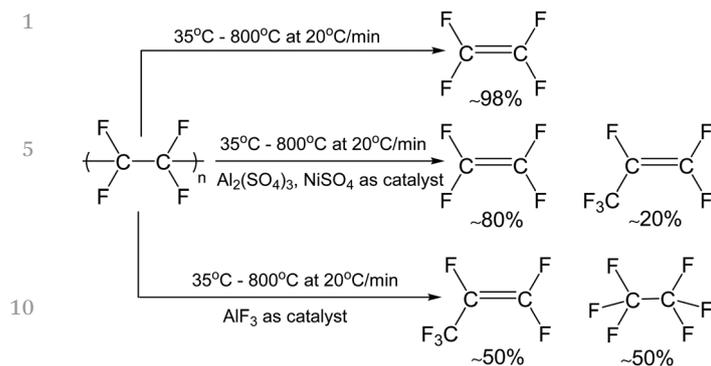
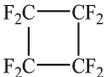


Fig. 16 Schematic diagram of the thermolysis experiment for various fluoropolymers¹¹⁷ (reproduced with permission from Elsevier).



Scheme 10 Thermal decomposition of PTFE in the absence or presence of various metals or salts (adapted from ref. 109).

Table 5 Various compounds released from the thermal decomposition of PTFE from 35 °C to 800 °C¹⁰⁹ (the abbreviations are defined at the end of the review) (adapted from ref. 109)

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

chains by electrochemically generated reactive oxygen species. These authors identified at least 20 thermolysis products in methanol and water (m/z fragments ranging from *ca.* 100 to 600) by means of liquid chromatography-electrospray ionization-tandem mass spectrometry (LC/ESI-MS/MS). The released fluorinated products (perfluorinated compounds, including PFCAs) were detected by an ion-chromatography system, while the thermal stability of the membrane was characterised by TGA. Hence, based on the 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 analytical evidence for the use of the LC/ESI-MS/MS method for characterising the degradation products of polymer electrolyte membranes.

Moreover, the degradation of this PFSA was reported and four graphical degradation mechanisms were proposed, as shown in Fig. 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 showed considerably improved durability. Furthermore, this improvement

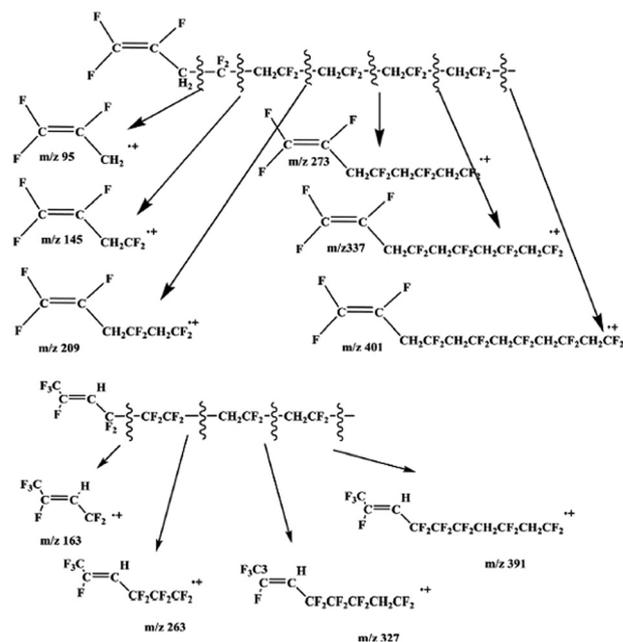


Fig. 17 Possible paths for the generation of some of the ions in the mass spectra of the major degradation products of poly(VDF-*ter*-HFP-*ter*-TFE) terpolymer FR17/75¹²¹ (reproduced with permission from Elsevier).

significantly increased with the release of the $-OCF_2CF(CF_3)$ group from the polymer dangling fragment.¹²⁶ This behaviour indicates the contribution of radical attack on the side chain to overall decomposition of the membrane (Fig. 18).¹²⁵

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

In 2005, Grot and Grot¹²⁸ pioneered the recovery of Nafion[®] membranes from the dissolution of used PFSA membranes in water and various solvents, and then heating the mixture under pressure, followed by the separation of the components.

Recently, the Chemours Company¹²⁹ announced three main goals to ensure a sustainable hydrogen economy involving PEMFCs, as follows: (i) to reach 60% absolute reduction of CO₂ emissions by 2030; (ii) to align with the climate goals (with the Paris 1.5 °C rule by process emission reductions, energy efficiency, and renewable energy) and (iii) to commit achieving net-zero CO₂ emission from operations by 2050. To achieve these goals, this company plans four main actions, as follows: (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

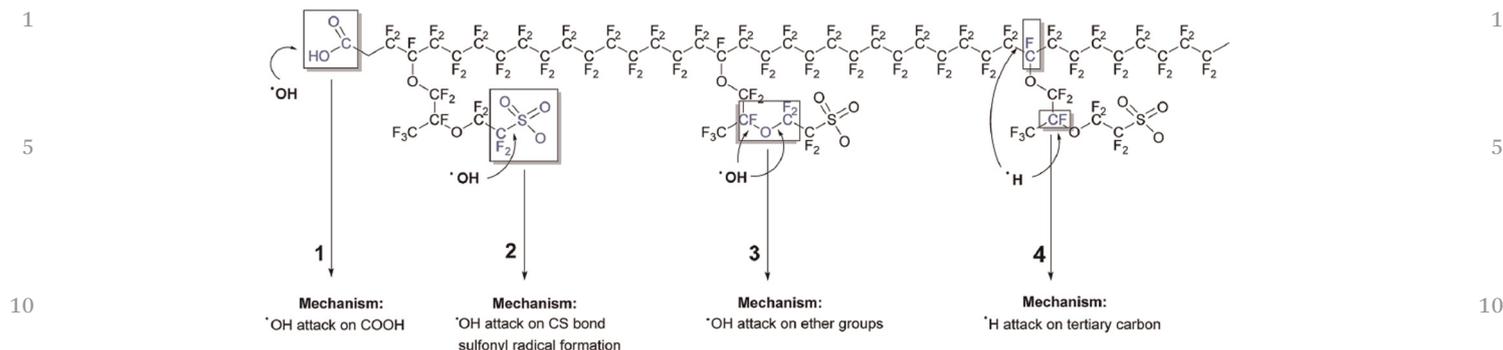


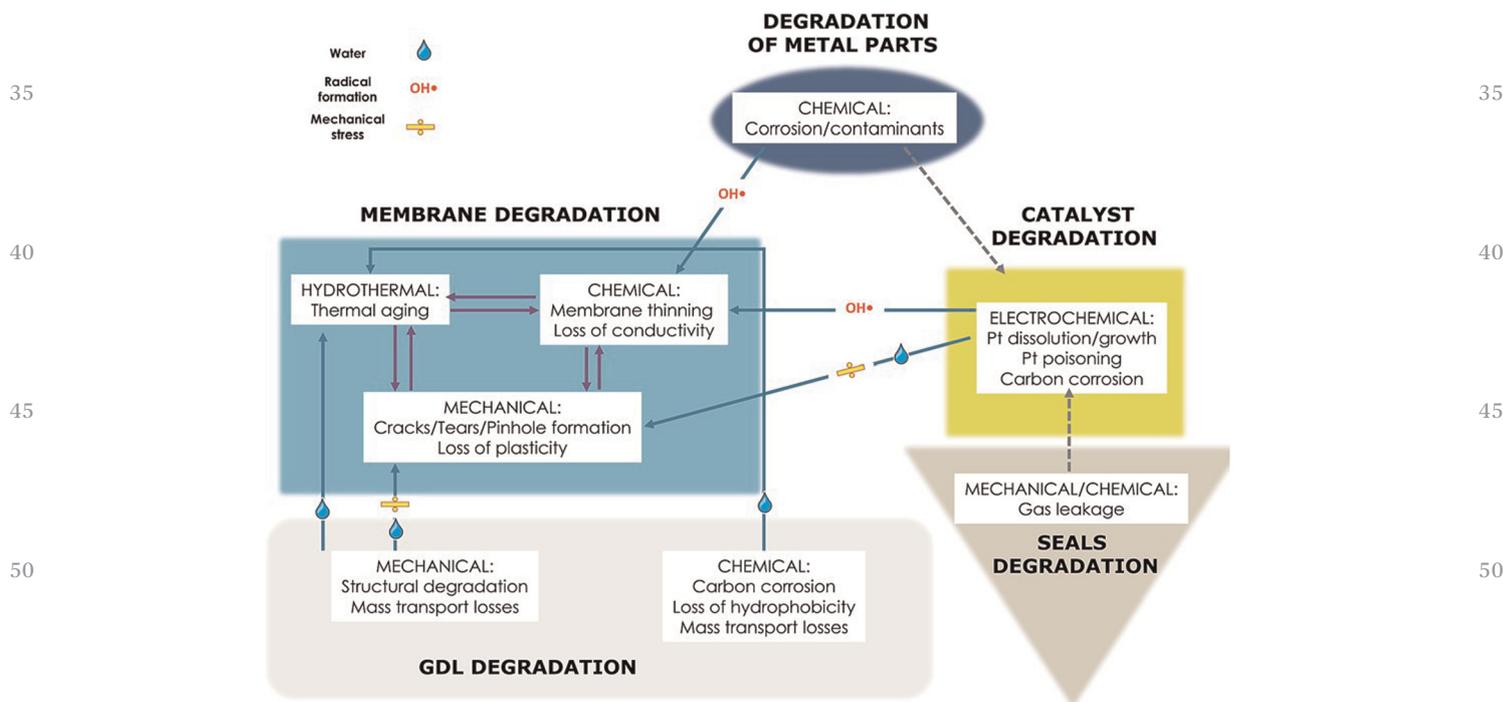
Fig. 18 Various mechanisms of HO• radical attack on Nafion® membranes¹²⁵ (reproduced with permission from The Royal Society of Chemistry).

15 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 the
process (ionomer broken down into elemental constituents and
20 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
25 above their melting point.⁵⁷ However, outside of normal, fore-
seeable use conditions, when FPs are extruded, injected, sin-
tered or calendared at temperatures much higher than their
appropriate processing temperatures, they may decompose.
Upon degradation, FPs generate volatile decomposition
30 products.¹³⁰ At 450 °C, the decomposition of PTFE only

proceeds at a slow rate on the order of 1% per hour. Alterna-
15 tively, significant degradation is only observed considerably
above the first-order transition temperature of the polymer
(329 °C).¹³¹ When the temperatures increase above suitable
processing temperatures, the rate of radical generation
increases, which may sufficiently degrade the polymer to
20 release dangerous gaseous by-products and polymer fume
fever.¹³⁰ Temperature, the presence of O₂, the morphology of
the polymer product, and the residence time at elevated tem-
perature are valuable parameters influencing the decomposi-
25 tion and the nature of the degradation products,¹³⁰ mainly
fluoroalkenes, hydrogen fluoride, oxides of carbon, and lower
molar mass FP particles. Similar to the above-mentioned stu-
dies, TFE is the main gaseous product observed from PTFE at
temperatures near 330 °C.



Scheme 11 Parameters influencing the degradation of perfluorosulfonic acid (PFSA) fuel cell membranes¹²⁵ (reproduced with permission from The Royal Society of Chemistry).

4.4. Incineration of FPs

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

The total penetration of FP waste by mass in mixed or commingled waste streams is typically very low (< 0.01%). Heat is directly applied to the FPs, which are contaminated (by soil, sediment, spent adsorbents, or waste), or liquids (water, wastewater, leachate, chemicals). The 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, the US EPA released a draft interim guidance on the destruction and disposal of PFAS.¹³⁴ Nowadays, this is an active area of research to evaluate the effective destruction temperatures and treatment time, the potential to generate products of incomplete combustion, stack gas analysis, deposition on 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 operations¹³⁵ (*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.

Regarding waste disposal options, energy costs, transportation costs, regulatory approvals, and final disposition of process, the waste residues should be evaluated given that they differ among incineration facilities.

Considering sustainability, the environmental footprint for incineration includes transportation and supplemental fuel for the incineration process. The incineration of contaminated soils, liquid waste, and investigation-derived waste (IDW) is energy-intensive and PFAS emissions, including potential PFAS combustion by-products, 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 to evaluate effective destruction temperatures and treatment time, the potential to generate products of incomplete combustion, stack gas analysis, deposition on 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. Although 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. Incineration or combustion differs from thermolysis in that a source of fuel is used to purposefully induce the 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 will result in the cleavage of most carbon-fluorine bonds. Alternatively, low-temperature burning of domestic waste, as an important source of furans and polychlorinated dioxins in the atmosphere, may analogously be a great source of fluorinated acids.

Several countries are currently using incineration. One example, achieved in Norway¹³⁶ though the municipal waste incineration is performed at *ca.* 850 °C, but the emissions of the FP degradation products from household waste incineration have not been studied to date. However, on the laboratory scale, severe degradation of FPs, mainly PTFE, were investigated in the temperature range of 700–1050 °C, leading to the release of CF₄, CHF₃, C₂F₆, TFE and HFP as the main products (Table 6).

As expected and mentioned in the section of pyrolysis, these generated products are strongly dependent on the incineration conditions such as temperature, moisture, oxygen content, and use of catalysts. A few surveys have been reported on the incineration degradation products of FPs besides 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-cyclic 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 their useful life, specifically as a result of the municipal incineration of PTFE.¹⁴² Although 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 on 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, including their 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 to the reactor to maintain a consistent thermal profile, as shown in Fig. 19.

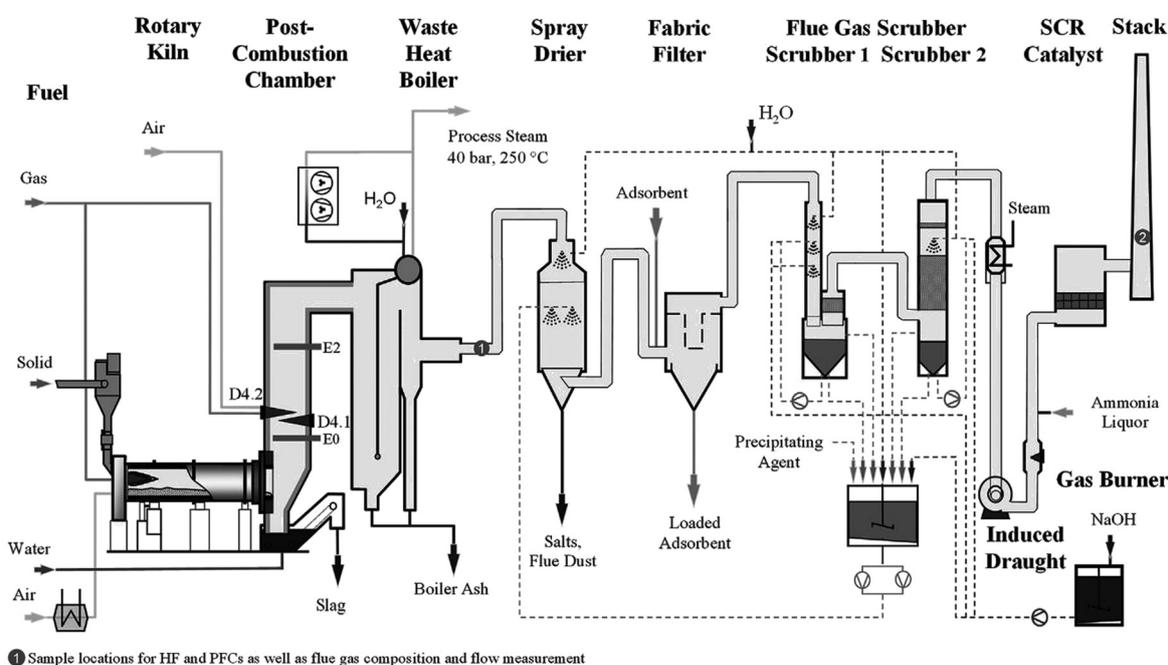
This study also attempted to evaluate 7 of 26 compounds to validate that PTFE almost entirely transforms fluorine into HF and a number of trace PFAS species in the concentration range of 0.3 to 24 µg Nm⁻³ using incineration under MSWI conditions.⁷² To reduce the probability of false results by

1 **Table 6** FPs and their main decomposition products at various temperatures from in the literature. In parenthesis: PFC-code¹³⁶ (reproduced with permission from Norwegian Institute of Air Research (the acronyms are defined at the end of the review))

Polymer	T (°C)	Main products	Ref.
PTFE	450	COF ₂ , HF	130
	400–500	TFE, HFP, PFIB	137
	500	HFP, TFA	36
	530	CF ₄ (PFC-14), C ₂ F ₆ (PFC-116), TFE, HFP, <i>c</i> -C ₄ F ₈ (<i>c</i> -OFB) (PFC-318)	138
	550	CF ₂ O, C ₂ F ₆ , CF ₃ CFO, C ₅ F ₄ , CF ₃ CF ₂ CFO, (CF ₂) ₃ O 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 ₂ F ₆ (PFC-116)	130
ETFE	850	HFP, TFE	101
	750–1050	C ₂ F ₆ (PFC-116), CF ₄ (PFC-14)	101
ECTFE	350	COF ₂ , PFBE, TFE, CO	130
FEP	500	TFA, CDFA	130
	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 ₂ F ₆ (PFC-116)	140

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 the PFAS concentration, flue gas samples were collected to test the compounds of interest after they cooled from *ca.* 850 °C 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. Although 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 given that the other 20 derivatives were below the detection limit. By using paired *t*-testing to determine the significance of these 11 compounds, the results showed no statistically significant evidence that the studied PFAS was noted during the incineration of PTFE. Based on 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 detected⁷² and that, within procedural quantitation limits, no statistically significant evidence was found that



1 Sample locations for HF and PFCs as well as flue gas composition and flow measurement

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

1 the studied PFAS were generated during the incineration of
PTFE. Therefore, MSWI of PTFE using the best available
technologies is not a relevant source of PFAS and should be
regarded as an acceptable form of waste treatment.

5 Moreover, Tsang *et al.* determined the unimolecular reaction rates to highlight that CF₄ molecules require 1440 °C for a little bit more than 1 s to achieve 99.99% destruction.¹⁴⁴ Therefore, CF₄ molecules represent a reference for the destruction removal efficiency testing of the required temperatures, times, and turbulence during incineration. Despite the ease of removing or oxidizing polar functional groups such as decarboxylation, the resulting products of incomplete combustion (PIC) are not well understood.¹⁴⁵

10 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 bypassing flame and packed bed reactor with Ca(OH)₂ to yield CaF₂.¹⁴² This approach provided a way to manage the HF, CO and CO₂ generated during decomposition in elevated pH media to investigate and characterise the reaction compounds.

15 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 release of HF as the only critical parameter. The limit values are for stack emissions.

20 Future work should investigate their incineration under a range of relevant conditions to more comprehensively determine the released substances and their amounts. Presently, this type of incineration study is underway (*e.g.*, by various companies including W.L. Gore Company¹⁴⁶). In addition, the practice of the open burning of FPs, or in this case any polymer, is unacceptable and unsafe. Alternatively, responsible incineration of FPs, adhering to regulatory guidelines, at the end of their life cycle is appropriate.

4.5. Smoldering

35 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 Although PFAS is commonly removed from water by sorption on carbon or other sorbents and many other techniques, as recently well summarised by the Interstate Technology and Regulatory Council (ITRC),¹⁴⁷ this 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. Major⁶⁹ found that granular activated carbon (GAC) could behave efficiently as a fuel and smolder at the 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

1 To avoid the possible formation of oligomers that present severe toxic and persistency issues, the total decomposition of FPs, while trying to minimize the release of greenhouse gases, will enable their total degradation. One possibility involves mineralization, which yields fluoride anions. Although 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 water¹⁴⁹ (*i.e.*, superheated water) as high-pressure liquid water in the temperature range of 100 °C and its critical temperature, 374 °C (while supercritical (sc) water is defined as water at temperature and pressure higher than the critical point: 374 °C and 22.1 MPa, respectively).^{149–155} Given that under 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.

5 In 2014, Hori *et al.*¹⁵⁰ described that PVDF could mineralize (*i.e.*, decomposed into F⁻ and CO₂) completely in sc water at 380 °C in the presence of a *ca.* 5.8-fold molar excess of O₂ relative to the fluorine or carbon atom content in PVDF. Furthermore, PVDF also led to complete mineralisation in subcritical water at 300 °C in the presence of H₂O₂, the amount of which was 31-fold molar excess relative to the fluorine and carbon contents in PVDF, respectively.¹⁵¹

10 Recently, a stronger treatment in basic medium favored this mineralisation.¹⁵⁵ To reduce the energy consumption, a lower temperature that enabled complete mineralisation was achieved by the same team using similar technology involving poly(VDF-*co*-HFP) and poly(VDF-*co*-PMVE) copolymers treated in subcritical water with the addition of KMnO₄.¹⁵³ As is known, KMnO₄ is a safe oxidizing agent, which is used in drinking water treatment plants to remove iron components and control the formation of trihalomethanes and other disinfection by-products.

15 This led to the *quasi*-complete mineralisation of PVDF at 250 °C as well as poly(VDF-*co*-HFP) and poly(VDF-*co*-CTFE) copolymers.¹⁵³ Table 7 summarizes the features of the mineralisation of these copolymers, while Scheme 12 presents the proposed mechanism. In these reactions, MnO₄⁻ was chemically modified into MnO₂. Compared to the above-mentioned method (combination of H₂O₂ and subcritical water), the reaction temperature to achieve complete mineralisation was reduced by 50 °C. Furthermore, these authors examined the formation of CaF₂^{153–155} from the reaction solutions to close the loop on the fluorine element, given that CaF₂ is the source for all the fluorinated compounds.

20 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 an excess amount of O₂¹⁵⁰ or a lower temperature in the presence of H₂O₂),¹⁵¹ VDF-

1 **Table 7** Decomposition of PVDF and VDF copolymers in subcritical water¹⁵³ (reproduced with permission from the American Chemical Society) 1

Entry	Polymer	Initial [KMnO ₄] (mM)	T (°C)	P (MPa)	F ⁻ (mol) [%]	[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]
5	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]
10	5	poly(VDF-co-HFP)	158	250	4.2	898 [96]	213 [24]		0.69	CHF ₃ (1.08) C ₆ H ₃ F 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]
15	8	poly(VDF-co-PMVE)	158	300	9.0	1.00 × 10 ³ [99]	299 [43]		1.04	n.d.	16.7 [2]

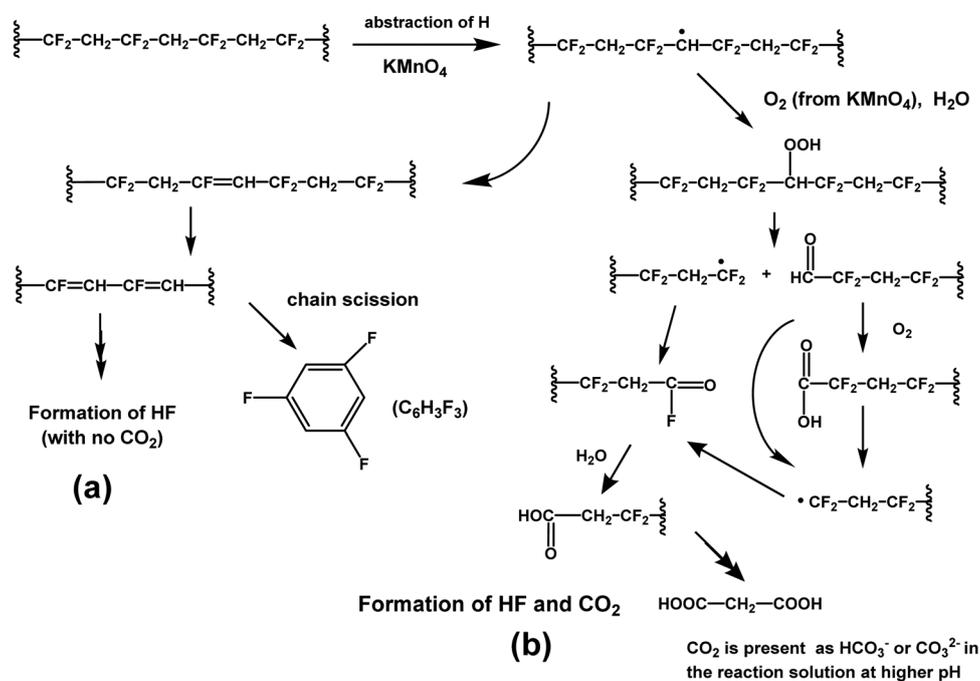
containing copolymers,¹⁵⁴ poly(VDF-*ter*-HFP-*ter*-TFE) fluoroelastomer¹⁵² and perfluorosulfonic acid (PFSA) membranes¹⁴⁹ (usually involved in ion-exchange polymer membranes, PEMFC, chloro-alkali process to produce chlorine and sodium hydroxide from brine, desalination for drinkable waters, *etc.*).

In addition, several authors reported that the degradation of PFSA membranes generates analogues of perfluoroalkanoic acids¹⁵⁶ and perfluoroalkane sulfonic acids.¹⁵⁷

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

More recently, Yanagihara and Katoha¹⁵⁸ used 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 *via* efficient mineralisation. However, this process seems a bit surprising given that it is well-known that liquid sodium can PTFE. In the first step, these polymers were decomposed to soluble alkaline fluorides *via* degradation in molten hydroxides at elevated temperatures (500 °C) and atmospheric pressure. In the latter step, CaF₂, which is an essential mineral for all organofluorine chemistry, was obtained by treatment of the former aqueous solution with CaCl₂. PTFE was mineralised using this strategy, as well as PVDF, PCTFE, and poly(VDF-co-HFP) copolymer. When PTFE was heated with a large excess of



55 **Scheme 12** Proposed reaction scheme for PVDF decomposition in subcritical water in the presence of KMnO₄¹⁵³ (reproduced with permission from the American Chemical Society). 55

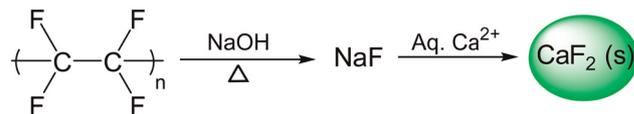


Fig. 20 Industrial supercritical water reactor for organic solvent treatment. This flow reactor can treat 1 metric tonnes waste per day. (This photograph was kindly provided by Organo Corporation (Tokyo). Permission for use was obtained from the company.)

NaOH at 500 °C for 3 h, 73.8% yield of CaF₂ was obtained (Scheme 13) with respect to the initial PTFE amount.

Actually, these temperatures are close to that 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, degradation should also occur, even without any base. These authors reported that (i) no decomposition was noted in the presence of molten NaOH below 400 °C, while ii) at 600 °C, the CaF₂ yields dropped to 46% (from 67% and 74% at 450 °C and 500 °C, respectively, Fig. 21).

For other FPs, under the same experimental conditions using NaOH, the CaF₂ 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 followed the order of 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 among the various tested FPs (*i.e.*, 140–145 °C), decomposed at 400 °C, giving the highest CaF₂ 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 O²⁻ generated from the molten NaOH. As well as being effective as a FP mineralisation reaction, this reaction involving molten NaOH



Scheme 13 Proposed procedure for the mineralisation of PTFE by molten NaOH¹⁵⁸ (readapted from The Royal Society of Chemistry).

also has the potential to treat other general-purpose polymers without any exhaust gas generation.

When the temperature increases to *ca.* 450 °C, the FP chains exhibit vigorous molecular motion, and chain scission occurs in the PTFE backbone. Subsequently, various small segments are generated *via* an unzipping mechanism.⁷⁹ The resulting small segments of the main chain undergo further scission to form oligomers and/or low molecular compounds. The obtained small molecules (*i.e.*, oligomers and monomers) then react with O²⁻, which attacks the carbon atom in a nucleophilic manner to generate CO₂ and eliminate F⁻.

5. Decomposition of FPs by irradiation

FPs can be affected by irradiation.^{159,160} Low molar-mass (M_n) PTFE micropowder is added to wax (*e.g.*, for use in automotive equipment, bike chain lubricants¹⁶¹ and printing machines) and is produced by radiation-initiated degradation. However, PFOA is produced as a by-product at concentrations greater than 25 ppb. Dams and Hintzer⁶¹ 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 formation of PFOA and could

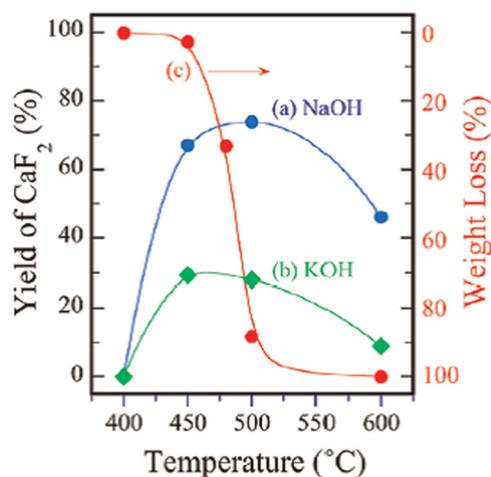


Fig. 21 Temperature dependence of PTFE degradation by molten alkaline hydroxides (curves a and b) and simple isothermal weight loss of PTFE (curve c). In each experiment, approx. 5 mmol of PTFE and an excess of MOH ($M = \text{Na}, \text{K}$) were placed in a crucible and reacted for 3 h at each reaction temperature¹⁵⁸ (reproduced with permission from The Royal Society of Chemistry).

1 **Table 8** Optimal experimental conditions and yields of CaF₂ for the mineralisation of PTFE and other fluorinated (co)polymers by molten NaOH¹⁵⁸ (reproduced with permission from The Royal Society of Chemistry)

5 (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

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upscale that manufacturing process for a novel low-*M_n* PTFE micropowder that contained traces of PFOA (less than 5 ppb). They could extend the production of the PFOA-free PTFE micropowder up to an 11 kg-scale. Fig. 22 presents the proposed mechanism for the formation PFOA by the irradiation of PTFE in an oxygen atmosphere. Irradiation under oxygen-free conditions resulted 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

1 alkyl radicals, occurs *via* β-scission to produce *R_f*-CF₃, *R_f*-CF=CF₂, 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 time, producing around 25 ppb PFOA (*i.e.*, REACH environmental limit¹⁵).

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 formation of PFOA became a minor component, and PFOA was formed at levels below the legal limit.

In contrast, when heat treatment was performed in the open atmosphere after irradiation (Fig. 22, process C), the peroxy radicals reacted with O₂ and water in the atmosphere to provoke thermal oxidative degradation, producing scission-

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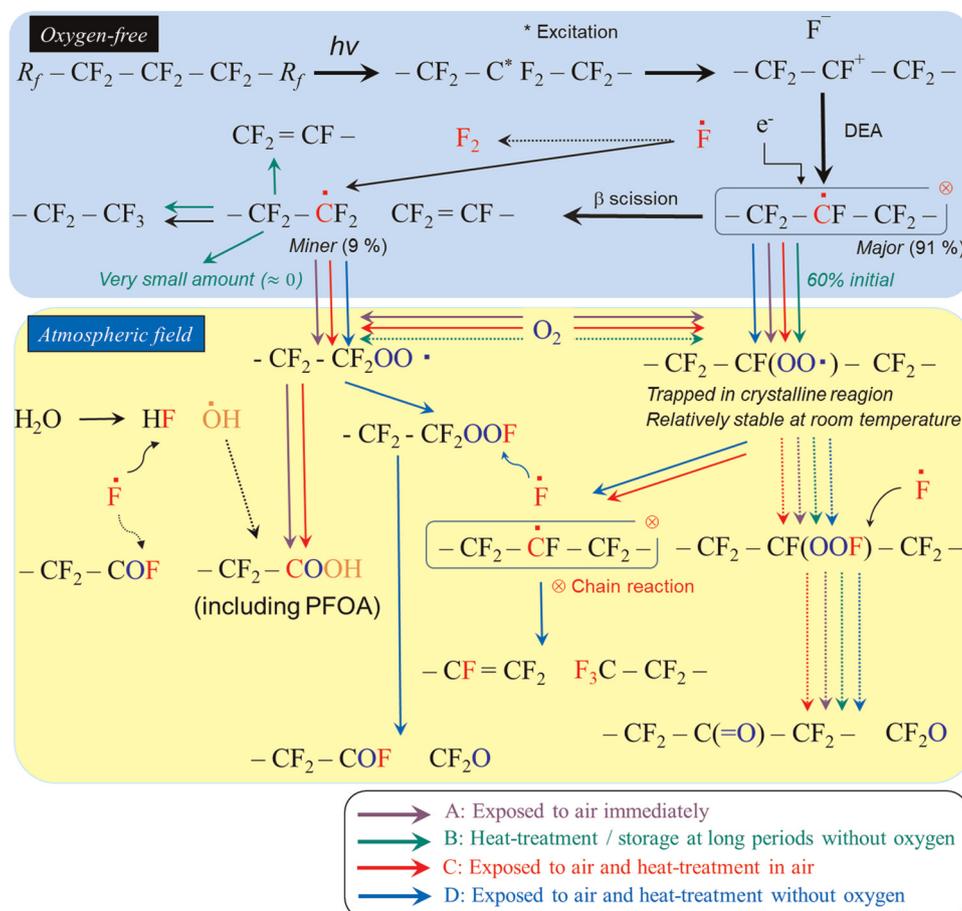
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Fig. 22 Reaction mechanism of PTFE irradiated in an oxygen-free atmosphere. Process A: exposure to air immediately after irradiation. Process B: heat treatment/storage for long periods in the absence of oxygen after irradiation. Process C: exposure 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 and dotted line: minor reaction (DEA stands for dissociative electron attachment)¹⁶² (reproduced with permission from Nature Group Publisher).

55

1 type peroxy radicals. Consequently, the released PFOA amount exceeded the environmentally regulated limit.¹⁶²

After irradiation, when the sample was exposed to the atmosphere, and then heat-treated without O₂ (Fig. 22, process D), both types of peroxy radicals were reconverted into alkyl radicals with very small amounts of chain-end radicals, as also previously reported.¹⁶⁶

In this case, because the radical yield was 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, were present as minor components, and the amount of PFOA released was much lower than the REACH limit.

The authors could extend their technology from the laboratory scale to a small pilot plant scale. Actually, 11 kg of PTFE was placed in tri-layer polymer bag comprised of PET/aluminum/polyethylene. Subsequently, the sample was 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. The PFOA content in the obtained PTFE micropowder was lower than 5 ppb (Table 10), similar to that noted from the above-mentioned lab-scale experimental result. Furthermore, even after a year stored in a closed container under ambient conditions, the PFOA content in this sample was still less than 5 ppb.¹⁶²

Specific irradiation tests were also achieved on Teflon[®] AF, an amorphous copolymer, and McKeen reported¹⁶⁷ the effect of the dose rate on its tensile strength, showing some progressive failure from 20 to 100 kGy (Fig. 23).

Alternatively, Van der Walt and Bruinsma¹⁰⁶ 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 in the vessel, where depolymerisation occurred. This continuous process enabled the production of TFE, hexafluoroethane, HFP, and OFCB from PTFE waste. The reactor could operate at various temperatures (ranging from 600 °C to 900 °C) as well as various pressures (5–80 kPa). Under certain conditions, a high TFE amount (>94%) was obtained concomitantly with a small amount of by-product.

Stefani *et al.*¹⁶⁸ compared the photo-oxidation degradation (which further favored the accumulation of a low amount of contaminants) 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

Table 10 Effect of re-heating of PTFE micropowder in air, which 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

climatic situation corresponding to Southern Italy (period considered: 15 years). The chemical contamination (assessed from titration of sulfur, iron and chlorine elements) of both films were reported after 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 by 5 to 10-times, with the further advantage of a significant recovery value for the used sheets.

Actually, the 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 due to their high chemical and ageing stability). One example is the case of poly(fluoroacrylate)s studied by Liu and Avendaño.¹⁶⁹ These polymers possessing ω -perfluorinated dangling moieties led to the formation of 8:2 fluorotelomer derivatives (Scheme 14), while several studies reported the decomposition and release of the fluorinated side chain under various conditions.^{18,170–173}

Moreover, FPs containing oxidizers have also been used in pyrotechnic compositions though fluorinated oxidizers, but less explored for metalised propellants and explosives despite their 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 these systems, including gases, polymers, and inorganic compounds, especially energetic formulations involving metals and FPs (Fig. 24). The characteristic morphologies and reaction sequences were observed in different metal-fluorinated oxidizer composites. Procedures probing the ignition and combustion of metal-fluorinated oxidizer composites under laboratory conditions were also reviewed, highlighting flash heating, impact, and shock ignition. Finally, several practical tests for energetic formulations have been described and the authors suggested the reaction mechanisms expected to govern ignition and combustion in various metal-fluorinated oxidizer composites.

Table 9 Various emitted PFCAs after γ -irradiation of 11 kg of PTFE with a 150 kGy-dose in air (reproduced with permission from Nature Group Publishing)¹⁶²

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

^a Acronyms are defined in the list at the end of the review.

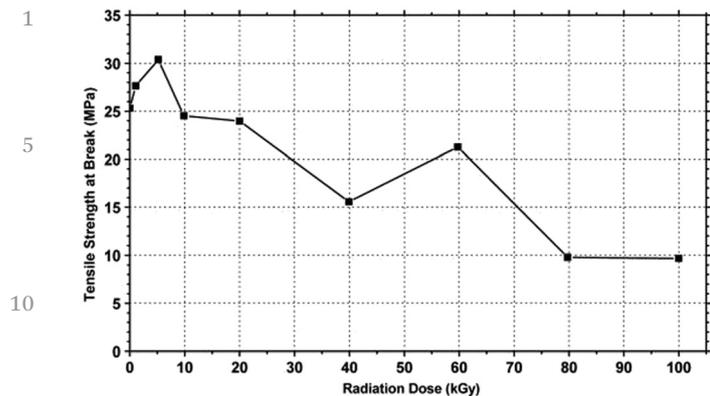


Fig. 23 Tensile strength at break versus radiation dose of DuPont PTFE (Teflon[®]AF1600) irradiated films¹⁶⁷ (reproduced from permission from Elsevier).

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 years¹⁶⁸

Film type	Cumulated film surface area (m ² ha ⁻¹)	Cumulated waste quantity range (kg ha ⁻¹)
LDPE or EVA, B class	195 000	22 669–27 203
LDPE or EVA, C class	130 000	18 135–21 158
LDPE or EVA, D class	91 000–104 000	14 810–19 344
LDPE or EVA, E class	65 000	12 090–13 601
ETFE	13 000	2210–2431

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, which were well-reviewed by the Interstate Technology and Regulatory Council.¹⁴⁷ Although these methods can be used to treat fluorinated waste, smoldering is a self-sustaining, and therefore is 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. In this case, the effectiveness of this process is dependent on 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 the successful destruction of toxic PFAS compounds, given that 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 complete degradation.^{72,73} Alternative methods to incineration such as mineralisation (see Section 4.6) of FPs during thermal treatment, or plasma-based water

treatment, are also being investigated given that they may be safer and more efficient to treat waste.

At its 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 is 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.

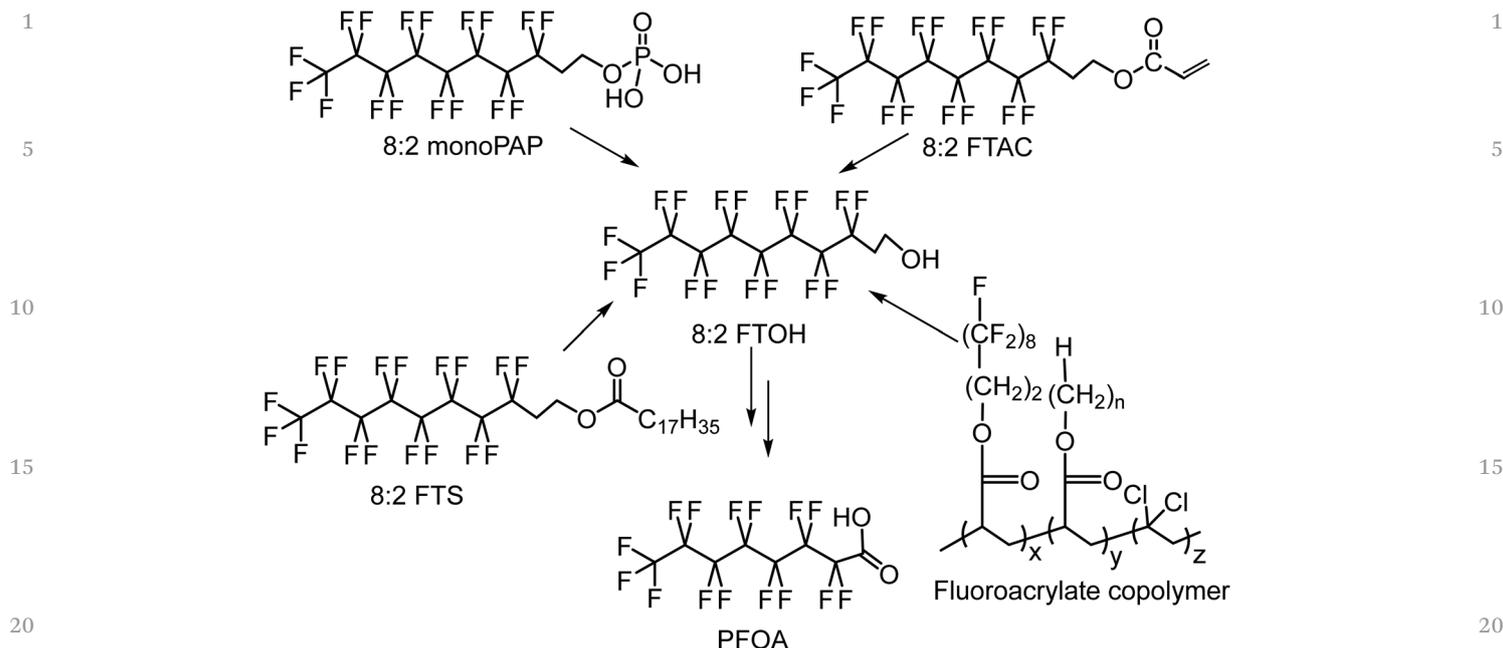
To improve the properties of PTFE, it is often compounded with glass fibers, carbon fibers, coal/soot, bronze, steel, molybdenum sulphide or polymers such as polyimides or poly(phenylene sulphide).^{79,178} As also observed in the above-mentioned processes (Section 3.2), the primary decomposition products are TFE and difluorocarbene radicals. Further products are formed by secondary reactions depending on the 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 such as perfluoroisobutylene (PFIB) or fluorophosphene are also formed under certain reaction conditions.

The global situation is represented in Fig. 25,⁹ showing that overall, *ca.* 23.5 kt of FP waste was collected in 2020 (<0.01% of the total waste collection). In comparison, about 29 450 kt of plastics was 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 was either thermally or (co-)incinerated destructed, while 3.1 kt (13.1%) was landfilled. Finally, 0.81 kt was collected separately for recycling, whereas a significant proportion was exported for recycling (*e.g.*, to Asian countries).⁴⁸

7. FPs fulfil 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 a basic consensus exists according to the following criteria.

(i) High number average molar mass (M_n) and oligomer content are the most commonly used criteria for PLC assessment. The EU assessment report¹⁸⁰ 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 percentages of oligomer, “*the distribution of potential health concern polymers showed an increased incidence of higher oligomer content, which began at 5% for <1000 Da and 2% for <500 Da oligomeric content.*”¹⁷⁹



Scheme 14 Illustration of microbial degradation of poly(fluoroacrylates) that generate 8:2 fluorotelomer derivatives.¹⁶⁹ (Reproduced with permission from Elsevier.)

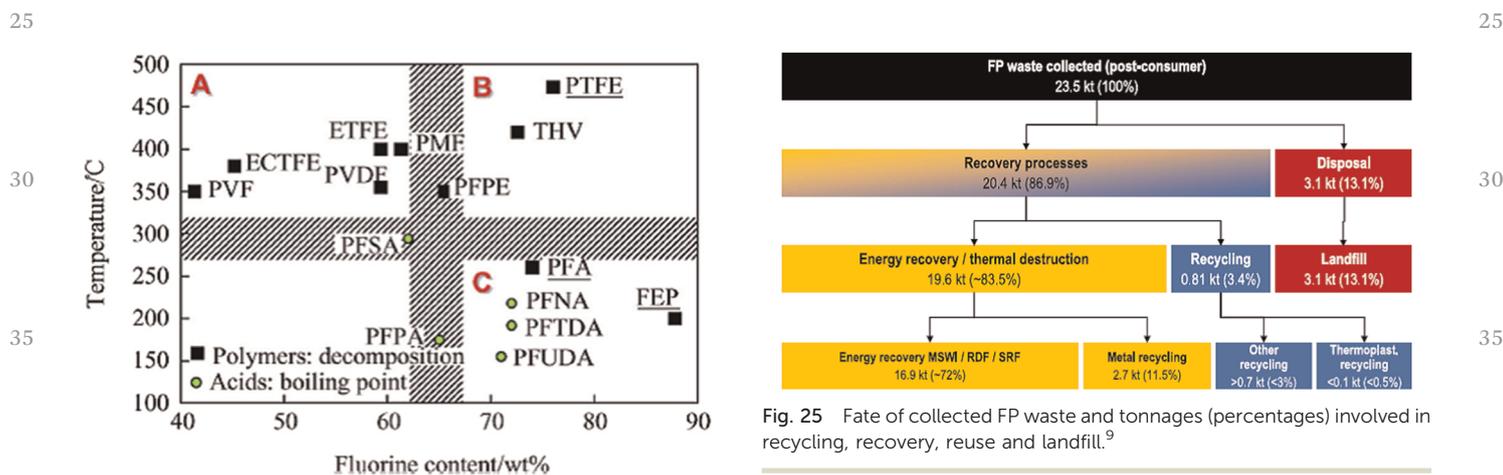


Fig. 24 Fluorinated polymers and acids based on their fluorine content and decomposition temperatures or boiling points¹⁷⁴ (PVF, PFNA, PFSA, PFPA, PFPE, PFTDA and PFUDA represent poly(vinyl fluoride), perfluorononanoic acid, perfluorosebacic acid, perfluoropentanoic acid, perfluoropolyether, perfluorotetradecanoic acid and perfluoroundecanoic acid, respectively. (Reproduced with permission from Elsevier.)

(ii) Reactive functional group (RFG) requirements. The RFG categories are low, moderate and high concern. Indeed, RFGs in the moderate concern category have evidence of reactivity in biological and/or aquatic media but their effects are not severe enough to place the functional group in the high concern category. If there is no, insufficient or contradictory information on an RFG, by default it is grouped in 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^{-1} .

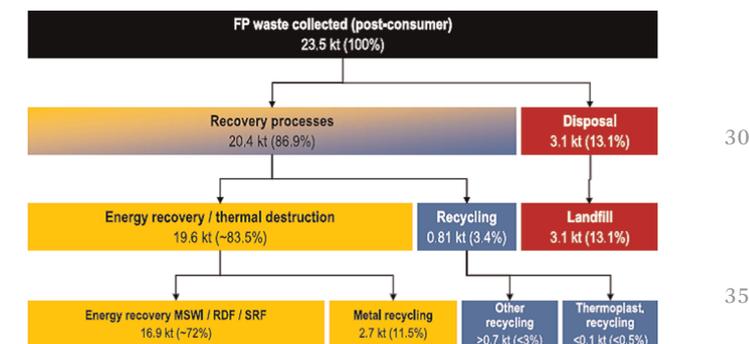


Fig. 25 Fate of collected FP waste and tonnages (percentages) involved in recycling, recovery, reuse and landfill.⁹

(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 these 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 ($\geq 10\,000 \text{ g mol}^{-1}$); and not have any known hazard classification.

FPs satisfy the PLC criteria related to RFGs and RFG ratio to M_n .^{180–182} PTFE typically has a terminal $-\text{CF}_3$ group,¹⁵ which is not an RFG. When this is not the case, the most common terminal group is $-\text{COOH}$, where M_n is an important predictor of biological effect because very large molecules ($> 1000\text{--}10\,000 \text{ Da}$) 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 can 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 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 these reactions/degradations.¹³

Based on these relevant properties and above-mentioned PLC criteria, Henry *et al.*¹⁵ provided some evidence 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 critical to the potential of a polymer to affect human health and the environment, given that they may migrate out of the polymer and cross the cell membrane to potentially react with biomolecules.

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 was 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.” However, in the case of high molar mass FPs, these characteristics are not observed (Table 12).

For PFAS and PFCA, the US EPA suggests clarification about the nature of the linkage, stating “How these materials are incorporated in the polymer is immaterial (they may be counterions, 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 US EPA review, the presence of the $-CF_3$ group is relevant given that it is a structural alert to consider potential degradation products. The US EPA¹³⁴ may make a determination whether the potential degradation of the polymer considered displays an unreasonable risk to human health and the environment under the Toxic Substances Control Act (TSCA). As shown in Table 12, these FPs are not subject to degradation.

With respect to applicability, among the FPs and as an example, PTFE is not a substance currently registered under REACH regulations, which usually gives the definition of a polymer substance as “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, similar to 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) will be applicable. Further, PTFE is highly stable in the environment and is resistant to thermal degradation. It is stable for years at temperatures up to 260 °C^{57,130} because it is stable to hydrolysis, oxidation, and light, as well as to anaerobic and aerobic degradations.¹⁸⁹ Therefore, PTFE fulfils the persistence criterion proposed by UBA. Advantageously, similar to most FPs, PTFE is insoluble in water, and therefore is not mobile in the environment. Using the descriptive solubility table by the US Pharmacopeia, the water solubility of PTFE can be classified as insoluble ($1-10^{-5}$ mg L⁻¹ or 0.01 mg L⁻¹) to very slightly soluble (10^{-4} mg L⁻¹ or 0.1 mg L⁻¹).¹⁹⁰ The mobility of PTFE is 1000 to 10 000 lower than the mobility criterion proposed by UBA. Therefore, PTFE does not fulfil the mobility criterion proposed by UBA and will not be classified as a PM or PMT substance.

Another advantage of PTFE deals with its non-toxicity. Actually, the average M_n of PTFE is too high (several million) for it to cross the cell membrane, which means it is not bioavailable or toxic. PTFE has been tested extensively in the USA and European Union to assess its 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 such as PTFE exhibit vastly different properties than other PFAS. Therefore, they are truly a separate class of materials that must be evaluated based on their own merits.

More recently, the American Chemical Council prompted the Fluoropolymer Industry Group (Fluoropolymergroup) to investigate a similar study on 14 additional fluorinated

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 ^a	Not detected	< 2% wt/wt (20 000 ppm)
Residual monomers ^b	Not detected	No limit established by OECD, 2009
Low molecular weight leachables & extractables	2 ppm ^c	No limit established by OECD, 2009

^a Polymers with potential health concern have an increased incidence of higher oligomer content, which begins at 5% for <1000 Da and 2% for <500 Da oligomeric content (OECD, 2009). The table lists the lower limit of 2%. ^b The data set used by OECD¹⁷⁹ to establish that the PLC criteria are insufficient to establish a universal limit for all residual monomers, although the residual monomer content was established as a PLC criterion.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 ^c Isopar K, an unavoidable ambient air contaminant adsorbed to PTFE fine powder, was detected at ≤ 2 ppm.

(co)polymers.¹⁸² FPs and the Stockholm Convention persistent organic pollutant (POP) criteria meet the persistence criterion only, not the bioaccumulative, toxic, and mobile criteria. Actually, their physico-chemical properties prevent their bioavailability, bioaccumulation, toxicity, and degradation. Presently, 96% of FPs fulfil these 13 PLC criteria.

Following the PLC criteria, the circular economy of FPs has not been studied except in one peculiar report by 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).

The Conversio report⁹ lists the treatment of FP waste by industry segments (automotive, aerospace, and chemical industries, electronics and semiconductors¹⁹¹) 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).

Lohmann *et al.*³⁰ identified and reported issues for environmental and human health resulting from possible emissions during the life cycle of FP (*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 bioinert, 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. Thus 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 compared to other polymers when exposed to harsh chemistries and high temperature. In addition, since the Challenger disaster in 1986, all the shuttle packing and gaskets have been made of fluoroelastomers. Moreover, FPs involved in electronics¹⁹¹ can also resist aggressive media in which all other materials fail. Actually, most of the FPs are safe during 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 FPs.

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

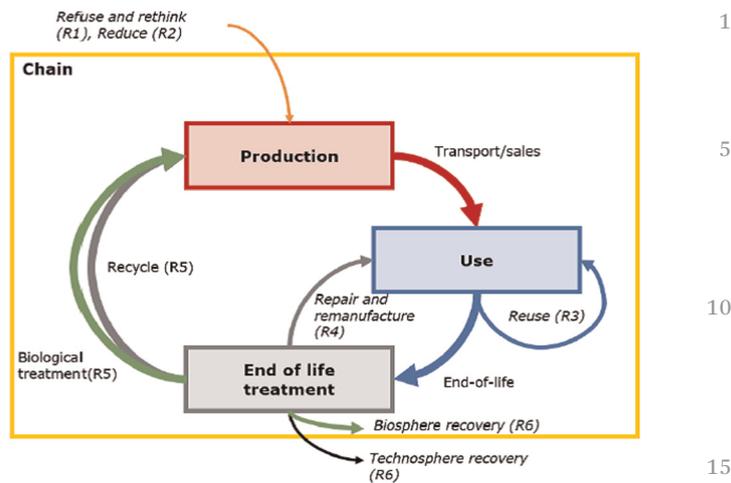


Fig. 26 Schematic view of possible flows of materials in a circular economy⁴ (reproduced with permission from the European Topic Centre Waste and Materials in a Green Economy).

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 was only 3.4% for FPs (yearly production of 320,300 tons in 2018).^{9,199} Although the recycling of clean FPs (*e.g.*, PTFE), FEP, PFA and PVDF waste or scraps generated during 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, given that these FPs are typically contaminated by other fillers and substances, which makes their recycling difficult. Moreover, the very slow decomposition of PTFE occurs above the application temperature of 260 °C for months. Alternatively, to favor its significant degradation, 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, total decomposition is observed without generating any PFAS. In December 2020, USEPA¹³⁴ released a draft interim guidance on the degradation and disposal of PFAS. This active area of research enables the evaluation of effective destruction temperatures and treatment time, the potential to generate products of incomplete combustion, stack gas analyses, deposition on land, and other risk factors. In addition, on melt processible polymers, reactive extrusion has been reported to be versatile technology to recycle these materials²⁰¹ and can be adapted to FPs.

To overcome the possible issues associated with incineration, recent alternative processes regarding the thermal treatment (mineralisation to release fluoride anions, precursor of CaF₂ as the starting point of fluorine chemistry) of FPs either under subcritical water or with molten sodium are 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

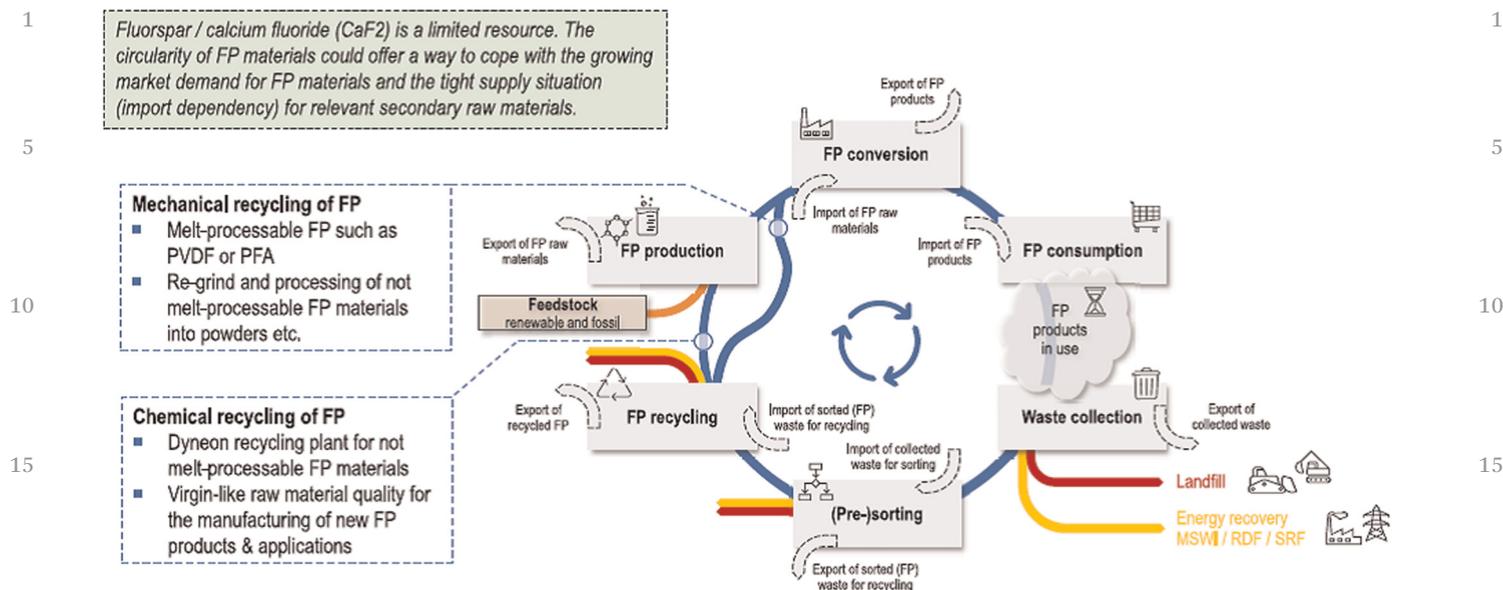


Fig. 27 Circular economy situation of FPs: lifecycle of FPs from feedstock extraction to end of life.⁹

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 Although the dossier is still under evaluation,²⁰² the restriction of FPs under REACH regulations may hamper the EU strategic sustainability ambition.²⁰³

Nevertheless, data showed that FPs (especially PTFE) have been extensively tested to satisfy US, Japanese⁴⁸ 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 only meet the persistence criterion, not the bioaccumulative, toxic, and mobile criteria.

Actually, due to the inertness, thermal, chemical, photochemical, hydrolytic, and biological stability of FPs (especially PTFE), they 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 FP manufacturers, and thus far, 96% of FPs fulfil 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 can be explored in future work. Research is needed to determine if emissions from the thermal disposal of FPs at temperatures consistent with OB, OD, or incineration contain PFAS. Furthermore, methods for the thermal degradation and

waste treatment of polymers containing PFAS can be greatly expanded 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, and activators, 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 bio-sourced derivatives for a couple of years.²⁰⁰ The toxicological and environmental properties (e.g., persistence, bioavailability, and mobility) of these alternatives merit further studies.

Although the demand for FPs is still increasing,²⁰⁴ future work should deal with FP manufacture, highlighting safety, health, and environmental management practices under applicable regulations. Also, substances used in FP manufacturers and their human health and environmental attributes should be assessed.

List of acronyms and abbreviations

APFO	Ammonium perfluorooctanoate
CDFA	Chlorodifluoroacetic acid
CPFP	Chloropentafluoropropene
CRM	Chemical recycling to monomers
CTA	Chain transfer agent

1	CTFE	Chlorotrifluoroethylene
	DCFB	Dichloroperfluorobutanoic acid
	DCFP	Dichloroperfluoropentanoic acid
	DCHFBCB	1,2-Dichlorohexafluorocyclobutane
5	DCTFP	1,3-Dichlorotetrafluoropropene
	DFA	Difluoroacetic acid
	DMA	Dimethyl acetamide
	DPn	Degree of polymerisation
	DSC	Differential scanning calorimeter
10	EB	Electron beam
	ECTFE	Poly(ethylene- <i>alt</i> -chlorotrifluoroethylene)copolymer
	FDCA	Fluorodichloroacetic acid
	FEP	Poly(tetrafluoroethylene- <i>co</i> -hexafluoropropylene)poly(TFE- <i>co</i> -HFP)
15	FP	Fluoropolymer
	HFP	Hexafluoropropylene
	ITRC	Interstate technology and regulatory council
	LCA	Life cycle assessment
	MFA	Monofluoroacetic acid
20	MSWI	Municipal solid waste incineration
	M_n	Average molar mass in number
	NMR	Nuclear magnetic resonance
	OECD	Organisation of Economic Co-operation and Development
25	OFCB	Octofluorocyclobutane
	PCTFE	Poly(chlorotrifluoroethylene)
	PEG	Poly(ethylene glycol)
	PEMFC	Proton exchange membranes for fuel cells
	PFA	Poly(tetrafluoroethylene- <i>co</i> -perfluoropropylvinyl ether)poly(TFE- <i>co</i> -PPVE)
30	PFCA	Perfluorocarboxylic acid
	PFDA	Perfluorodecanoic acid
	PFDoDA	Perfluorododecanoic acid
	PFHpA	Perfluoroheptanoic acid
35	PFHxA	Perfluorohexanoic acid
	PFIB	Perfluoroisobutylene
	PFNA	Perfluorononanoic acid
	PFOA	Perfluorooctanoic acid
	PFOS	Perfluorooctane sulfonic acid
40	PFPeA	Perfluoropentanoic acid
	PFPEs	Perfluoropolyethers
	PFTeDA	Perfluorotetradecanoic acid
	PFTrDA	Perfluorotridecanoic acid
	PFUnDA	Perfluoroundecanoic acid
45	PLC	Polymer of low concern
	PMT	Persistent, mobile and toxic
	PMVE	Perfluoromethyl vinyl ether
	POP	Persistent organic pollutants
	PPRA	Processing and recycling aid
50	PTFE	Poly(tetrafluoroethylene)
	PVDF	Poly(vinylidene fluoride)
	REACH	Registration, evaluation, authorisation and restriction of chemicals
	RT	Room temperature
55	SVHC	Substances of very high concern
	TCTFE	1,1,2-Trichloro-1,2,2-trifluoroethane

	1,1,3-TCTFP	1	
	1,1,3-Trichlorotrifluoropropene		
	TFE	Tetrafluoroethylene	
	TFA	Trifluoroacetic acid	
	TPE	Thermoplastic elastomers	5
	TSCA	Toxic substances control act	
	VDF	Vinylidene fluoride	
	VF	Vinyl fluoride	

Conflicts of interest



Q8

Acknowledgements

H. H. thanks the financial support from Japan Science and Technology Agency (JST) CREST grant number JPMJCR21L1 and BA thanks the French Fluorine Network (GIS) and co-workers cited in the references. The authors thank the Organo Corporation (Tokyo) to grant the permission to reproduce the reactor in Fig. 20.

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