

Christopher Correnti

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CHEMISTRY OF FLUOROCARBON ELASTOMERS

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1. GENERAL INTRODUCTION

Fluoropolymers, although discovered 50 years ago, are still growing in volume and in new compositions to meet industrial needs. They represent an

active field of research where there is a great promise for new discoveries in the form of macromolecules with unusual properties. A greater understanding of this fascinating area of polymer science will lead to new applications.

Amorphous compositions having glass transition temperatures below room temperature represent a small segment of the fluoropolymer field. These materials, having little or no crystallinity, derive their strength by being crosslinked into a permanent network. They are used predominantly in sealing applications in hostile environments requiring extreme resistance to oxidation, high temperatures, aggressive fluids and chemicals. Although quite expensive relative to other elastomeric materials, their exceptional properties make them the most effective and least costly answer to sealing problems demanding resistance to corrosive high temperature environments. Fluoroelastomeric parts are extensively used by the aircraft, aerospace, automotive, chemical, petroleum and energy industries. The higher performance requirements in these industries have created greater opportunities involving fluoroelastomers.

This paper will summarize only the chemistry of the commercial fluorocarbon elastomers and those which are currently under development. These fluoroelastomers are characterized by having carbon-carbon bonds in the backbone. They also share some of the same monomers. The similarities extend to the crosslinking chemistry of these materials and the physical properties obtained upon curing. Fluorosilicones and fluorophosphazenes are very different in chemistry from the carbon-carbon fluorocarbon elastomers and they will not be described. The same is true with the alternating copolymers made by copolymerizing trifluoronitrosomethane with tetrafluoroethylene,¹ the poly(perfluorothioacyl fluorides)^{2,3} and perfluoroalkyltriazines.⁴ These latter fluoroelastomers have some serious deficiencies and they have not been developed commercially as yet.^{5,6}

The purpose of this review paper is to describe the chemical structures of the various fluorocarbon elastomers, the monomers used, the polymerization techniques utilized and the crosslinking chemistry developed for curing these materials. The information sources searched include scientific and technical publications as well as patents and trade literature. An attempt has been made to cover the literature reasonably well to the middle of 1987.

2. FLUOROELASTOMERS

2.1. *Chemical structures*

Homopolymers derived from tetrafluoroethylene (TFE) or vinylidene fluoride (VF_2) are long chain macromolecules with high crystallinity which are unsuitable as elastomers. Copolymers of TFE or VF_2 with suitable fluoromonomers have reduced crystallinity and are elastomeric, amorphous materials

	$\begin{array}{c} \text{CF}_3 \\ \\ \text{CF}_2=\text{CF} \end{array}$	$\begin{array}{c} \text{ORf} \\ \\ \text{CF}_2=\text{CF} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CH} \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ \text{CF}_2=\text{CF} \end{array}$
$\text{CF}_2=\text{CH}_2$	x	x (+ TFE)		x
$\text{CF}_2=\text{CF}_2$	x (+ VF_2)	x	x	

FIG. 1. Combination of two or more fluorocarbon monomers to give elastomeric structures.^{7,8} The sign X indicates commercially available fluoroelastomers.

with low intermolecular forces. Figure 1 shows the monomers which constitute today's commercially important fluorocarbon elastomers. In order to confer elastomeric properties, the basic monomers VF_2 and TFE are copolymerized with other monomers which have a certain topological similarity, a bulky group attached to the vinyl functionality. The X's indicate monomer combinations which give commercially available fluorocarbon elastomers. In some cases an additional monomer (cure site monomer) is added in small amounts to render curability to the composition.

The present knowledge of rubber elasticity and of the solid-state behavior of organic polymers allows us to set out general structural characteristics necessary to make useful elastomers. Long, linear chain molecules of high intrinsic flexibility are desirable over those which are highly branched. Branching often leads to slow recovery, particularly at low temperatures, and large hysteresis loops in the stress-strain curves of the materials. The absence of groups exhibiting strong intermolecular forces and absence of crystallinity are very important to minimize intermolecular attraction and keep the energy barriers low between conformational states of the chain. Since the polymers are amorphous, the elastomers initially consist of randomly coiled macromolecules which deform on stretching and recover upon removal of force. In order to ensure complete recovery from large strains and avoid occurrence of a large permanent set, it is important to establish a permanent three-dimensional network.⁹

2.2. Syntheses of perfluorovinyl ether monomers

Most of the monomers shown in Fig. 1 are commercially available and need no further elaboration (Table 1). Some of the perfluorinated alkylvinyl ethers,

TABLE 1. Structural formulas of fluoromonomers

$\text{CH}_2=\text{CF}_2$	Vinylidene fluoride (VF_2)
$\text{CF}_3\text{CF}=\text{CF}_2$	Hexafluoropropylene (HFP)
$\text{CF}_2=\text{CF}_2$	Tetrafluoroethylene (TFE)
$\text{ClCF}=\text{CF}_2$	Chlorotrifluoroethylene (CTFE)
$\text{CF}_3\text{CF}=\text{CFH}$	1-Hydropentafluoropropylene (HFPE)
$\text{ROCF}=\text{CF}_2$	Perfluoroalkyl vinyl ethers (PFVE)

3. FLUOROELASTOMERS DERIVED FROM VINYLIDENE FLUORIDE COPOLYMERS

3.1. *General description*

Most commercially available fluoroelastomers consist of copolymers of vinylidene fluoride (VF_2) with hexafluoropropylene (HFP) and optionally tetrafluoroethylene (TFE).¹⁴⁻¹⁷ Presently approximately 12 million lb/yr of fluoroelastomers of these compositions are sold worldwide. In very special applications, other monomers like perfluoroalkyl vinyl ethers (Rf-O-CF=CF_2), chlorotrifluoroethylene (CTFE) and 1-hydropentafluoropropylene (HFPE) have been co- or terpolymerized with vinylidene fluoride to give specialty rubbers. These highly fluorinated polymers containing 62–70 wt% fluorine have remarkable resistance to flame, chemicals, solvents and oxidative attack. The stability has been attributed to the strength of the carbon–fluorine bond compared to that of the carbon–hydrogen bond, to steric hindrance due to the presence of fluorine and to strong van der Waals forces between hydrogen and fluorine atoms present in the macromolecules.^{18,19}

Copolymers of VF_2 /CTFE were prepared under contract from the Army Quartermaster Corps and described in a series of papers in 1955.²⁰⁻²² These were the first commercial fluoroelastomers with vulcanizate properties superior to any of the then existing elastomers. Copolymers of VF_2 /HFP were described by Du Pont and M. W. Kellogg Co. workers shortly after.²³⁻²⁵ Commercial acceptance of this later fluoroelastomer rapidly surpassed that of VF_2 /CTFE. A terpolymer of VF_2 /HFP/TFE was introduced in the late 1950s by Du Pont^{26,27} with even better solvent and thermal resistance than the dipolymers. In the 1960s elastomeric copolymers of VF_2 /HFPE and terpolymers of VF_2 /HFPE/TFE were introduced by Montecatini-Edison S.p.A.²⁸⁻³⁰ These fluoroelastomers are inferior in heat and fluid resistance to those of VF_2 /HFP and VF_2 /HFP/TFE compositions, most likely due to their lower fluorine content.

In the mid-1970s workers at Du Pont introduced VF_2 /HFP, VF_2 /HFP/TFE and VF_2 /RfOCF=CF₂/TFE compositions which contain small amounts of a bromine-substituted olefin as cure site monomer.^{16,17,31-33} These polymers are curable with dinucleophiles or peroxides and have advantages in making certain compositions with higher fluorine content (70 wt%) and better lower temperature performance. Table 1 shows the fluorine-containing monomers which are being used to make fluorocarbon elastomers. The monomer selection is based on the required properties. Vinylidene fluoride is always one of the monomers. However, if better low temperature flexibility is needed, perfluoroalkyl vinyl ethers are preferred over hexafluoropropylene. On the other hand, introduction of TFE in the fluoroelastomer composition contributes better thermal stability to the detriment of the low temperature flexibility.

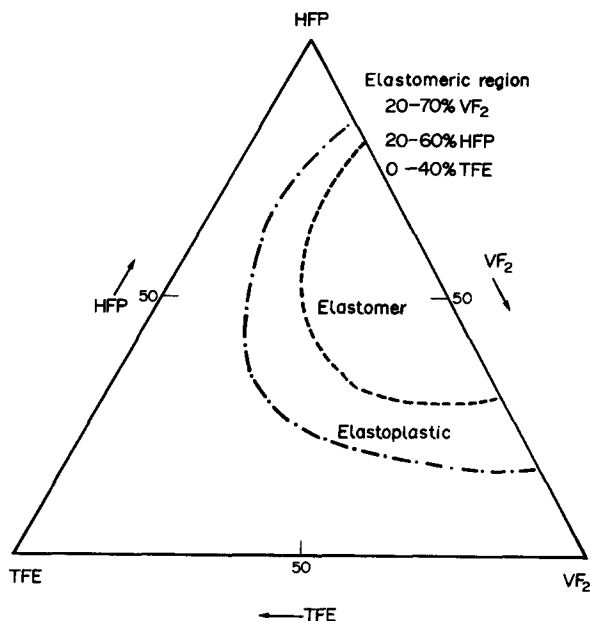
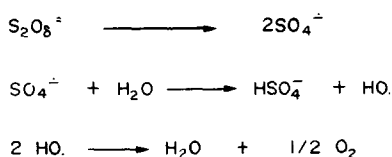
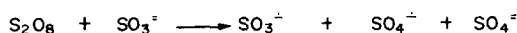


FIG. 3. Fluoroelastomeric compositions of polymers made from vinylidene fluoride (VF_2), hexafluoropropylene (HFP) and tetrafluoroethylene (TFE).^{7,8}

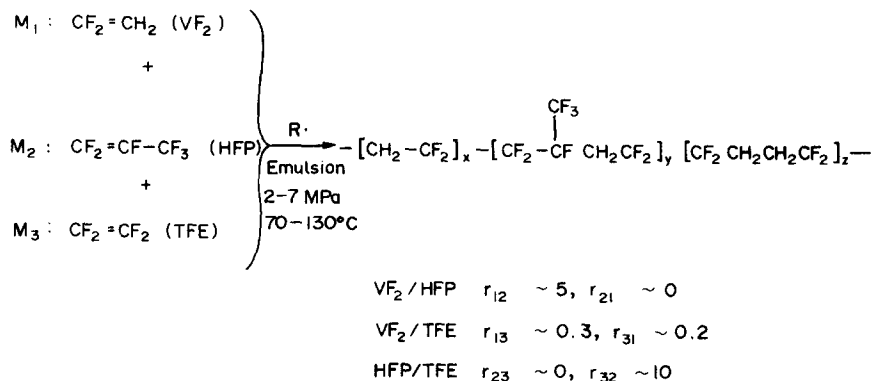
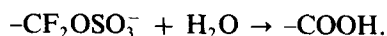
3.2. Polymerizations

The useful compositional range for elastomeric structures from the three key monomers, VF_2 , HFP and TFE is shown in Fig. 3.^{7,8} The region of interest is the one encompassing a composition of 20–70 wt% VF_2 , 20–60 wt% HFP and 0–40 wt% TFE. On a molecular scale it is important to have about one HFP unit for every 2–4 of the other monomers present to prevent crystallization of the polymer and to assure an amorphous material. The terpolymerization of VF_2 /HFP/TFE is shown in Fig. 5. As the reactivity ratios indicate, when an HFP radical is at the end of the chain, it reacts slowly with the other monomers present and hardly at all with another HFP monomer. The rate limiting step in such polymerizations is the addition of the radical on an HFP unit to either a VF_2 or TFE monomer, of about the same reactivity. This is supported by the observation that two adjacent HFP units in the polymer are not found by NMR analysis.^{35,36} In fact, an HFP unit flanked on both sides by VF_2 or VF_2 and TFE, respectively, turns out to be a very important structure in the curing of these elastomers with dinucleophiles.

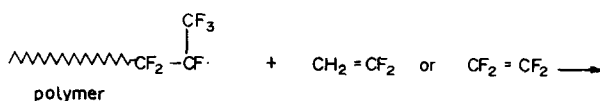
3.2.1. Initiation — The fluoroelastomers are prepared by free radical polymerization in an emulsion system.^{7,8,14,15} The most common free-radical initi-

Thermal decompositionRedoxFIG. 4. Radicals in thermal and redox aqueous initiating systems.³⁴

ators are the water soluble ammonium or potassium persulfate or the redox system persulfate/sodium sulfite. The thermal and redox decomposition of persulfates in aqueous solutions has been described by Kolthoff and Miller,³⁴ and the chemical equations are shown in Fig. 4. In thermal initiation, the sulfate radical acts as initiator in the presence of the fluoromonomers. The end groups, therefore, are mostly acid groups resulting from the hydrolysis of the sulfate intermediates as shown below:



Rate limiting step

FIG. 5. Synthesis of vinylidene fluoride copolymers.^{7,8}

To a varying degree there are also non-ionic end groups resulting from chain transfer or disproportionation of the growing radical.

In the redox system, initiation can take place via either the sulfate or sulfite radicals, resulting in carboxylate and sulfonate as the predominant end groups. In both cases these strong ionic end groups act as internal surfactants resulting in relatively stable emulsions. The use of surfactants — the most commonly used are salts of C_8 – C_{10} perfluorocarboxylic acids — is therefore optional. Buffers like monosodium or disodium are also used to keep the pH within the 3–8 range in order to maintain emulsion stability in the system. A high concentration of ionic end groups result in strong ionomer formation which in turn gives high raw polymer and compound viscosities. High viscosity polymers usually have processing difficulties during the manufacture of rubber parts.

It is possible to minimize the ionic end group concentrations of these polymers by running the polymerizations in the presence of small amounts of chain-transfer agents. Hydrocarbon-based alcohols, esters and halogens as well as fluoroalkyl iodides have been used successfully. They react with the growing radical in the particles as well as with the initiating species in the aqueous phase, affecting the rate of polymerization and the molecular weight. It is important, therefore, that for each polymerization system and combination of monomers the kind and amount of chain transfer agent be selected carefully to give the optimum balance of molecular weight, polymerization rate and ionic end group concentration.

The polymerizations may be carried out under steady-state conditions in which the monomers, water, surfactants, buffers and catalysts are fed continuously to a stirred reactor under optimum pressure and temperature conditions while the resulting emulsion is removed continuously. An alternative technique is batch or semibatch polymerization by feeding the ingredients into a stirred reactor and allowing them to react at a set temperature for a specified length of time or until the pressure is equalized. Both systems appear to be used commercially from the indications in the patent literature.

Thermal initiation with persulfates usually requires temperatures above 75°C to give a satisfactory initiation rate. The redox initiation systems have the advantage of being effective at lower temperatures (50 – 70°C). The disadvantage of the sulfite based redox systems is that they give strong ionic end groups in the form of sulfonic acids, in contrast to thermal initiation which gives carboxyl end groups. Redox systems that give low levels of ionic end groups are also possible. Selection of one initiation system over the other depends, therefore, on what kind of polymer is desired and what kind of polymerization facilities are available.

The resulting emulsions are usually coagulated by addition of electrolytes. The precipitated polymer is thoroughly washed with water and then dried in an air oven. Salts such as sodium chloride, magnesium sulfate, and aluminium sulfate act effectively as coagulants. Depending on the stability of the emulsion, the amount and kind of the electrolyte to be added have to be determined. The least stable emulsions can be coagulated simply by shear.

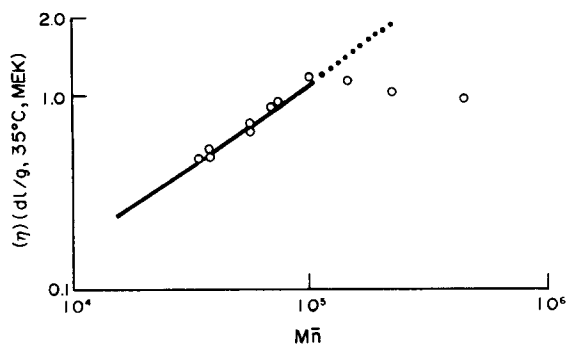


FIG. 6. Relationship between intrinsic viscosity (η) and number average molecular weight, M_n , of fluoroelastomers made in a semibatch polymerization system.³⁸

3.2.2. Molecular weight control and chain transfer agents — In persulfate-initiated polymerization, the molecular weight of the polymer usually increases with decreasing initiator concentration. The extent of the increase of the molecular weight may not be as obvious if only solution viscosity measurements are utilized. In batch or semibatch type polymerizations intrinsic viscosity measurements show a deviation from linearity in the high molecular weight range, caused by gel formation (Fig. 6). Use of chain-transfer agents is an effective way to eliminate the gel by eliminating chain transfer between growing polymeric radicals and polymer chains. Some of these effective chain-transfer agents and their chain transfer coefficients are shown in Table 2. Because of the high reactivity of fluorocarbon radicals, almost any kind of compound is more or less a chain transfer agent except the highly fluorinated ones. Among the most desirable ones are the iodo-substituted fluorocarbons because they have the added advantage of giving iodo-terminated polymeric chains.³⁷⁻⁴² The reactivity

TABLE 2. Chain transfer coefficients in fluoromonomer polymerization

Fluoromonomers	Chain transfer coefficients (Cs) of various agents			
	C-----H Neo-C ₅ H ₁₂	iso-C ₅ H ₁₂	CCl ₄	C-----X (CF ₃) ₂ CFI
CH ₂ =CHF		0.09	15	
CH ₂ =CF ₂		0.22	1.7	0.8-1.6
CF ₂ =CF ₂		0.73	0.02	0.6-0.7
VF ₂ /HFP*	0.012	0.69	0.1†	
TFE/HFP†		10	0.004‡	

*HFP content in the polymer 25 mol%.

†HFP content in the polymer 10 mol%.

‡Suspension polymerization at 25°C.

At 80°C in an emulsion system. Data from Ref. 38.

of the polymer terminal iodine is about the same as that of the chain transfer agent, RfI. Thus, successive chain transfers of the terminal iodine make the system behave like a living radical polymerization. By this process the low molecular weight polymers formed at the initial stage are extended to high molecular weight polymers. To prepare high molecular weight species with iodine as the predominant terminal group, termination reactions other than chain transfer involving iodine are to be avoided as much as possible. Consequently, the least amount of iodo compounds in relation to the initiator should be used throughout the polymerization to keep the kinetic chain as long as possible. Photoinitiation is most favorable from this point of view.³⁸

The relationship between intrinsic viscosity and molecular weight of unmodified and modified polymerizations carried out in a semibatch process is shown in Fig. 7. The regular unmodified co- and terpolymers of VF₂ obtained at low initiator concentrations are of relatively broad molecular weight distribution (MWD) and contain large amounts of gel. By using isopentane as modifier, gel formation is eliminated but the M_w/M_n ratio of 12.7 indicates that the MWD is still broad. Modification by perfluoroalkyl iodides, on the other hand, makes the MWD considerably narrower, $M_w/M_n = 1.4$. These data developed by workers at Daikin³⁸ are shown in Fig. 8. The diiodo-substituted molecular weight modifiers, I(CF₂)_nI, are preferred over the monoiodides because they give narrower MWD polymers substituted with iodine at both ends of the molecular chain. The diiodo-substituted fluoroelastomers cure more efficiently in the presence of peroxides.^{37,38}

The terminal iodine atoms on these polymers are capable of undergoing many

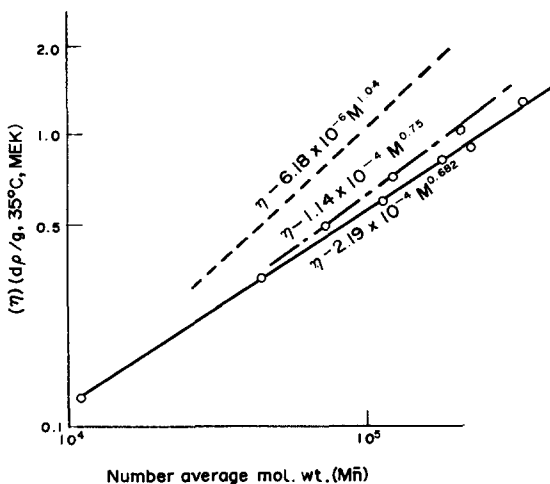


FIG. 7. Relationship between intrinsic viscosity (η) and mol. weight (M_n) for I(CF₂)₄I regulated (—Δ—), C₄F₉I regulated (—O—) and non regulated (---) fluoroelastomers.³⁸

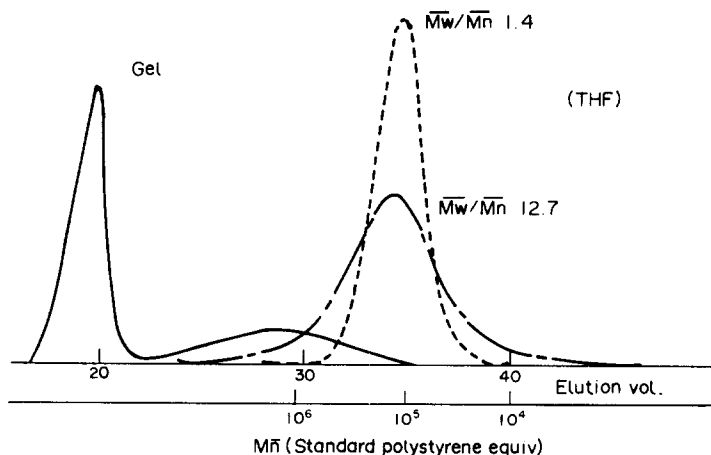
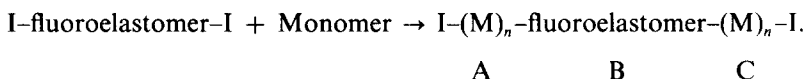


FIG. 8. Gel permeation chromatography (GPC) of iodo-regulated (IFKM, ----), isopentane-regulated ($\text{iso-C}_5\text{H}_{12}$, - · - ·) and non-regulated (FKM, —) fluoroelastomers in THF solvent.³⁸

reactions characteristic of the carbon–iodine bond.³⁸ For example, olefins can be added across the carbon–iodine bond, the iodine can be replaced with a hydrogen, and it can be coupled or reacted in the presence of peroxides with other monomers to give block copolymers. Thus the diiodo-terminated polymers of VF_2/HFP and $\text{VF}_2/\text{HFP}/\text{TFE}$ have been further reacted with TFE or mixtures of TFE and E or mixtures of TFE and VF_2 or just VF_2 to give ABA type thermoplastic block fluoroelastomers where A is the crystalline hard segment (polyTFE, polyTFE/E, poly VF_2) and B is the soft elastomeric segment (VF_2/HFP , $\text{VF}_2/\text{HFP}/\text{TFE}$, TFE/P) as shown below:



This reaction can be carried out sequentially in an emulsion system batchwise in a stirred reactor, running first the initial polymerization to make the elastomeric segment. When this part of the polymerization is complete, the monomers which make up the elastomeric segment are vented off and the monomers which make up the crystalline segment are introduced. The polymerization is then allowed to continue to give the hard segment by introducing additional initiator. Thus, the polymers can be made in high molecular weight in a manner reminiscent of living anionic polymerizations. Daikin, which developed this technology, refers to it as “Segmented Polymerization” and has introduced commercial products based on polymers in which the soft segments are either VF_2/HFP or $\text{VF}_2/\text{HFP}/\text{TFE}$. When the hard segments are E/TFE/HFP, the polymer has a melting point of 220°C and an apparent melt viscosity of 100 Pa at 280°C . On the other hand, when the hard segment is poly VF_2 , the melting point is only

160°C and the apparent melt viscosity is 300 Pa at 230°C. These polymers can be processed at about 20–50°C above the melting point of the crystalline (hard) segment. Although curing is not necessary, radiation curing is recommended to improve the high temperature properties.

3.2.3. Special compositions — A number of interesting fluoroelastomers have been made by copolymerizing tetrafluoroethylene (TFE), vinylidene fluoride (VF₂) and perfluoroalkyl vinyl ethers. Perfluoroalkyl vinyl ethers are ordinarily very difficult to homopolymerize to high molecular weight polymers. Copolymers and terpolymers, on the other hand, are relatively easy to make and macromolecules of intrinsic viscosity > 0.5 have been synthesized. Thus elastomeric copolymers of VF₂/RfO-CF=CF₂ have been synthesized (Fig. 9) with mol ratio of the two monomers ranging from 95:5 to 50:50.^{43,44} In addition elastomeric terpolymers of TFE/VF₂/RfOCF=CF₂^{16,31–33} with molecular ratios from about 25:50:25 to 33:33:33 have also been made. All these copolymers need a cure-site monomer in order to be cured satisfactorily. Bromine-containing fluoroolefins like 2-bromoethyl vinyl ether, bromotrifluoroethylene and 4-bromo-3,3,4,4-tetrafluorobutene are such cure site monomers rendering the polymers capable of peroxide curing. Ionizing radiation is another way of curing these polymers. The advantage of the perfluoroalkyl vinyl ether-containing macromolecules is their very good low temperature properties (*T_g* of –30° to –40°C) compared to the other fluorocarbon elastomers (*T_g* of –10° to –20°C). The

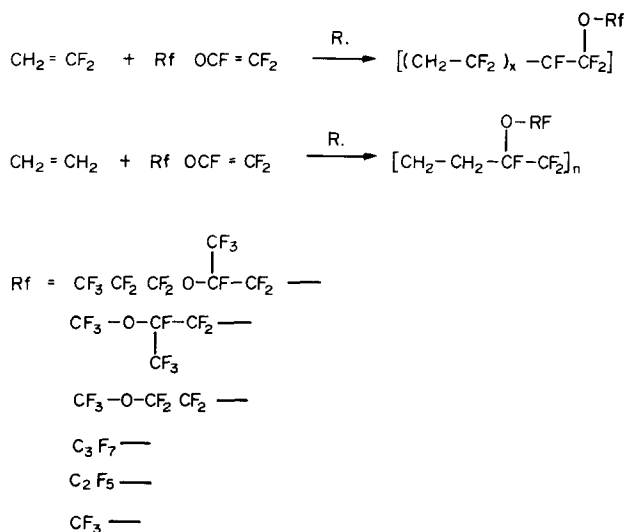


FIG. 9. Copolymers of perfluoroalkyl vinyl ethers with vinylidene fluoride (VF₂) and ethylene (E).^{43,44} Terpolymers can also be made by adding tetrafluoroethylene (TFE) to the monomer mixture.^{16,31–33,43,44}

presence of the perfluoroalkyl vinyl ethers in the polymers contributes greatly to lowering the glass transition temperature (T_g).

Copolymerization of ethylene and perfluoroalkyl vinyl ethers resulted in the formation of fluoroelastomers of $E/RfOCF=CF_2$ with molar ratios ranging from 67 : 33 to 55 : 45. Because of the high molecular weights of perfluoroalkyl vinyl ether monomers and the low molecular weight of ethylene, the weight content of the fluoromonomer component is in the range of 95%. Terpolymers in which the third component is VF_2 or TFE have also been reported.^{43,44} These polymers are attractive because of their low T_g values (around $-40^\circ C$) leading to the synthesis of good low temperature fluoroelastomers. The polymerization of these polymers is carried out under 75–200 psi pressure in an emulsion system at $25-40^\circ C$ with ammonium perfluorononanoate as surfactant and a redox initiator consisting of ammonium persulfate, ferrous salt, ethylenediamine tetraacetic acid and sodium hydroxymethanesulfinate. The low polymerization temperatures help to minimize chain transfer reactions, thus enabling the formation of relatively high molecular weight polymers suitable for elastomeric uses. These fluoroelastomers can be cured by irradiation or by incorporating a bromine-containing cure site monomer.

3.3. *Curing chemistry of vinylidene fluoride based fluoroelastomers*

Fluoroelastomers, like all other thermosetting elastomers, require curing in order to get useful properties. A considerable amount of effort has been devoted over the 30 years of existence of fluoroelastomers towards the development of practical crosslinking systems. Fluoroelastomers can be cured by nucleophiles such as diamines^{45–50} or bisphenols^{35,36,51} and with peroxides.^{16,17,31–33} Irrespective of the curing system the best vulcanizate properties are obtained by a two-step process. The first step entails the application of both heat and pressure, by molding a specimen in a press (press cure). The second step (postcure) is carried out in air or under nitrogen at higher temperatures than the press cure and at atmospheric pressure. For thick sections, the temperature of the oven is usually raised stepwise to prevent fissuring of the part. A typical curing condition would be 5–15 min in a press at $150-180^\circ C$ followed by 12–24 hr at $200-250^\circ C$ in an air oven. Postcuring contributes substantially toward improving the compression-set resistance, as well as tensile strength, fluid, and chemical resistance properties.

3.3.1. *Curing with diamines* — Diamine curing,^{14,45–50} originally introduced in the late 1950s, was the predominant way of crosslinking fluoroelastomers until the late 1960s, when curing with bisphenols was introduced. The most commonly used diamine is hexamethylenediamine, utilized conveniently as its carbamate salt (“Diak” 1) or *N,N'*-dicinnamylidene-1,6-hexanediamine (“Diak” 3). The chemistry involved is the initial removal by the amine of the elements of hydrogen fluoride from the polymer chain. The resulting highly polarized

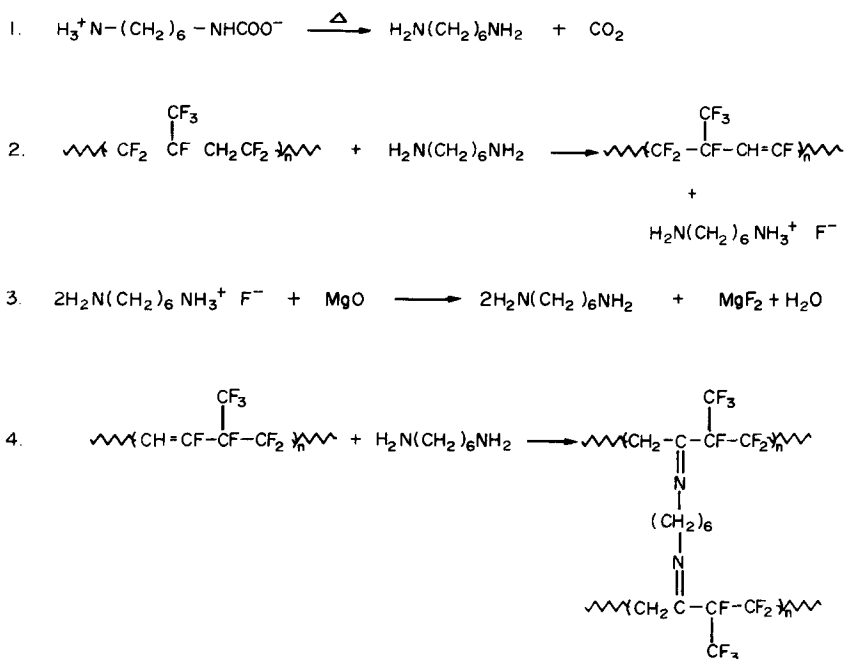


FIG. 10. Curing of vinylidene fluoride-containing fluoroelastomers with diamines.¹⁴

–CH=CF– units are susceptible to addition by the diamines to form a highly crosslinked network (Fig. 10). It is advantageous to provide a metal oxide (MgO, PbO, CaO) as acid acceptor to react with the hydrogen fluoride generated during the curing step. These metals give insoluble, non-volatile metal fluorides which are thermally and chemically stable and are not detrimental to the physical properties of the cured fluoroelastomer.

Typical compounds contain, per hundred parts of rubber (phr), 4–20 parts of a metal oxide (MgO being the most common), 10–30 phr carbon black and 1–3 phr diamine either as the carbamate or as the *N,N'*-dicinnamylidene derivative. Because of processing difficulties and relatively poor retention of physical properties at high temperatures (> 200°C) after long exposures, the importance of the diamine cures has diminished and they have been slowly replaced by the bisphenol curing system.

3.3.2. Curing with bisphenols — Bisphenols are presently the predominant cross-linking agents for curing fluorocarbon-based elastomers. Bisphenol cure was developed in the late 1960s and started replacing the diamine cure in the early 1970s.⁵⁰ Because of processing and property advantages, the most commonly used compound is “bisphenol AF” (2,2-bis(4-hydroxyphenyl)hexafluoropropane). Others, like hydroquinone, substituted hydroquinones and 4,4'-

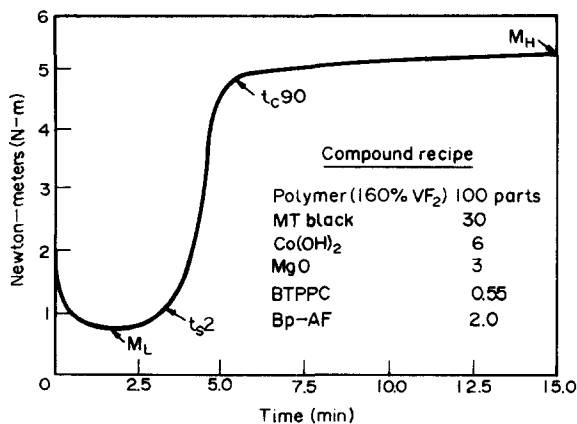
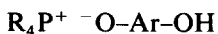
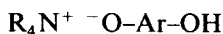


FIG. 11. Cure response by oscillating disc rheometry at 177°C of a compound optimized for use in O-rings.¹⁷

disubstituted bisphenols also work well and are used commercially to a lesser degree. A typical curing recipe and the rate of cure are depicted in Fig. 11. The maximum cure rate is the initial slope of the curve; t_{s2} , the time to initiation (increase of torque by two points from minimum); t_{c90} , the time to 90% completion of cure; M_L , the minimum torque; M_H , the maximum torque; and $M_H - M_L$, the degree of state of cure. This system is very scorch safe, that is no curing reaction is detected for 30 min at 121°C. However, at 177°C after a 2.5 min induction period, the reaction is practically over after 5 min. The induction time, t_{s2} , is shortened with increase of temperature as is the slope of the curve that indicates the cure rate. The final state of cure, however, remains essentially unchanged with increasing temperature. The shape of the curve does not change much for copolymers of VF₂/HFP composition or terpolymers like VF₂/HFP/TFE or VF₂/RfOCF=CF₂/TFE. Schmiegel^{17,35,36} described the curing chemistry of these polymers and explained the various steps by using ODR, IR and NMR measurements on the polymers and on model compounds. He found that the diphenol does not react with the polymer without an accelerator, which can be a phosphonium or tetraalkylammonium salt, in combination with a metal oxide. The diphenol reacts with the metal oxide to give the phenolate ion which, in turn, reacts with the phosphonium or tetraalkylammonium ion to give the intermediates I or II. These intermediates are strong bases which have some compatability with the polymers and abstract hydrogen fluoride from the polymer backbone.



I



II

The double bonds rearrange and a second molecule of hydrogen fluoride is

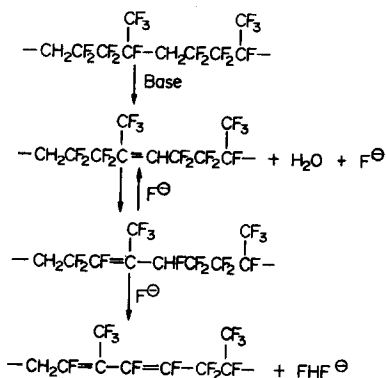


FIG. 12. Proposed reaction sequence of selectively base-sensitive site in VF_2/HFP polymers.¹⁷

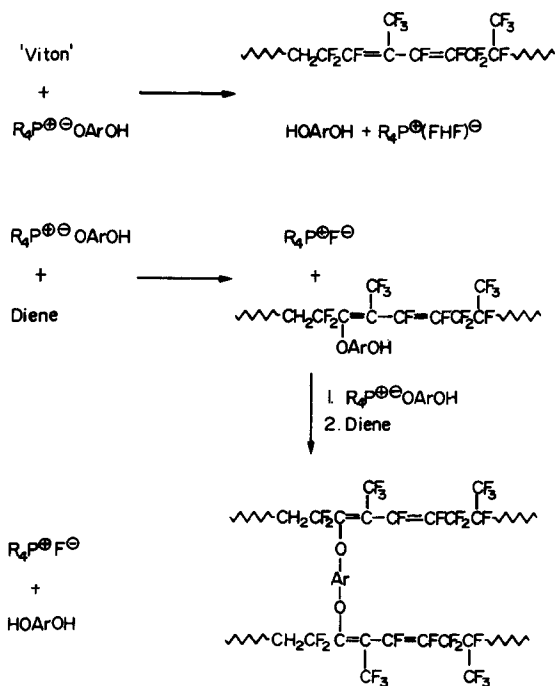


FIG. 13. Proposed scheme for crosslinking VF_2/HFP polymers with bisphenols in basic media.¹⁷

abstracted from the polymer to give a diene (see Fig. 12 for the reaction sequence). Such reactions are only possible when the $-\text{CH}_2-$ group on the backbone is flanked by CF_2 or $\text{CF}(\text{CF}_3)$ groups, rendering the hydrogens acidic enough to be abstracted by the base. The resulting anion will then eliminate a fluoride ion and form a double bond and eventually a diene. Formation of the unsaturation in the polymeric backbone is the rate determining step of the curing reaction. Addition of the diphenol to the diene is relatively fast and proceeds essentially to completion. It is interesting to note that according to Fig. 13 which describes the crosslinked structure, the network contains conjugated vinyl ethers. Surprisingly enough the cured compounds show extremely good properties, particularly with regard to oxidative and hydrolytic stability. A possible explanation is that the double bonds are hidden in the polymeric network due to the relatively large size of the fluorine atoms and become inaccessible for reactions with chemical reagents. In addition such reagents may not be soluble in the fluoropolymer and thus cannot penetrate the network and get to the reaction site in sufficient concentrations.

In compositions of $\text{VF}_2/\text{CF}_3\text{OCF}=\text{CF}_2/\text{TFE}$, Schmiegel showed^{17,36} that the anion generated by the abstraction of a proton from the polymeric backbone eliminates trifluoromethoxide as well as fluoride ion to give double bonds. Trifluoromethanol is further degraded to hydrogen fluoride and carbon dioxide, which results in the formation of large amounts of volatiles. The cured specimens, therefore, show excessive porosity and poor vulcanizate properties due to the volatiles produced during the curing process. For this reason it is advisable that the VF_2 -based polymers containing perfluoroalkyl vinyl ethers have a special cure site with curing chemistry different from nucleophilic attack on the backbone. Such chemistry is the peroxide induced crosslinking which was specifically developed to bypass these kinds of problems and is described below.

3.3.3. Curing with peroxides — A cure site monomer susceptible to free-radical attack is required to render peroxide curable the elastomeric co- and terpolymers of vinylidene fluoride. Du Pont workers found that bromine-containing fluoroolefins such as bromotrifluoroethylene, 1-bromo-2,2-difluoroethylene and 4-bromo-3,3,4,4-tetrafluorobutene-1 are excellent cure site monomers because they are easily polymerized with fluoromonomers to give high molecular weight polymers. The resulting polymers readily give free radical intermediates on the polymeric backbone upon attack by peroxides,^{16,17,31-33} which in turn, crosslink into a network in the presence of a radical trap. Thus, an efficient curing system requires not only the presence of a peroxide but also of a coagent to trap the polymeric radicals. Daikin workers utilized modification of the fluorocarbon elastomers with perfluoroalkyl iodides (described earlier under "Polymerization") to introduce iodine end groups on the polymeric chain.³⁷⁻⁴² These polymers also give free radical intermediates upon attack by peroxides. Thus

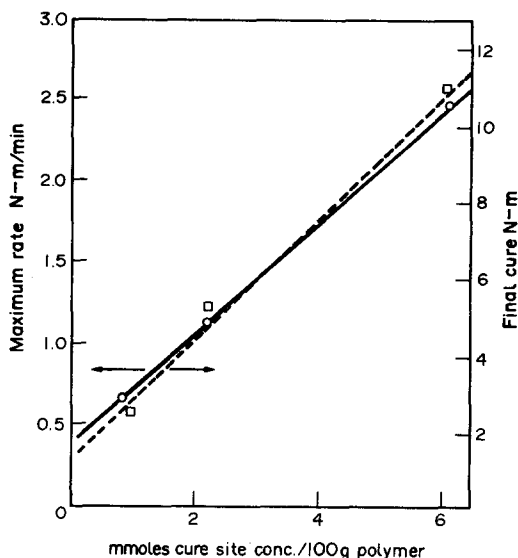


FIG. 14. The cure rate (open circles) and final cure state (squares) as obtained from ODR measurements at 177°C plotted as functions of cure site concentration.¹⁶

fluoroelastomers containing bromine or iodine functional groups can be cured with peroxides.

Among the peroxides found to work well are aliphatic and aromatic ones like 2,5-bis(*t*-butylperoxy)-2,5-dimethylhexane (Luperco 101XL), 2,5-bis(*t*-butylperoxy)-2,5-dimethylhexyne-3 (Luperco 130XL) and α,α' -bis(*t*-butylperoxy)diisopropylbenzene (VUL-Cup). The crosslinking agents are usually di- or trifunctional electron-rich olefins. Among the ones that have been described to work the best in terms of optimum cure rate, cure state and physical properties are triallyl isocyanurate ("Diak" 17), triallyl cyanurate, trimethallyl isocyanurate ("Diak" 8), tetramethyltetravinylcyclotetrasiloxane and *m*-phenylenebismaleimide ("HVA-2").¹⁶ Metal oxides like $\text{Ca}(\text{OH})_2$, CaO , MgO , ZnO and PbO are useful in absorbing traces of hydrogen fluoride generated during the curing process. The rate and degree of curing is followed by measurements with a Monsanto Oscillating Disc Rheometer (ODR), and a typical curve is very similar to that of Fig. 11 shown earlier for the bisphenol cure recipe. The characteristics of this cure described by the Du Pont workers^{16,17} are given below:

- The cure rate and final cure state are directly proportional to the cure-site monomer concentration in the polymer. This is shown in Fig. 14 for the bromine-containing polymers.

- The peroxide concentration has little effect on the final state of cure above a certain minimal level (Fig. 15) but has a pronounced effect on the rate of cure.

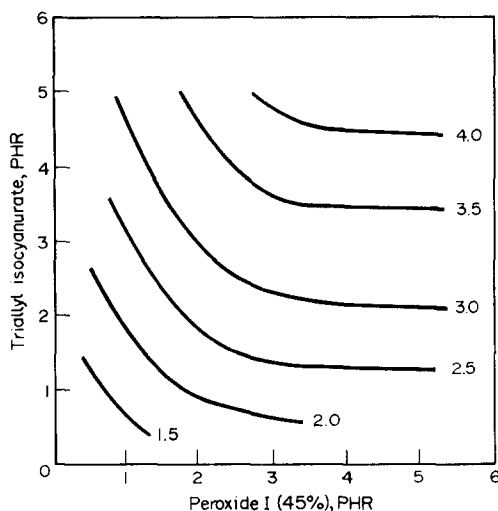


FIG. 15. Final cure state contours (N.m) as a function of peroxide (2,5-bis(*t*-butylperoxy) 2,5-dimethylhexane; 45% active ingredient) and coagent (triallyl isocyanurate) concentrations.¹⁶

Table 3 compares two peroxides with different half-lives in an identical cure system.

● The radical trap (coagent) concentration is important in maintaining a good cure rate and final cure state.

The most informative technique for following reactions that involve free

TABLE 3. Effects of peroxide type and cure temperature

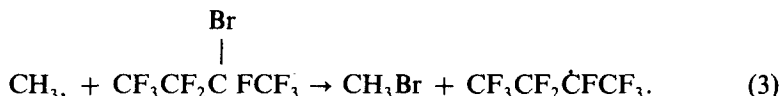
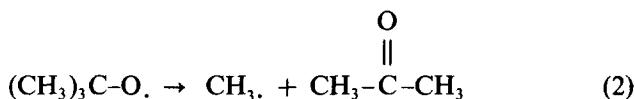
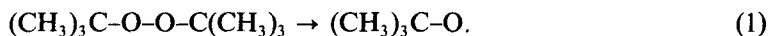
Cure temp (°C)	Peroxide half-life* (min)	ODR values		
		$t_c 2$ (min)	$t_c 90$ (min)	Cure state, $M_H - M_L$ (N-m)
2,5-bis(<i>t</i> -butylperoxy)-2,5-dimethylhexane				
160	4.8	4.0	24	8.0
177	0.80	1.6	8.3	8.6
190	0.24	1.4	4.6	8.2
204	0.07	0.8	2.8	7.9
2,5-bis(<i>t</i> -butylperoxy)-2,5-dimethylhexyne-3				
160	18.7	7.1	41†	—
177	3.4	3.4	14	7.7
190	1.0	2.1	7.5	7.7
204	0.30	1.2	4.2	7.5

*In dilute benzene solution.

†Extrapolated value.

Ref. 16.

radical chemistry is ESR. Upon ultraviolet irradiation of a dilute solution of 2-bromoperfluorobutane and di-*t*-butyl peroxide in cyclopropane in an ESR cavity at room temperature, an intense spectrum of 2-perfluorobutyl radical is observed.¹⁶ If the peroxide is omitted or the temperature is lowered, very weak ESR spectra are observed. This is explained by assuming that direct abstraction of a bromine atom by the *t*-butoxy radical is unlikely to occur. Most likely the bromine atom abstraction is caused by the methyl radical produced from the beta-scission of the *t*-butoxy radical. This beta-scission is a thermally activated process and does not take place readily at low temperatures. The steps are described in eqs 1-3 shown below:



Analyses of the volatiles generated during a typical peroxide cure of a fully compounded stock are given in Table 4. The total amount of volatile materials

TABLE 4. Volatiles generated during peroxide cures*

Compound	Amount generated (mmol)
Acetone	9.45
<i>t</i> -C ₄ H ₉ OH	0.78
CH ₃ Br†	0.18
CH ₄	2.68
C ₂ H ₄	0.26
C ₃ H ₆ (+ C ₃ H ₈)	0.41
<i>i</i> -C ₄ H ₈ ‡	0.39
H ₂ O§	16.6

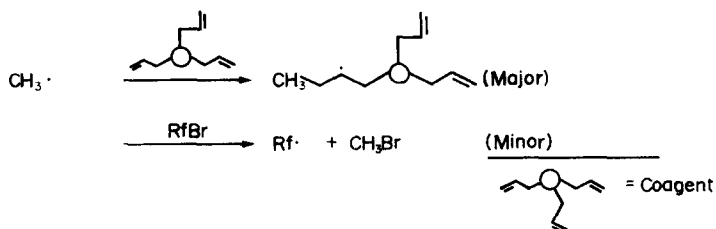
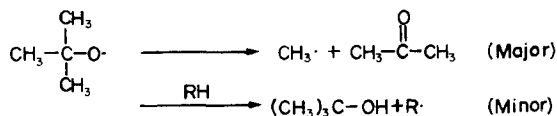
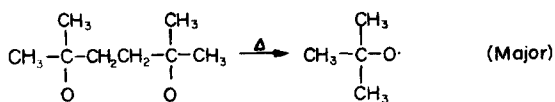
*Recipe: polymer 100; MT black, 30; Ca(OH)₂, 4; peroxide, 4; triallyl isocyanurate, 4. The polymer contained 5.6 meq. of bromine and the bisperoxide (2,5-bis(*t*-butylperoxy)-2,5-dimethylhexane) was present in a 5.5 mmol quantity. The container with the stock was heated to 190°C at a rate of 40°C/min and held at 190°C for 10 min under a helium sweep. Data from Ref. 16.

†When triallyl isocyanurate is omitted from the recipe, CH₃Br evolution is 50-100% greater.

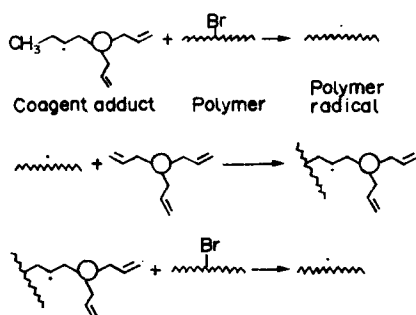
‡When both triallyl isocyanurate and calcium hydroxide are omitted from the recipe, isobutene formation increases dramatically.

§When the peroxide is omitted from the recipe, water is the only volatile product.

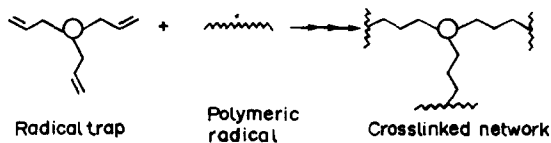
Initiation



Propagation



Crosslinking reactions


 FIG. 16. The main reactions of the proposed crosslinking mechanism.¹⁶

formed is proportional to the amount of peroxide present. Among organic fragments, acetone is the largest component. Surprisingly, methane and methyl bromide are present in relatively low concentrations. The water comes from the metal oxides and equilibrium water present in the polymer. When the radical trap (triallyl isocyanurate) is omitted, the methyl bromide concentration increases. When the peroxide is omitted, the only volatile produced is water, while when the radical trap and metal oxide are omitted, the isobutene concentration increases (dehydration of t-butanol). The most probable reactions are outlined in Fig. 16. The primary decomposition product is the t-butoxy radical which may abstract a hydrogen to give t-butanol (minor product) or decompose to acetone and methyl radical (major product). The methyl radical may in turn abstract a bromine atom from the polymer to give methyl bromide (minor reaction) or add to the radical trap (TAIC) to give a more stable radical. These more stable radical intermediates, in turn, abstract bromine atoms from the polymer, generating polymeric radicals. The driving force for such a chain reaction during propagation is the transfer of a bromine atom from the electron-poor fluoropolymer to the electron-rich hydrocarbon radical on the radical trap. The radical trap, therefore, becomes the crosslinker and in order to give optimum properties, it should be efficient (multifunctional and electron-rich) and thermally and oxidatively stable.

3.4. Postcuring

Fluorocarbon vulcanizate properties, as mentioned earlier, are improved by postcuring the press cured specimens in an oven at atmospheric pressure at temperatures above the cure temperature. This postcuring step is commonly used commercially and the property improvements obtained are independent of the cure recipe. Thus a VF₂/TFE/HFP terpolymer containing bromine func-

TABLE 5. Postcure effect on properties*

Properties	Bisphenol		Peroxide	
	Press cure†	Postcure‡	Press cure†	Postcure‡
Modulus at 100% strain, MPa	5.0	7.9	5.0	7.9
Tensile strength at break, MPa	10.0	13.8	9.7	15.9
Elongation at break, %	225	175	165	150
Compression set, % (70 hr/200°C)				
O-rings	63	25	50	27
Pellets	85	20	52	20

*Data from Ref. 16.

†Press cure, 10 min at 177°C.

‡Postcure, 24 hr at 232°C.

TABLE 6. Compression set resistance* measured in air or nitrogen

Compound†	Compression set, %		
	Press cured‡	Postcured§	
		air	N ₂
A	71	38	20
B	70	37	25
C	59	27	12
D	52	21	9

*At 70 hr/204°C, O-rings, %.

†Compounds A and C: Polymer, 100; Peroxide II, 3; triallyl (TAIC), 3; PbO, 3. Compound B: PbO replaced by MgO, 2; ZnO, 2. Compound D: PbO replaced by Ca(OH)₂, 6; MgO, 3. The bromo cure site in A and B differed from that in C and D.

‡Press cured 15 min at 177°C.

§Postcured under nitrogen 24 hr at 232°C after press cure.

Ref. 16.

tionality and cured with bisphenol and peroxide was tested before and after postcuring and the results are shown in Table 5.¹⁶ The tests showed a 50% increase in the modulus (M_{100}) and tensile-at-break (T_b), a 50% decrease in the elongation at break and a substantial improvement (two to three fold) in the compression set resistance after postcuring. Additional improvement is noticed when the compression set resistance test is run under nitrogen (see Table 6). It is not very clear what actually happens during postcuring. A number of processes may contribute to the property improvement. One of the essential functions of postcure is the removal of water and other volatile products generated

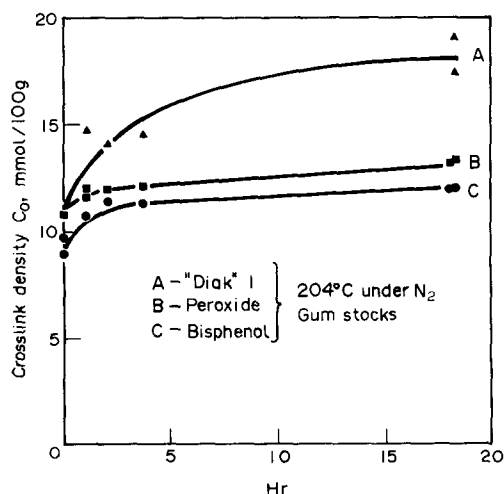


FIG. 17. The crosslink density of various cure systems plotted as a function of postcure time at 204°C under nitrogen.¹⁶

during the press curing step. In addition to the removal of by-products, it appears that postcure contributes to a thermally induced bond-breaking and bond-making process that results in a more stable network.^{16,52-54} Thus an annealing type process is occurring which relieves the stress points in the crosslinked network created during the curing process in a mold under heat and pressure. This is particularly noticeable in the bisphenol and peroxide curing systems where the overall network density remains essentially the same before and after postcure (Fig. 17). In the case of the diamine cures, there is a definite increase of the crosslink density, indicating that more bond making than bond breaking is taking place. The actual mechanism of such a process is not well understood, and additional work is needed to clarify it.

4. FLUOROELASTOMERS DERIVED FROM TETRAFLUOROETHYLENE AND PROPYLENE

4.1. *Introduction*

In the early 1960s, it was found that TFE readily copolymerizes with propylene in a nearly alternating manner to give fluoroelastomers.⁵⁵⁻⁵⁷ These copolymers require the presence of a cure-site monomer in order to be cured with chemical crosslinking agents. It is also possible to cure them with peroxides in the presence of a radical trap and, in such cases, no special cure-site monomer is needed. Most of the reports in the literature involve just the copolymers which are cured by free radicals. These copolymers have shown good resistance to heat and chemicals, particularly to strong bases.

4.2. *Polymerizations*

The copolymers have been prepared by emulsion polymerization with the ammonium salts of perfluorooctanoic or perfluorononanoic acids as emulsifier and a modified persulfate redox system as initiator.⁵⁸⁻⁶⁰ This redox system makes it possible to run the polymerizations close to room temperature and get molecular weights in the range of 100,000–180,000. At higher temperatures chain transfer reactions begin to occur, and it is difficult to make high molecular weight polymers suitable for elastomeric uses (Fig. 18). At temperatures of 70–80°C the common ammonium persulfate/sodium sulfite redox system gives relatively good polymerization rates but the molecular weights are limited to about $\bar{M}_n$ 70,000. The preferred redox system reported by the Asahi Glass workers⁶⁰ consists of ammonium persulfate, ferrous sulfate, ethylenediamine tetraacetic acid and sodium hydroxymethanesulfinate operating in the 25–35°C temperature range. Disodium hydrogen phosphate buffer and sodium hydroxide are used to keep the pH between 5.5 and 10.0. The kinetic study indicates that the reduction of the ferric ion seems to be the rate determining step.

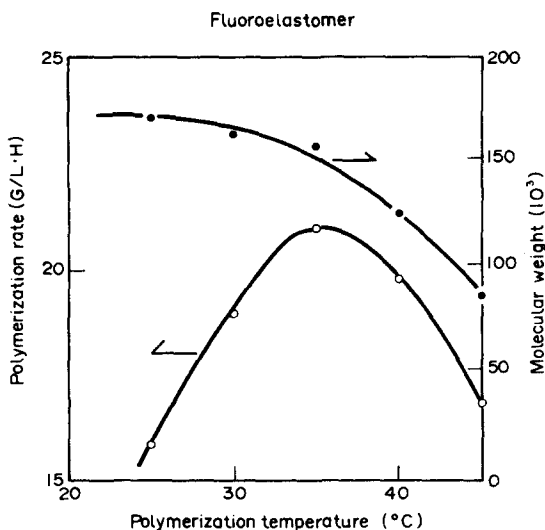


FIG. 18. TFE/propylene copolymers. Dependence of polymerization rate and molecular weight on polymerization temperature at TFE/ C_3H_6 (85:15) molar ratio of monomers.⁵⁹

Analysis of the resulting polymer showed that the monomers have entered the macromolecular structure predominantly in an alternating manner (Fig. 19). This tendency for alternation is supported by the measured monomer reactivity ratios, $r_{C_2F_4} = 0.05$ and $r_{C_3H_6} = 0.10$ and is ascribed to the very different electronic characters of these monomers ($Q_{C_2F_4} = 0.05$, $e_{C_2F_4} = 1.22$, $Q_{C_3H_6} =$

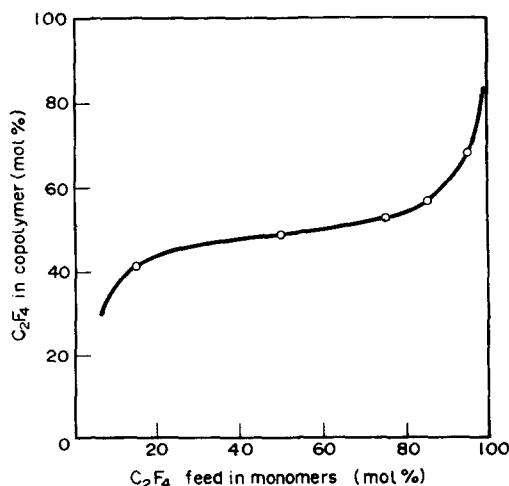


FIG. 19. Copolymerization curve of the TFE/propylene system. Polymerization in emulsion at 25°C and under 2.5 MPa pressure.⁵⁹

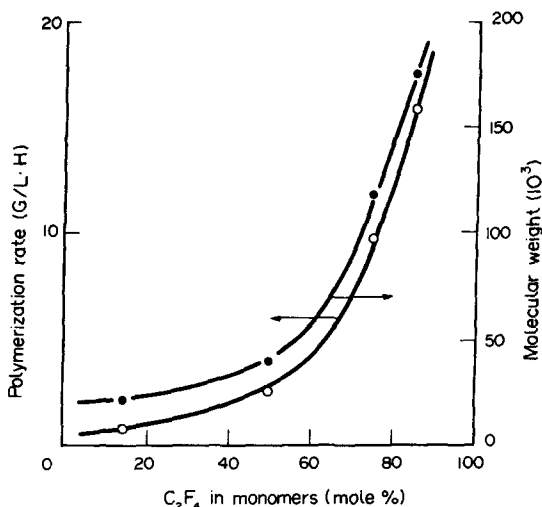
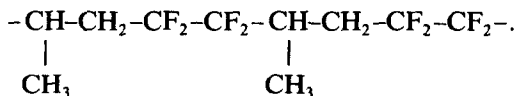


FIG. 20. TFE/propylene copolymers. Dependence of polymerization rate and molecular weight on the C_2F_4 fraction in monomers at 25°C.³⁹

0.002, $e_{C_3H_6} = 0.78$). It has also been reported⁶⁶ that radiation induced polymerization of TFE and propylene gives high molecular weight polymers with excellent properties.

The amount of tetrafluoroethylene in the monomer feed does not affect the polymerization composition to any great extent but affects the rate and the molecular weight of the polymer (Fig. 20). For this reason the optimum molar ratio in the monomer feed appears to be 85:15 for TFE/propylene in order to get a polymer composition of 55:45 TFE/propylene and $\bar{M}_n$ 100,000–180,000. Thus almost every propylene unit is isolated between two tetrafluoroethylene units as shown below:



The 1H and ^{19}F NMR spectra indicate that nearly 70% of the TFE units are alternating with C_3H_6 units in terms of tetrads. The methyl groups appear to be in a random configuration which helps in giving the polymers an amorphous morphology in spite of the highly regular alternating structure.

The polymer has a T_g of $-2^\circ C$ and is stable in air up to $400^\circ C$ for short periods of time, as indicated by thermogravimetric analyses. Once decomposition begins, the rate is about the same in air or in nitrogen.

4.3. Curing chemistry of tetrafluoroethylene/propylene fluoroelastomers

Since the TFE/propylene copolymer contains no double bonds or any other reactive site, any curing process has to involve the hydrogen atoms on the propylene units. Researchers at Asahi Glass Co. found that heat treatment of the copolymer causes some unsaturation in the backbone, making the fluoroelastomer easier to process and cure.⁶² A peroxide/radical trap system similar to that developed for the bromine- or iodine-containing vinylidene fluoride based fluoroelastomers described earlier, has been shown to work well with the TFE/propylene copolymers. Among the various peroxides tried, the α,α' -bis(*t*-butylperoxy)diisopropylbenzene (Vul-Cup), and among the radical traps triallyl isocyanurate and triallyl cyanurate are recommended. Some other radical traps, like 1,2-polybutadiene (MW 2000), divinylbenzene, *N,N'*-*m*-phenylenedimaleimide and diallylmelamine may also be used.⁶¹ The performance of the various curing systems was determined by the amount of gel fraction formed and by the compression set resistance values of fully compounded stocks as shown in Table 7. Figure 21 shows the relationship between the amount of peroxide in the compound and the amount of gel formed. The amount of gel formed depends on the efficiency of the radical trap. When the radical trap is absent, larger amounts of peroxide are required to reach the desired gel fraction levels. A comparison of the cured properties of these materials with those of vinylidene fluoride based fluoroelastomers shows that the TFE/propylene copolymers have about equal tensile properties but poorer compression set resistance, poorer resistance towards aromatic hydrocarbon solvents, poorer low-temperature properties, but superior resistance towards acids, bases and polar solvents (Table 8).

The suggested curing mechanism⁶¹ for TFE/propylene fluoroelastomers is very similar to the mechanism proposed earlier for the peroxide cured vinylidene

TABLE 7. Effect of coagents on peroxide vulcanization of TFE-propylene copolymers*

Coagent	Gel fraction	Compression set (%)
None	0.44	100
Divinylbenzene	0.50	100
<i>N,N'</i> - <i>m</i> -Phenylenedimaleimide	0.70	98
1,2-Polybutadiene (MW = 2000)	0.66	100
Trimethylolpropane trimethacrylate	0.77	94
Diallylmelamine	0.76	95
Triallyl cyanurate (TAC)	0.80	85
Triallyl isocyanurate (TAIC)	0.84	75
Triallyl isocyanurate + calcium carbonate	0.89	62

*Copolymer $\bar{M}_n$, 100 000. Recipe phr: polymer, 100; α,α' -bis(*t*-butylperoxy)-*p*-diisopropylbenzene, 5; coagent, 3; manesium oxide, 10; MT carbon black, 35. Vulcanization: Press, 160°C for 30 min; oven, 200°C for 2 hr. Data from Ref. 61.

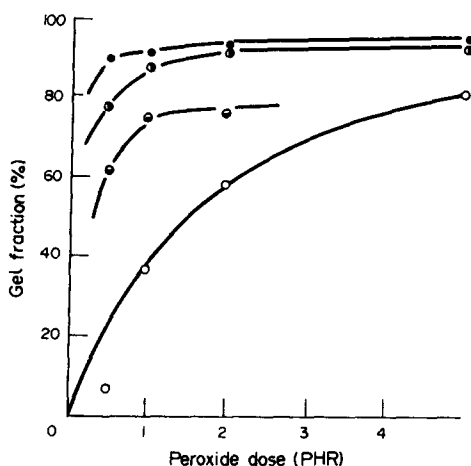


FIG. 21. Curing of TFE/propylene elastomers. Relation between peroxide level and gel fraction of an M_n 180,000 polymer; (O) without triallyl isocyanurate (TAIC); (●) with 3 phr TAIC; (⊖) with 2.4 phr divinylbenzene; (⊙) with 3 phr triallyl-cyanurate (TAC).⁶¹

TABLE 8. Properties of standard vulcanizates

	"Bisphenol AF" or peroxide cured vinylidene fluoride based fluoroelastomers*	Peroxide cured C_2F_4/C_3H_6 elastomer†
Physical properties		
Specific gravity, g/cm ³	1.9	1.6
Tensile strength, MPa	14–20	20–25
Elongation at break, %	150–400	200–400
Tensile modulus at 100% strain, MPa	4–6	2.5–3.5
Hardness, shore A	60–90	70
Compression set resistance, %	15–40	35
Brittle point, °C	–45	–40
Retraction temp. TR-10, °C	–20	–3
Chemical resistance		
	Volume increase after immersion (%)	
95% H_2SO_4 , 100°C, 3 days	5–25	4.4
60% HNO_3 , 70°C, 3 days	12–47	10
H_2O , 150°C, 3 days	5–10	8.7
Steam, 160°C, 7 days	1–8	4.6
Fuel oil B, 25°C, 7 days	1	58.6
Benzene, 25°C, 7 days	5–12	40
Methanol, 25°C, 7 days	4–30	0.2
Ethyl acetate, 25°C, 7 days	> 100	88

*From Viton® Trade Bulletins VT-230.B and VT-250.GF.

†Reported in Refs 60–62, 65 and 68.

fluoride based polymers. It also involves formation of polymeric radicals via abstraction of a hydrogen atom from the backbone by the peroxide and the eventual trapping of these radicals into a crosslinked network by the coagent (radical trap).

TFE/propylene fluoroelastomers with small amounts of a cure site monomer have also been reported. Du Pont workers have shown that aryloxyalkyl vinyl ether-containing polymers can be cured with paraformaldehyde,⁶³ and vinylidene fluoride (VF₂)-containing polymers can be cured with dinucleophiles⁶⁴ to give satisfactory properties. Recently, Kojima and coworkers at Asahi Glass Co.⁶⁵ have shown that a cure site monomer like glycidyl vinyl ether may be introduced in the polymer without disturbing the predominant alternating structure of the copolymer. These TFE/propylene/glycidyl vinyl ether terpolymers can be cured at room temperature with tris(dimethylaminomethyl)phenol in the presence of phenol accelerators or at higher temperatures (170°C) by diamines. The same workers also reported TFE/propylene/VF₂ terpolymers⁶⁶ as a means of improving the low-temperature properties. Thus, the T_g can be lowered from -2°C for the TFE/propylene copolymer to -13°C for the TFE/propylene/VF₂ without changing substantially any of the physical properties. This VF₂-containing terpolymer can be cured either with the peroxide/radical trap system or with dinucleophiles.

Copolymers of TFE/alkyl vinyl ethers containing chloroalkyl vinyl ethers as cure site monomer have also been reported to be curable with diamines.⁶⁷

5. PERFLUOROELASTOMERS

5.1. Introduction

The extreme thermal stability and chemical, fluid and oxidative resistance of Teflon[®] perfluorinated plastics is largely attributed to the absence of C-H bonds. The fluoroelastomers described in the earlier sections all contain C-H bonds in the backbone and are, therefore, limited to 200–230°C for extended service and are attacked by certain fluids even at room temperature.

Perfluoroelastomers that match the oxidative, thermal and chemical inertness of "Teflon" are currently based on copolymers of TFE and perfluoroalkyl vinyl ethers. Because of the low reactivity of hexafluoropropylene or other perfluoroolefins, it is very difficult to make amorphous copolymers with TFE. Only perfluoroalkyl vinyl ethers have enough reactivity to copolymerize with TFE in a random fashion to give high molecular weight amorphous copolymers having low temperature flexibility. When 20–40 mol% of the perfluoroalkyl vinyl ethers are incorporated, the copolymers are true elastomers with T_g below room temperature. The most readily copolymerizable homolog is perfluoromethyl vinyl ether, which is the cornerstone of Du Pont's commercial Kalrez[®] perfluoroelastomer.^{69–75} Higher perfluoroalkyl vinyl ethers also give elastomeric copolymers of TFE with lower T_g values. They have the disadvantage, however, that the

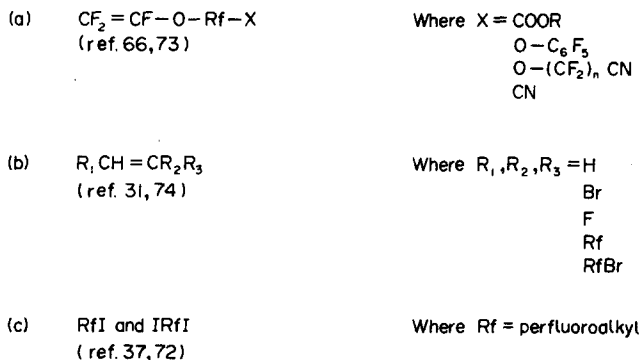
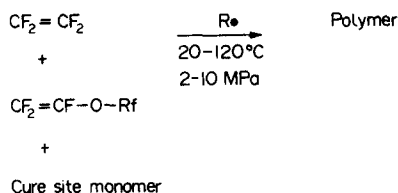


FIG. 22. Classes of cure site monomers as described in published articles and patents.

rate of polymerization is reduced substantially and that it becomes progressively more difficult to make polymers of adequately high molecular weight for good elastomeric properties. For example Uschold⁷ was able to prepare copolymers of TFE with $\text{C}_3\text{F}_7\text{O} - [\text{CF}(\text{CF}_3) - \text{CF}_2 - \text{O}]_n - \text{CF} = \text{CF}_2$ where $n = 3-11$. The T_g values of such polymers were in the range of -33 to -76°C . Tatemoto and coworkers⁷⁶ reported high molecular weight copolymers similar to those reported by Uschold where $n = 1-3$ with T_g values around -32°C .

A third monomer is usually added in small amounts (1 mol%) to make these polymers curable. It is very important that the cure site monomer copolymerizes with TFE and perfluoroalkyl vinyl ether in a random fashion, that it does not cause chain transfer, and that it leads to high molecular weight polymers. It should also be capable of forming a thermally and oxidatively stable network inert to aggressive fluids. Three classes of monomers that meet the above requirements have been reported in the literature and are shown in Fig. 22. The substituted perfluorinated alkyl vinyl ethers shown in eq. (a) are the most useful because they allow the most versatility in the curing chemistry. They are easily incorporated in a random fashion and do not compromise the inertness of the resulting perfluoroelastomers since they are also perfluorinated. The substituted fluoroolefins containing a hydrogen, a bromine or both functionalities as shown in eq. (b), have limited utility. Substituted fluoroolefins are not very reactive in copolymerizing with TFE and Rf-O-CF=CF_2 , so only the simplest types like vinylidene fluoride or trifluoroethylene can be used. When the olefin also contains a bromine atom as a substituent, there is the added complication of chain transfer during polymerization. Perfluoroiodo compounds shown in eq. (c) act predominantly as very efficient chain transfer agents. The same chemistry described previously for the vinylidene fluoride based fluoroelastomers can be applied with the TFE/Rf-O-CF=CF₂ copolymers. Thus perfluoroelastomers with bromo- and iodo-substituents have been prepared and cured with peroxides and a radical trap. The crosslinking chemistry for all these different cure sites will be described in a later section.

FIG. 23. Polymerization of perfluoroelastomers.⁷²⁻⁷⁴

5.2. Polymerizations

Polymerizations are usually carried out in an aqueous system by feeding the monomers under pressure into a stirred reactor using either redox or thermally generated free radicals (Fig. 23). The initiation systems and polymerization conditions are very similar to those described in the fluoroelastomer section. A persulfate/sodium sulfite redox initiator operating in the range of 50–70°C is used when it is difficult to attain high molecular weight polymers. This initiating system, however, gives sulfonic acid end groups, which in turn form “strong” ionomeric domains, making the polymers difficult to process. Thermally initiated free-radical polymerizations using ammonium or potassium persulfate at temperatures of 70–120°C are suitable in systems where chain transfer is less important. The end groups formed when this initiator system is used are mostly carboxylic acids which also form ionomers but these ionomers disassociate at lower temperatures than those from sulfonic acid end groups, thus making the polymers easier to process. All aqueous polymerizations require a surfactant, usually a salt of a perfluorinated acid (C₈–C₁₂), and a buffer to maintain the pH close to neutral.

Anhydrous polymerizations using chlorofluorocarbon (“Freon”) type solvents and an organic peroxide as initiator have been described as well.^{7,76} The advantage of such systems lies in the low concentrations of ionic end groups formed and the subsequent good processing behavior of the polymers. On the other hand, solvent-based systems are less practical because of the low solubility of perfluorinated polymers and they usually give polymers with lower molecular weights. A hybrid suspension polymerization system of tetrafluoroethylene (TFE) and perfluoroalkyl vinyl ethers in a medium comprising water and a fluorocarbon-type solvent at room temperature using (Cl(CF₂)_nCOO)₂ initiator has also been reported.⁷⁷ The copolymers made this way also have low concentrations of unstable ionic end groups.

The polymerizations can be run in a batch or continuous fashion, and both types have been described in the literature. Standard spectroscopic techniques, infrared or NMR, have been used to determine the composition of the polymers.

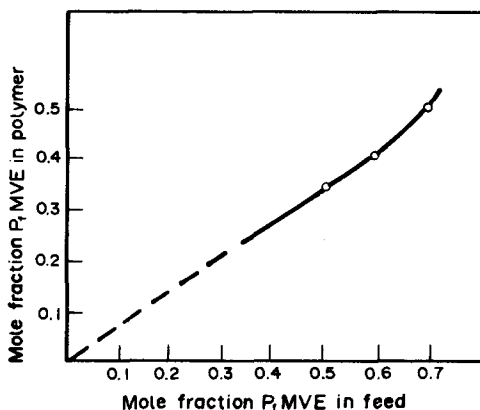


FIG. 24. TFE/perfluoromethyl vinyl ether (PFMVE) copolymers. Polymer composition as a function of monomer feed ratio at 60°C in an aqueous system at about 50% conversion.⁶⁹

5.3. Raw polymer properties

Barney and coworkers⁶⁹ have described the polymerization of TFE/ $\text{CF}_3\text{-O-CF=CF}_2$ to give copolymers of various compositions as a function of monomer feed (Fig. 24). The effect of perfluoromethyl vinyl ether content on the T_g and thermal stability of the raw polymer is shown in Figs 25 and 26. Addition of small amounts of a cure site monomer like perfluorophenoxyalkyl vinyl ethers does not change the glass transition relationship substantially but lowers the thermal stability somewhat. Thus, it is reported⁶⁹ that perfluorophenoxy-containing polymers lost about 12% weight on heat aging at 340°C for 7 days in an air oven, while the TFE- $\text{CF}_3\text{OCF=CF}_2\text{CO}$ polymer lost only 6.5% under identical conditions.

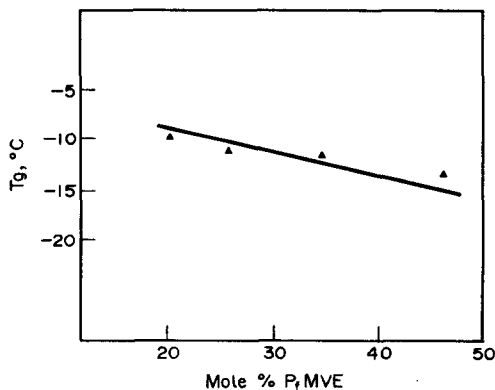


FIG. 25. T_g of TFE/perfluoromethyl vinyl ether (PFMVE) copolymers.⁶⁹

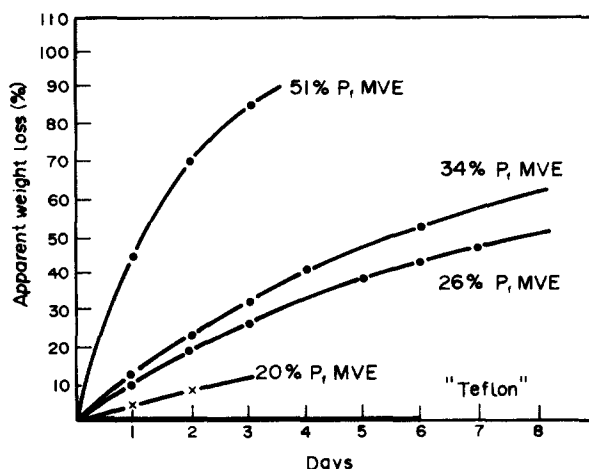


FIG. 26. Thermal stability of TFE/perfluoromethyl vinyl ether (P_fMVE) in air in a glass vessel at 340°C.⁶⁹

The raw polymer density is 2.04 ± 0.01 and changes very little with the composition. The raw polymer is insoluble in practically all solvents except those of the "Freon" type. Thus, dilute solutions can be prepared in "Freon"-113 or 2,2,3-trichloroheptafluorobutane in combination with small amounts (2–3%) of a polar solvent like dialkyl ethers of glycols and triglycols or tetrahydrofuran or methanol. The inherent viscosities can be determined in such sys-

TABLE 9. Raw polymer properties*

Stress-strain, original	
Modulus at 100% strain, MPa	1.65
Tensile strength at break, MPa	4.65
EB, %	240
Low temp. properties	
Brittle pt, °C	–45
T _g , °C	–8
Wt increase (10 days at 25°C), %	
Diethylamine	0.61
Fuming nitric acid, 90%	0.75
Freon [®] 113	40
Skydrol 500	0.41
Permeability (mg/mcl/hr/cm)	
Benzene	0.061
CCl ₄	0.051
Ethyl acetate	0.065
MeO	0.011
Water	< 0.05

*Data from Refs 69 and 70.

TABLE 10. Dielectric properties of gum perfluoroelastomer*

Property	Perfluoroelastomer	TFE
Dielectric constant "E"	2.8-3.2	2.1
Dissipation factor "D" (50% RH, 25°C)	1×10^{-3}	3×10^{-4}
D.C. Resistivity "P", ohm-cm	10^{18}	10^{18}
Dielectric strength (volts/mil) (breakdown)	> 2000	400

*Cured gum stock. Data from Ref. 75.

tems, and it was found that polymers with values > 0.4 are suitable to give good vulcanizate properties.⁷⁰ Raw polymer properties for TFE/CF₃-O-CF=CF₂ are shown in Tables 9 and 10.

5.4. Curing chemistry of perfluoroelastomers

In spite of the very small volume of these materials used commercially, a relatively large number of cure site monomers is used and quite a number of ways of crosslinking them have been developed. Examples of the various curing systems are described in the sections that follow. Similar to that for fluoroelastomers, the curing process for perfluoroelastomers consists of two steps: (a)

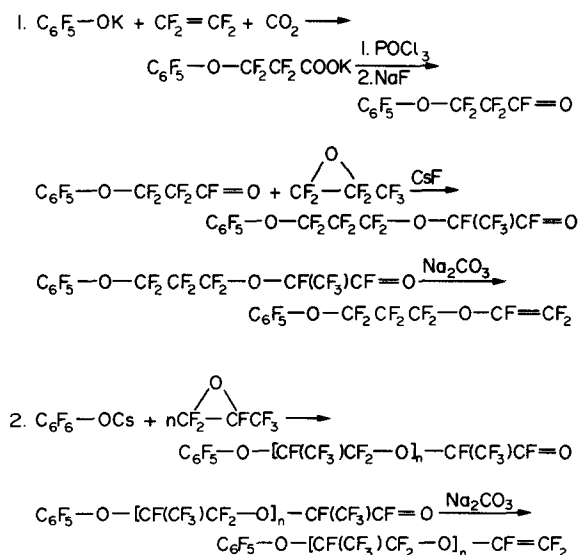


FIG. 27. Synthesis of perfluoro(3-phenoxypropyl vinyl ether) and perfluoro(2-phenoxypropyl vinyl ether).⁷⁰

press curing done in a mold at 150–200°C under pressure for 10–60 min and (b) the postcure done in an oven in air or under nitrogen at 200–300°C for 24–120 hr. The purpose of the postcure is to improve the physical properties of the vulcanizates (tensile properties, compression-set resistance, and fluid resistance) which are somewhat deficient after the press cure. As discussed in detail in the fluoroelastomers section, the actual chemical processes taking place during the postcure step are not well understood. It is believed that completion of the curing reactions, removal of the volatile by-products generated in the curing step, improved interaction between polymer and fillers, and some thermal rearrangement of the crosslinking network to relieve stresses, all contribute to the considerable improvement in properties.

5.4.1. Crosslinking of perfluorophenoxy-containing perfluoroelastomers — The cure site monomers used to make the above polymers were prepared by a multiple step synthesis as outlined in Fig. 27. The potassium salt of pentafluorophenol and hexafluoropropylene oxide are the key starting materials. The cost of the final product is quite high because of the expensive ingredients and the number of steps needed.

Curing of these polymers takes place by a dinucleophilic attack. Workers at Du Pont⁷⁰ found that diamines such as *p*-phenylenediamine, tetraethylenepentamine or hexamethylenediamine carbamate are quite effective. The elastomer, fillers and curing ingredients are mixed on a rubber mill and the desired shape is molded in a press at 3–7 MPa for 30 min at 160–180°C. The piece is then removed from the press and postcured for 5–6 days at elevated temperatures. The present concept of the crosslinking reaction is described by Du Pont workers.^{70–75} The diamine reacts with the active fluorine atom *para* to the oxygen linkage on the aromatic ring to liberate hydrogen fluoride. The hydrogen

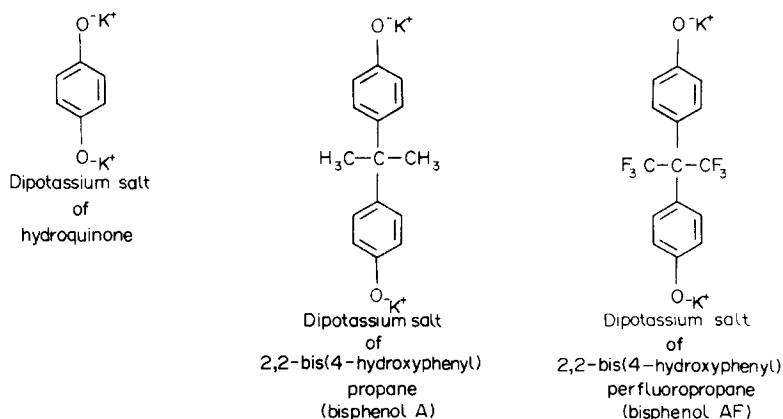


FIG. 28. Typical bisphenols dinucleophiles used in curing phenoxy-containing perfluoroelastomers.⁷⁰

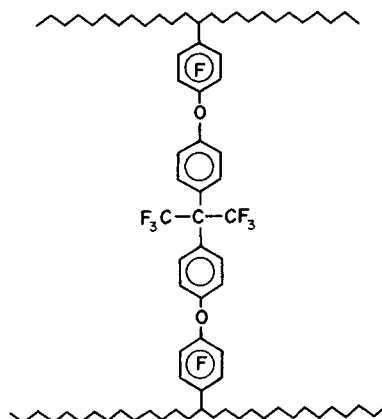


FIG. 29. The structure of the crosslinks formed after curing perfluorophenoxy-containing perfluoroelastomers with bisphenol AF.⁷²⁻⁷⁴

fluoride, in turn, reacts with magnesium oxide or other metal oxides present (PbO, CaO or ZnO may also be used) to form water and metal fluoride. Under the conditions required to complete the curing, water must be expelled from the molded piece, and because of the low permeability of the perfluorinated elastomer to moisture, the temperature of the postcure oven must be raised stepwise to prevent sponging. The aliphatic diamines which are the crosslinks are not thermally stable and the upper temperature resistance of the diamine cured perfluoroelastomers is limited.

Better dinucleophiles are the more thermally stable bisphenols. Examples of such species (used as their potassium salts) are shown in Fig. 28. These crosslink-

TABLE 11. Typical physical properties of perfluoroelastomers*

Specific gravity, g/cm ³	2.05
Tensile strength, MPa	16
Elongation at break, %	160
Tensile modulus at 100%, MPa	9
Hardness, shore A	75
Compression set, %	
70 hr at 121°C	23
70 hr at 288°C	45
Clash-Berg stiffness temp., °C	-2
(66.6 MPa torsional modulus)	
Brittle temp., °C	-38
Retraction temp., °C	
TR-10	-1
TR-50	+8

*Polymer recipe: polymer, 100; SAF black, 10; MgO, 4; accelerator, 3; bisphenol AF, 3. Data from Ref. 70.

TABLE 12. Permeability of perfluoroelastomers*

Test material	Temp. (°C)	Permeability (cc/cm ² -sec-atm)	Diffusivity (cm ² /sec)	Solubility (cc/cm ² -atm)
Benzene vapor	150	4.9×10^{-6}	1.6×10^{-6}	3
Isooctane	150	1.51×10^{-6}	6.83×10^{-7}	2.22×10^{-2}
Jet fuel II	30	0.5×10^{-11}		
Jet fuel II	150	2.88×10^{-8}		
O ₂	32	9.6×10^{-8}	3.8×10^{-7}	0.25
N ₂	30	2.6×10^{-8}	1.8×10^{-7}	0.14

*Data from Ref. 75. Black compounded stock cured with bisphenol AF.

ing agents require an accelerator to function well, such as polyethers like polyethylene ether glycols $[\text{CH}_3\text{-O-(CH}_2\text{CH}_2\text{-O)}_n\text{-H}$, of MW 350, Carbowax 350] or the cyclic polyether compounds of "crown" structure. The role of the accelerators is not well understood. It is assumed they act as complexing agents to solubilize the phenolic metal salts. The press cure conditions are similar to those described with the diamines and the postcure is carried out for 2–4 days under nitrogen at about 250°C. The diphenol curing system is superior to that of the diamines in processing (milling, preforming and curing) and in the final properties. A typical set of the properties obtained are shown in Tables 11 and 12. The most likely structure of a "bisphenol AF" crosslink is shown in Fig. 29.

5.4.2. Crosslinking of nitrile-containing perfluoroelastomers — The preparation of perfluoroalkyl vinyl ethers containing nitrile groups involves many steps and two such processes are shown in Fig. 30. The final monomers are expensive because of the high cost of the starting materials and the multistep processes. They are, however, convenient monomers to handle because they readily copolymerize with TFE and perfluoroalkyl vinyl ethers in an aqueous free radical polymerization, the nitrile groups being unaffected by the polymerization conditions. The infrared spectra of these polymers show typical nitrile peaks at 2271 cm^{-1} and this peak is calibrated to estimate quantitatively the amount of the cure site monomer incorporated in the polymer. A typical nitrile-containing cure-site monomer is perfluoro-(8-cyano-5-methyl-3,6-dioxo-1-octene), whose synthesis is described in Ref. 78. This monomer has about the same reactivity towards TFE as perfluoromethyl vinyl ether, thus making it easy to incorporate in a random fashion the amount of nitrile functionality needed for optimum properties. Crosslinking is brought about by the catalytic interaction of tetraphenyltin or silver oxide on the pendant nitrile groups. The structure of the crosslinks is assumed to be mainly triazine as shown in Fig. 31. This is supported by the work of Henne⁸⁰ who showed unequivocally that monomeric perfluorocarbonitriles form triazine rings in the presence of catalysts like tetraphenyltin or silver oxide. The crosslinked polymers showed an infrared band at

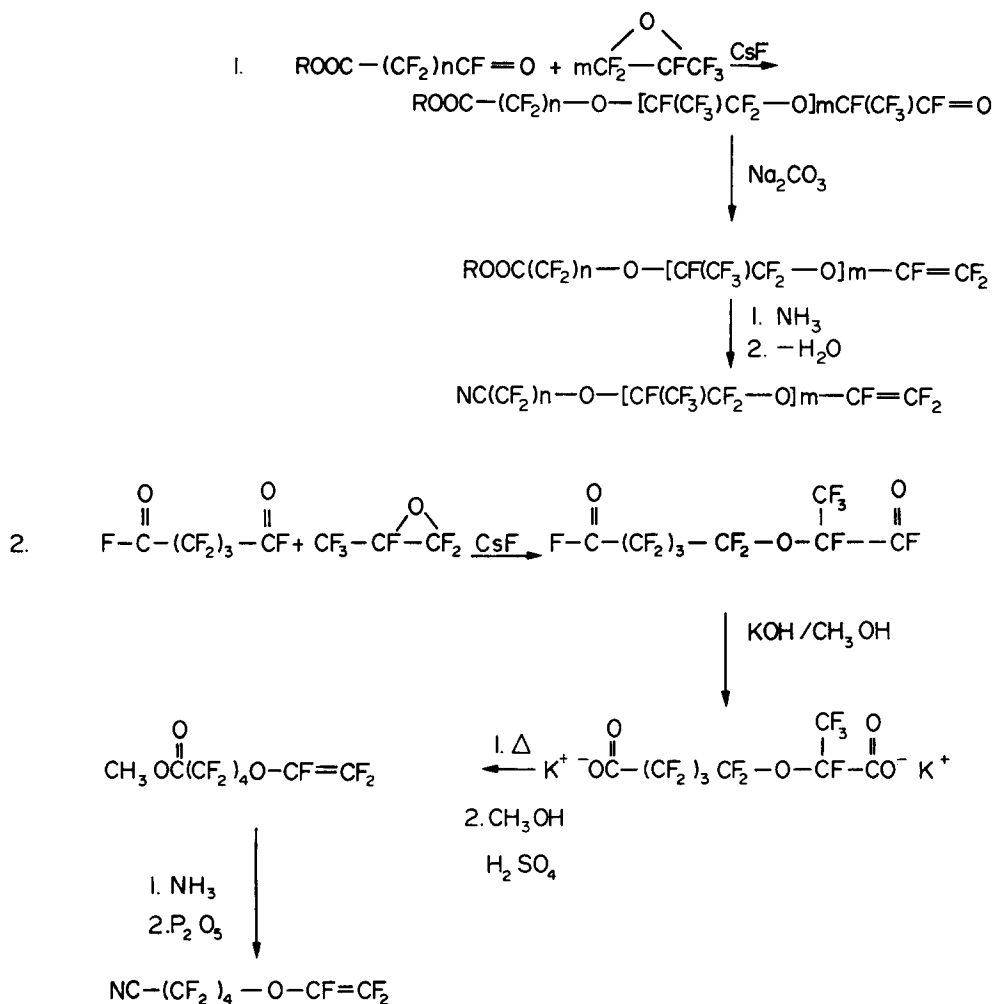


FIG. 30. Synthesis of perfluoro-(8-cyano-5-methyl-3,6-dioxo-1-octene) and perfluoro-(9-cyano-5-methyl-3,6-dioxo-1-nonene) where $m = 1$ and $n = 2, 3$ and perfluoro(4-cyanobutyl vinyl ether).^{70,77}

1560 cm^{-1} , typical of triazine, supporting the assumption that triazine is the main crosslinking structure.

5.4.3. Crosslinking of halogen-containing perfluoroelastomers — The finding that bromine- or iodine-containing vinylidene fluoride based fluoroelastomers can be peroxide cured in the presence of a radical trap prompted the extension of this technology to the perfluoroelastomer field. Du Pont workers^{31,32,72-74} were first to demonstrate that perfluoroelastomers containing small amounts of randomly

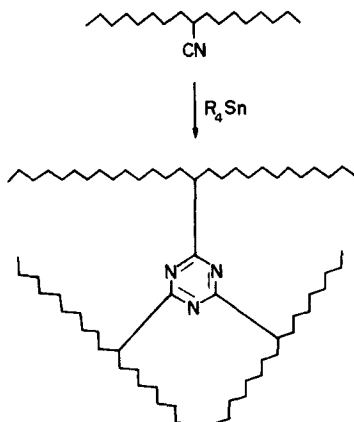


FIG. 31. The structure of the crosslinks formed after curing nitrile-containing perfluoroelastomers.⁷²⁻⁷⁴

distributed bromine atoms on the backbone or in side chains can be peroxide cured. The curing recipe has certain similarities to that used with the fluoroelastomers but had to be extensively modified for optimum properties. Daikin workers extended their end-group modification of fluoroelastomers with perfluoroalkyl iodide compounds to the perfluoroelastomers.^{37,76} The polymers containing iodine substituents at the end groups are crosslinkable with peroxides in the presence of radical traps. Aliphatic or aromatic peroxides have been used successfully and among the many radical traps tried, triallyl isocyanurate is preferred. The mechanism of crosslinking is similar to that described for the fluoroelastomers, indicating that the radical trap becomes part of the crosslinking structure (Fig. 32). The rate of cure of these polymers is faster than that of

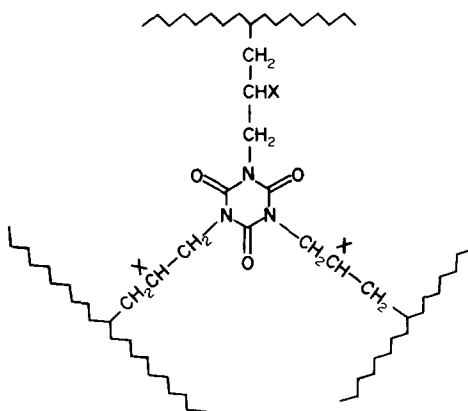


FIG. 32. The assumed structure of the crosslinks formed after curing of halogen-containing perfluoroelastomers with peroxides in the presence of a radical trap (triallyl isocyanurate).⁷²⁻⁷⁴

TABLE 13. Effect of postcure on physical properties*

Original properties at 25°C	After press cure (190°C/15 min)	After postcure (232°C/26 hr)
Tensile strength, MPa	7.1	10.5
Elongation at break, %	387	225
Tensile modulus at 100%, MPa	4.1	5.7
Tensile modulus at 200%, MPa	5.0	9.2
Compression set, % (200°C/70 hr)	89	51

*Bromine-containing perfluoroelastomer. The recipe: polymer, 100; SAF black, 10; metal oxide, 3; peroxide, 4; triallyl isocyanurate, 4. From Ref. 74.

the phenoxy- or nitrile-containing types. After 15 min at 180°C, the maximum torque has been reached for the peroxide curing system while it is still rising for the others. However, postcure is still required in order to develop optimum properties (Table 13). The physical properties improved substantially upon postcuring; for example, the modulus and tensile strength increase by 50–80%, and the elongation-at-break and compression set decrease by 50–80%.

5.4.4. Crosslinking of hydrogen-containing perfluoroelastomers — One of the main reasons for the excellent thermal and oxidative resistance of the perfluoroelastomers is the absence of carbon–hydrogen bonds on the polymer backbone. The C–H bond is the weak point where oxidative and thermal attack may be initiated. Thus it is possible to utilize small concentrations of C–H on the polymer as cure site, very much like the perfluorophenoxy, nitrile and Br or I groups described earlier. Finlay⁷⁹ introduced just enough C–H bonds (0.5–2.0 mol%) to generate adequate crosslinking without causing deterioration in oxidation and thermal resistance properties of the elastomer. The hydrogen atoms, being located adjacent to –CF₂– groups, are acidic enough to be susceptible to nucleophilic attack. These polymers can be cured with strong dinucleophiles, either diamines or the bis(metal salts) of bisphenols. The strong base presumably eliminates a molecule of hydrogen fluoride to create unsaturation on the polymer, and then the bisnucleophile adds across the double bonds to form the crosslinks. The satisfactory curing of such copolymers was somehow surprising in view of Schmiegel's work.^{17,36} He found excessive porosity when he tried to cure with nucleophiles VF₂/TFE/RfOCF=CF₂ elastomers where VF₂ was 40–60 wt% of the composition. Finlay's success was probably due to the limited amount of VF₂ present in the polymer.

5.5. Property differentiation between curing systems

Perfluoroelastomers are stable macromolecules because they contain predominantly carbon–fluorine bonds which are thermally and oxidatively stable and

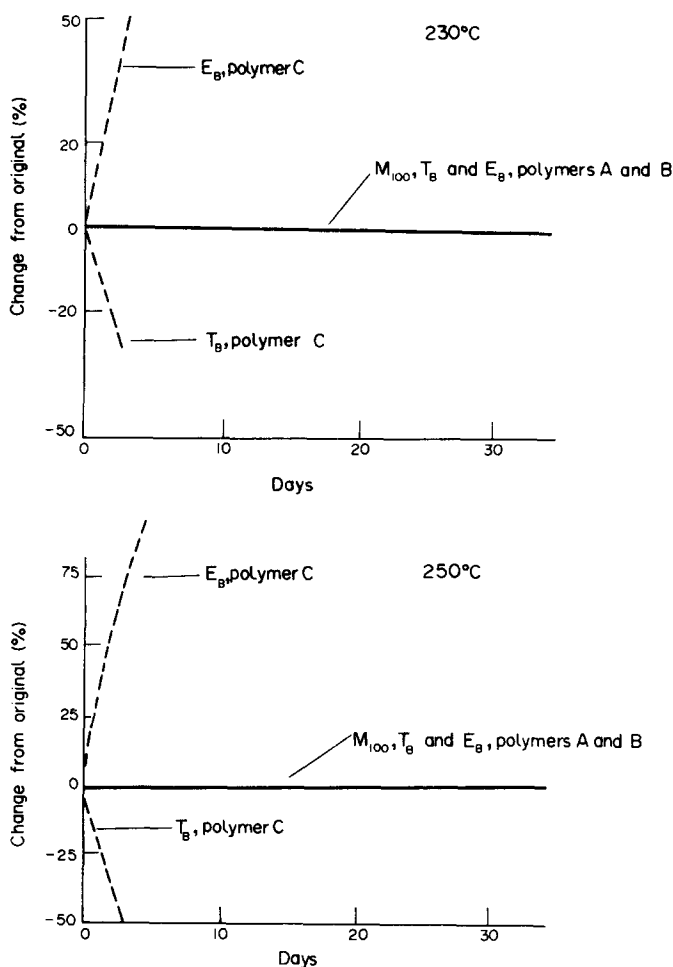


FIG. 33. Tensile properties after heat aging cured stocks of perfluoroelastomers: polymer A (nitrile-containing); polymer B (bisphenol AF cured); polymer C (halogen-containing, peroxide cured).⁷² M_{100} = modulus at 100% strain; T_B = tensile strength at break; E_B = tensile elongation at break.

very much inert to any chemical attack. The weak points in these polymers are the cure sites because they are designed to be chemically attacked under the curing conditions so that the crosslinking takes place. The four different ways of curing these polymers give four different crosslinking structures. In the perfluorophenoxy- and hydrogen-containing polymers, the network contains "bisphenol AF" as the crosslinking structure. The nitrile-containing polymer utilizes triazine as the crosslinking structure and the peroxide curable types (Br- or I-containing polymers) have alkyl isocyanurate-type structures in the network. The thermal, oxidative and chemical stability of these crosslinks varies

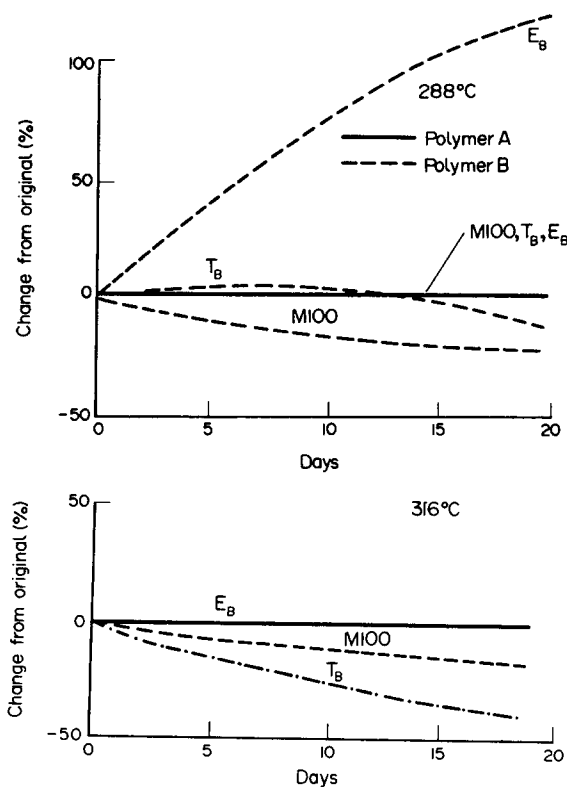


FIG. 34. Tensile properties after heat aging cured stocks of perfluoroelastomers: polymer A (nitrile-containing); polymer B (bisphenol AF cured); polymer C (halogen-containing, peroxide cured).⁷² Footnotes as in Fig. 33.

considerably, depending on the chemical structure of the crosslink. "Bisphenol AF" and triazine, being aromatic structures, are expected to be thermally and oxidatively stable, while the alkyl isocyanurates which contain aliphatic hydrogens are expected to be relatively unstable. At room temperature, the tensile properties and compression set resistance values are about the same and independent of the cure site used. After exposure to air at higher temperatures the property differences become pronounced. Figures 33 and 34 show the change of tensile properties after cured stocks of perfluoroelastomers with different cure systems were heat aged in air at different temperatures.⁷²⁻⁷⁶ The results show that the perfluoroelastomers containing Br or I and peroxide cured have an upper use temperature of about 220–225°C. The perfluoroelastomers with "bisphenol AF" crosslinks, with either perfluorophenoxy or carbon-hydrogen as the cure site, are stable in the range of 270–290°C. The most thermally stable perfluoroelastomers are those that contain triazine crosslinks. These still maintain their properties quite well even after exposure to 316°C.

TABLE 14. Chemical and fluid resistance of perfluoroelastomers*

	Temperature (°C)	Time (hr)	Curing system		
			Triazine (% swell)	Bisphenol AF (% swell)	Peroxide (% swell)
Fluids					
Nitric acid	85	70	3	8	9
Acetic acid	100	70	3	32	16
Aniline	100	166	5	2	6
Butyraldehyde	70	70	13	10	14
Toluene	100	70	7	7	7
Skydrol 500B	125	70	9	5	6
Methyl ethyl ketone	70	70	6	4	4
Water	225	70	27	60	7

*Black loaded stocks. Data from Ref. 74.

There is also differentiation in fluid resistance under aggressive conditions. The swelling data for perfluoroelastomer samples cured with different systems are shown in Table 14. The fluid resistance towards most of the chemicals and organic solvents is excellent for all types. There are, however, some distinct differences. For example, towards glacial acetic acid (at 100°C) and water (225°C under pressure) the "bisphenol AF"-crosslinked material showed considerably higher swell than the other types. At the same time, the peroxide-cured material showed outstanding resistance to water at 225°C under pressure. All perfluoroelastomers show fair to poor resistance towards chlorofluorocarbon-type solvents, although they are quite resistant towards hydrogen-containing fluorocarbons. Thus, one has to be careful in using perfluoroelastomers in sealing applications with "Freon" type liquids or gases.

6. USES OF FLUOROELASTOMERS

The commercial use of fluoroelastomers and perfluoroelastomers is largely the result of their excellent resistance to heat, fluids, and oxidizing media as well as their excellent physical properties. Elastomeric seals for industrial, aerospace and automotive equipment constitute the largest applications. These are mostly O-rings of all sizes, V-rings, flat or lathe-cut gaskets and lip-type rotating or reciprocating shaft seals. Coated fabrics for diaphragms, sheet goods, expansion joints, chimney and duct coatings account for considerable consumption. Hose-linings, tubing and industrial gloves for chemical service, extruded goods for such purposes as autoclave and oven seals, electrical connections and wire coatings constitute examples of the varied end uses. Their value in use has been confirmed in numerous applications that require a combination of chemical, thermal, fluid and oxidation resistance where no other material can do the job.

These polymers are relatively difficult materials to process and sometimes require high temperatures and special techniques to do so. Vigorous exothermic decompositions of fluoroelastomeric compounds during processing have occurred on rare occasions. These have occurred at extremely high processing temperatures ($> 260^{\circ}\text{C}$) and when divided metals (aluminium or lead powder) were present or when a large amount of curing ingredients was added accidentally.^{14,81}

Fluoroelastomers based on co- or terpolymers of vinylidene fluoride have been compounded for optimum performance.⁸² In applications where the flexing life is important, decreasing the carbon black content and increasing the molecular weight of the base polymer help to extend the use life.⁸³ Keeping the strain to relatively low values also helps in prolonging the fatigue life. These elastomers can be compression molded, injection molded or extruded.⁸⁴⁻⁸⁶ The peroxide curable fluoroelastomers are extremely good in sealing applications where the parts are exposed to steam and acids at high temperatures and pressures.⁸⁴

7. SUMMARY

Fluorocarbon elastomers represent a broad class of high performance elastomers which combine excellent thermal, oxidative and fluid resistance with very good tensile and compression-set resistance properties. These polymers are characterized by having carbon-carbon bonds in the backbone and a considerable amount of fluorine (50–73 wt%). They are made by using different combinations of some of the same fluoroolefin monomers. The commercially important types are classified into three categories:

(a) Random copolymers of vinylidene fluoride with perfluoroolefins such as hexafluoropropylene, tetrafluoroethylene, and perfluoroalkyl vinyl ethers. Cure site monomers may also be incorporated.

(b) Copolymers of tetrafluoroethylene and propylene (in about equal molar amounts) which have mostly an alternating structure. Cure site monomers may also be incorporated.

(c) Copolymers of tetrafluoroethylene with perfluoroalkyl vinyl ethers. Cure sites are imperative for curing these highly inert materials.

Curing chemistry suitable for each composition has been developed. The polymer structure is very important in determining the physical properties of an elastomer. However, the crosslinking chemistry used in curing determines to a great extent the properties of the final rubber part. Because of their excellent properties these polymers are being increasingly used in applications where no other material is suitable. In spite of their higher costs, fluoroelastomer uses are expected to keep growing in volume at an estimated rate of 10% per year.

Most of the current research effort is aimed towards improving the processability of the polymers and the properties of the resulting rubber parts. It is expected that new polymeric compositions and new curing chemistry will appear in the future.

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PROTECTING OUR ENVIRONMENT, PRESERVING THE ENCHANTMENT

Air Quality Bureau

Ozone Pollution Health Effects

Is ozone pollution harmful?

Ground-level ozone is a public health concern. Prolonged exposure to low-level ozone concentrations is as harmful to human health as exposure to higher levels for shorter durations.

Although certain groups of people are considered most at risk from ozone pollution due to developing or compromised cardiovascular systems, even healthy people can be affected.

What are the main health effects of ozone pollution?

Ozone can inflame the airways, causing symptoms such as chest pain, coughing, wheezing and shortness of breath, even in healthy people. These effects can be more serious in people with lung diseases, such as asthma.

Ozone can harm the respiratory system by inflaming cells that line the upper airways and the lungs, much like a sunburn damages skin.



- Short-term exposures to ozone can make it more difficult to take a full, deep breath and can cause adverse respiratory symptoms. These short-term exposures also can aggravate asthma and other lung diseases and can make people more susceptible to respiratory infections.
- Long-term exposure to ozone is linked to the development and aggravation of asthma and a variety of other effects on the respiratory system. New studies warn of serious effects from breathing ozone over longer periods (days, months or years). With more long-term data, scientists are finding that long-term exposure (i.e., for periods longer than eight hours) may increase the risk of early death.

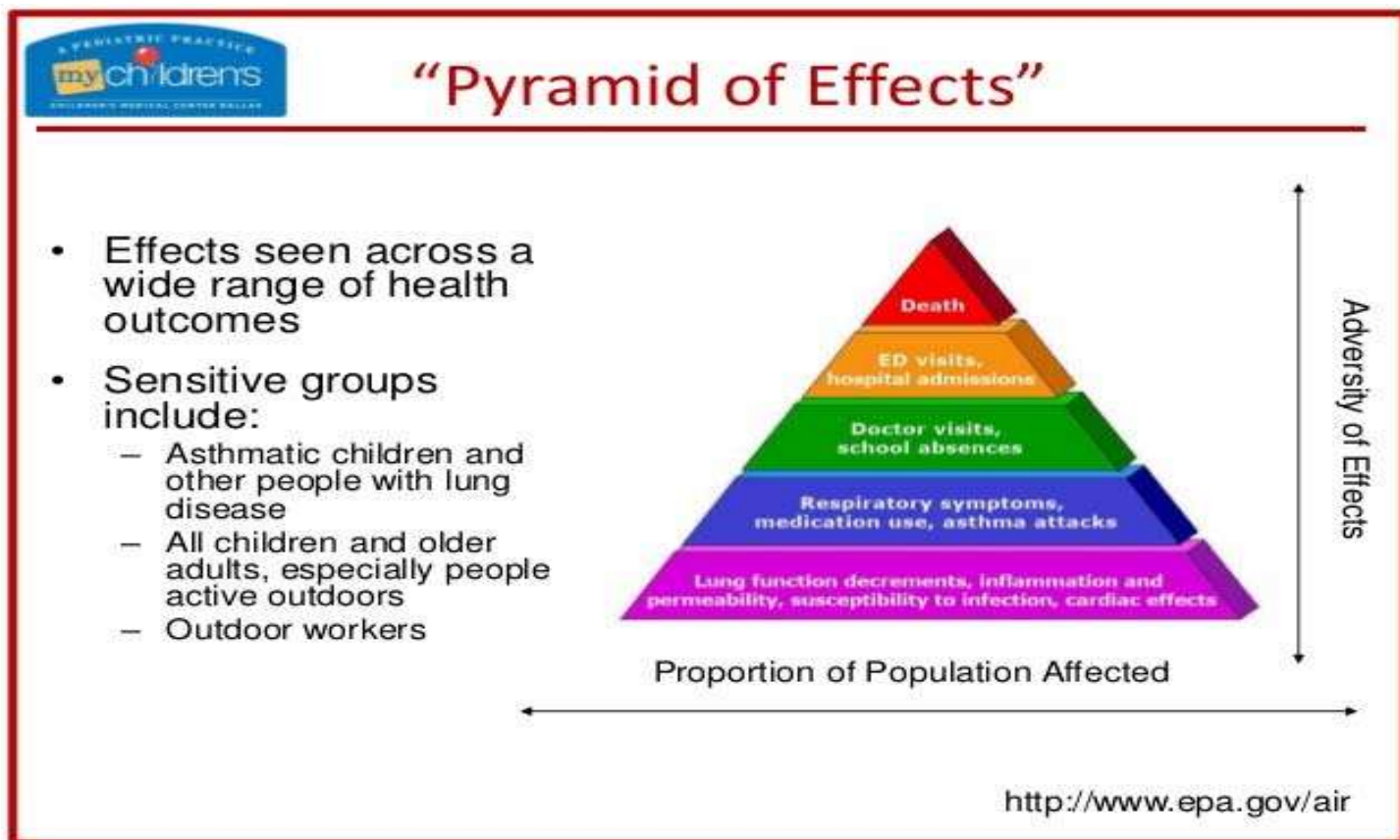
Anyone who spends time outdoors where ozone concentrations are high may be at risk of experiencing health effects. Five groups of people are especially vulnerable to the effects of breathing ozone:

- children and teens;
- adults 65 and older;
- people who work or exercise outdoors;
- people with existing lung diseases, such as asthma and chronic obstructive pulmonary disease (also known as COPD, which includes emphysema and chronic bronchitis); and
- people with cardiovascular disease.

Because children and teens spend nearly twice as much time outdoors and engage in vigorous activities twice as much as adults, their risk of health impacts is increased relative to adults. Children breathe more rapidly than adults and inhale

Ozone Pollution Health Effects

more pollution per pound of body weight than adults, increasing their exposure to pollution. Also, children are less likely than adults to notice their own symptoms and avoid harmful exposures. Repeated ozone exposure to developing lungs can affect children into adulthood, contributing to permanent reductions in the lungs' ability to function. Older adults may be more affected by ozone exposure due to already decreased lung tissue elasticity; effects are heightened if they have pre-existing lung conditions.



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Polymers of Low Concern

Background information

Work on polymers was undertaken at the OECD starting in the early 1990s. The First Meeting of the Expert Group on Polymer Definition held in Toronto, Canada (January 1990), developed the polymer definition. This was reconfirmed at the Second Meeting of the Expert Group on Polymer Definition held in Paris, France (October 1991), and in the Second Meeting of the OECD Expert Group on Polymer Definition: Chairman's Report [ENV/MC/CHEM(91)18], it is stated in paragraph 5:

In considering the report and subsequent comments the Group reconfirmed the agreed definition on polymers for use in new chemicals notification procedures i.e.":

An OECD definition developed to distinguish discrete substances from polymers:

A 'POLYMER' means a substance consisting of molecules characterized by the sequence of one or more types of monomer units and comprising a simple weight majority of molecules containing at least three monomer units which are covalently bound to at least one other monomer unit or other reactant and consists of less than a simple weight majority of molecules of the same molecular weight. Such molecules must be distributed over a range of molecular weights wherein differences in the molecular weight are primarily attributable to differences in the number of monomer units. In the context of this definition a 'MONOMER UNIT' means the reacted form of a monomer in a polymer."

1. A Third Meeting of OECD Experts on Polymers, held in Tokyo, Japan (April 1993), further clarified some of the terms of the definition to avoid ambiguity and set criteria for identifying polymers of low concern [ENV/MC/CHEM/RD(93)4].
2. The document states in paragraph 8:

The Working Group recommended the following addition to the polymer definition

Sequence: means that the monomer units under consideration are covalently bound to one another and form a continuous string within the molecule, uninterrupted by units other than monomer units.

Monomer: means a molecule which is capable of forming covalent bonds with two or more like or unlike molecules under the conditions of the relevant polymer-forming reaction used for the particular process.

Other reactant: means a molecule linked to one or more sequences of monomer units but which, under the relevant reaction conditions used for the particular process, cannot become a repeating unit in the polymer structure.

1. The meeting of this working group also discussed criteria for decision-making regarding low concern for polymers. Seven main criteria were discussed, although others were mentioned, but particular parameters were not agreed for each criterion. From the same report:

The Working Group, as asked, discussed criteria.

(1) Concerning MW: the range of 1,000 - 10,000 Mn was agreed as a range within which the concern value was likely to lie.

(2) Concerning MW of low MW compounds giving rise to concern: the agreement was MW below 1,000.

(3) Concerning percentage of low MW compounds of concern: no agreement

(4) Concerning functional groups: only one value, applicable to epoxy and anhydride groups was mentioned (it was 1 reactive group in 20 monomer units); no general conclusion was reached.

(5) Metal content: no value agreed.

(6) Extractivity in water: 10mg/l was seen as acceptable, provided that test conditions were standardized

(7) Cationic charge density: the 5,000 equivalent weight value was accepted (as defined by EPA: not more than one cationic charge in 5000 monomer units).

Several countries implemented criteria for reduced regulatory requirements for polymers that depended on the nature of their regulatory systems. In March 2007, the then OECD Task Force on New Chemicals Notification and Assessment organised an Expert Group Meeting on polymers. The meeting was organised to (i) share information on national legislative schemes; (ii) review commonalities and differences in criteria, approaches and methodologies with a focus on low concern polymers; (iii) consider the merits of various approaches; and (iv) investigate the potential for a common approach [ENV/JM/NWCH(2007)1] [ENV/JM/MONO(2009)1].

At the meeting, the Expert Group recommended that a scientific examination of the polymer of low concern concept be performed, through an analysis of polymer data submitted by OECD regulatory authorities. This

work was carried out in 2007 and 2008, and published in 2009 [[ENV/JM/MONO\(2009\)1](#)]. The initial analysis supported the contention that polymers meeting low concern criteria have insignificant human health or environmental impacts, which in turn, supports reduced regulatory requirements for these polymers. However, gaps in data to support the analysis were also noted. Further work has not been carried out at the OECD.

Recent developments

A number of countries including Australia, Canada, Japan, Korea, New Zealand and the United States have introduced reduced regulatory requirements for some polymers based on criteria. A summary of the history and criteria applied in these approaches can be found in recent reports such as [Groh et al. \(2023\)](#) and [Wood \(2020\)](#). See [table](#) below for an overview.

Criteria for polymers of low concern have received increased attention in recent years, mainly for two reasons. First, the EU is discussing the introduction of reporting requirements for polymers under the EU REACH regulation. Many of the elements under consideration for identifying polymers requiring registration under REACH draw from the application of criteria in other countries. This discussion has also highlighted new information, data and considerations since many of the polymer of low concern criteria were established in the early 1990s.

Second, many countries are planning to regulate PFAS and will need to decide on how to deal with fluoropolymers. Criteria for polymers of low concern have recently been applied to justify low concern for some fluoropolymers ([Henry et al. \(2018\)](#)). While not focused on fluoropolymers, since 2010, the [US EPA excludes from exemption rules polymers containing as an integral part of their composition, except as impurities, certain perfluoroalkyl moieties consisting of a CF₃- or longer chain length](#). Initial EU discussions on criteria for registration of polymers under REACH would require all fluorinated polymers to be registered.

Third, at the international level, countries have started negotiations to develop an [international legally binding instrument to end plastic pollution](#). In that context, agreed criteria for polymers of low concern may be particularly relevant.

Access the [presentation on the OECD Communication on Polymers of Low Concern](#).

Table: Overview of criteria used for identifying polymers of low concern (PLC) in jurisdictions worldwide:

Criteria ^{a,c}	Jurisdictions									
	OECD PLC	AUS	CAN	PRC	TWN	JPN	KOR	PHL	USA	EC's draft ^d
Molecular weight										
Oligomer content										
Reactive functional groups										
Metal content										
Extractivity / solubility in water										
Cationic charge density										
Stability / degradability										
Chemical structure classes										
Hazard classifications										
Fluorinated polymers										
Water absorption										
Unreacted monomers										
Surface activity										

Note: ^a A shaded cell indicates that metrics related to the respective criterion are part of the respective jurisdiction's approach to PLC identification; an unshaded cell indicates that the respective criterion is not being used. ^b All criteria apart from the last five below the bold line have been discussed by the OECD Expert Group already in the early 1990s. ^c Additional criteria that have been discussed by the OECD Expert Group but have so far not been included in the PLC criteria set adopted by any of the analyzed jurisdictions include: (i) lipophilicity (though high bioaccumulation potential is considered in Japan), (ii) particle size/respirability, (iii) production volume, (iv) intended uses. ^d In the current EC proposal (April 2022), polymer assessment criteria are not used to identify PLCs, but to identify polymers requiring registration (PRRs) instead. ^e Abbreviations: AUS, Australia; CAN, Canada; EC, European Commission; JPN, Japan; KOR, Republic of Korea; PHL, Philippines; PLC, polymer of low concern; PRC, People's Republic of China; PRR, polymer requiring registration; TWN, Taiwan; USA, United States of America.

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Recommendations

Based on the absence of harmonised application of criteria and recent scientific advances in this area, OECD guidance is that the regulatory schemes of individual countries should be consulted.*



Synthesis Report on Understanding Fluoropolymers and Their Life Cycle

OECD Series on Risk Management of Chemicals



OECD Series on Risk Management of Chemicals

Synthesis Report on Understanding Fluoropolymers and Their Life Cycle

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This publication was developed in the IOMC context. The contents do not necessarily reflect the views or stated policies of individual IOMC Participating Organizations.

The Inter-Organisation Programme for the Sound Management of Chemicals (IOMC) was established in 1995 following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. The Participating Organisations are FAO, ILO, UNDP, UNEP, UNIDO, UNITAR, WHO, World Bank, Basel, Rotterdam and Stockholm Conventions and OECD. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organisations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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Executive Summary

This report, developed under the framework of the Global PFAS Group, synthesises scientific and technical data collected between 2023 and 2025 on fluoropolymers—a subset of per- and polyfluoroalkyl substances (PFASs). Emphasizing a life-cycle perspective, the report outlines fluoropolymer production, use, degradation, and environmental emissions, including the role of polymerisation and processing aids. It does not address regulatory status or alternatives but focuses on enhancing understanding through six chapters covering chemical identity, life cycle, presence of other PFASs in products, degradation processes, environmental releases, and recommendations for future research and policy actions.

Fluoropolymers, commercially available since the late 1930s, starting with polychlorotrifluoroethylene (PCTFE) and polytetrafluoroethylene (PTFE), have evolved into a diverse group of substances and a wide array of commercial products. Identifying and characterizing these fluoropolymers is complex but crucial for understanding their properties and potential environmental impacts. Addressing key knowledge gaps requires collaboration with manufacturers to clarify commercial formulations and focus on high-volume, actively produced fluoropolymers. Additionally, developing more precise chemical identifiers could improve tracking and assessment of individual fluoropolymer substances throughout their life cycles.

Fluoropolymers are widely used across industries as standalone materials, coatings, or additives, often in small amounts within complex products. Global consumption has increased, led by China, with PTFE remaining the most used but gradually declining in favour of other fluoropolymers. The life cycle stages of fluoropolymers, from monomer synthesis to end of life treatment are overviewed in the report and each stage involves particular risk management challenges. These include minimisation of hazardous byproducts during monomer production, continuing the phase out of PFAS polymerisation aids and controlling processing methods with technologies that help to mitigate environmental impacts. End-of-life management presents significant challenges, with substantial portions of production scraps recycled internally or externally, while post-use waste is predominantly incinerated or landfilled due to complex product integration and material composition. Chemical recycling shows potential but remains in early stages of development and scaling.

The report also examines the presence and persistence of various PFAS impurities in fluoropolymer products throughout their life cycle. Comprehensive data on the specific PFAS compounds present and their concentrations in commercial fluoropolymers remain limited, complicating assessment. To mitigate PFAS releases and their associated impacts, enhanced source identification, monitoring, improved process controls, and targeted strategies throughout the fluoropolymer life cycle—particularly during polymerisation, processing, and end-of-life management—are essential. These actions will support ongoing industrial transitions and regulatory efforts aimed at minimising PFAS environmental releases and exposure.

Finally, the report examines both degradation of fluoropolymers and the understanding of the release of fluorinated substance throughout the fluoropolymer life cycle. Overall, the analysis stresses a need for deeper investigation into degradation mechanisms, emissions pathways, and environmental behaviour of PFAS released across fluoropolymer life-cycle stages. Fluoropolymer production sites have been identified as key sources of environmental PFAS emissions and contamination in air, water, and soil, with both legacy

and emerging compounds present. Analytical gaps, particularly around novel PFASs, impede comprehensive understanding and assessment. PTFE and other fluoropolymers are also increasingly recognized as microplastics in various environmental media, including aquatic systems. However, data on microplastic forms of fluoropolymers beyond PTFE remain scarce. Addressing these challenges requires enhanced monitoring, broader chemical tracking, and mitigation efforts to limit environmental releases and better understand the long-term impacts of fluoropolymer-related contamination.

Existing information relevant to risk management of fluoropolymers is of a fragmented nature and is dispersed across regulatory documents, scientific literature, and proprietary industry sources. This fragmentation hampers efforts to form a coherent understanding of fluoropolymers' environmental and health impacts. As such, the report underscores the value of creating a centralized, multidisciplinary data repository to support better knowledge sharing among regulators, scientists, industry and civil society. Furthermore, the interconnectedness of PFAS presence in products, their degradation, and their environmental distribution calls for a holistic, life-cycle-based approach. Effective environmental and health assessment requires mass balance analysis and advanced analytical techniques to track fluorinated substances across all stages of production, use, and disposal. The report emphasizes that improved data access, integrated methodologies, and coordinated global efforts are essential for informed decision-making and the development of sustainable fluoropolymer management practices.

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List of Acronyms

1H-PFHx	1-hydroperfluorohexane
6:2 FTs	6:2 fluorotelomers
6:2 FTSA	6:2 fluorotelomer sulfonic acid
ADONA	2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]propanoic acid (CASRN 958445-44-8)
APFO	Ammonium salt of perfluorooctanoic acid
AOF	Adsorbable organic fluorine
BPAF	Bisphenol AF
CAS	Chemical Abstracts Service
CASRNs	CAS Registry Numbers
CDR	Chemical Data Reporting
CFCs	Chlorofluorocarbons
CFC-113	1,1,2-trichloro-1,2,2-trifluoroethane
Cl-PFECAs	Chlorine-substituted perfluoroalkylether carboxylic acids
CPT	Terpolymer of TFE, perfluoroalkyl trifluorovinyl ether and chlorotrifluoroethylene
CTFE	Chlorotrifluoroethylene
DOSS	Dioctyl sodium sulfosuccinate
ECA	Enforceable consent agreement
ECHA	European Chemicals Agency
ECTFE	Ethylene chlorotrifluoroethylene copolymers
EFEP	Ethylene tetrafluoroethylene hexafluoropropylene copolymers
EOF	Extractable organic fluorine
E-PRTR	European Pollutant Release and Transfer Register

ePTFE	Expanded PTFE
ETFE	Ethylene tetrafluoroethylene copolymers
EU	European Union
FCN	Inventory of Effective Food Contact Substance Notifications
FEP	Fluorinated ethylene propylene copolymers
FEPM	Tetrafluoroethylene propylene copolymer
FEVE	Fluoroethylene vinyl ether copolymers
FFKM	Perfluoroelastomers of the polymethylene type
FKM	Fluorine kautschuk material, vinylidene fluoride-based fluoroelastomers
GWP	Global warming potential
HCFCs	Hydrochlorofluorocarbons
HCFC-132b	1,2-dichloro-1,1-difluoroethane
HCFC-142b	1-chloro-1,1-difluoroethane
HCFC-21	Dichlorofluoromethane
HCFC-22	Chlorodifluoromethane
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HFCs	Hydrofluorocarbons
HFC-143a	1,1,1-trifluoroethane
HFC-152a	1,1-difluoroethane
HFC-23	Trifluoromethane
HFC-32	Difluoromethane
HFIB	Hexafluoroisobutylene
HFP	Hexafluoropropylene
HFPO	Hexafluoropropylene oxide
HFPO-DA	Hexafluoropropylene oxide dimer acid
HFPO-TrA	Hexafluoropropylene oxide trimer acid
HRMS	High resolution mass spectrometry
HTE	Hexafluoropropylene tetrafluoroethylene ethylene copolymers
ICCM	International Conference on Chemicals Management

IVD	In vitro diagnostics
MFA	Perfluoromethylalkoxy copolymers
MW	Molecular weight
NaPFO	Sodium salt of perfluorooctanoic acid
N.A.	Not available
n.d.	No date
OECD	Organisation of Economic Co-operation and Development
PAVEs	Perfluoro(alkyl vinyl ethers)
PBSF	Perfluorobutanesulfonyl fluoride
PBVE	Perfluoro(butenyl vinyl ether)
PCTFE	Polychlorotrifluoroethylene
PDD	Perfluoro(2,2-dimethyl-1,3-dioxole)
PE	Polyethylene
PEMFC	Polymer electrolyte membrane fuel cell
PEMWE	Polymer electrolyte membrane water electrolyzers
PEVE	Perfluoro(ethyl vinyl ether)
PFA	Perfluoroalkoxy alkanes / perfluoroalkoxy copolymers
PFASs	Per- and polyfluoroalkyl substances
PFCAs	Perfluoroalkyl carboxylic acids
PFCs	Perfluorocarbons
PFC-318	Octafluorocyclobutane / $c\text{-C}_4\text{F}_8$
PFECAs	Perfluoroalkylether carboxylic acids
PFHxA	Perfluorohexanoic acid
PFIB	Perfluoroisobutylene
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFP	1H-pentafluoropropylene
PFPEs	Perfluoropolyethers
PFPE-K	Perfluoropolyethers, type K

PFTTrDA	Perfluorotridecanoic acid
PFSAs	Perfluoroalkane sulfonic acids
PFUnDA	Perfluoroundecanoic acid
PMVE	Perfluoro(methyl vinyl ether)
Poly(CTFE-VDF)	Chlorotrifluoroethylene vinylidene fluoride / CTFE-VDF copolymers
POSF	Perfluorooctanesulfonyl fluoride
PP	Polypropylene
PPVE	Perfluoro(propyl vinyl ether)
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
PVF	Polyvinyl fluoride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SDS	Safety data sheet
SEI	Solid electrolyte interphase
SPI	Plastics Industry Trade Association
SPIN	Substances in Preparations in Nordic Countries
t	Tonnes
TBPH	t-butyl hydroperoxide
TFA	Trifluoroacetic acid
TFE	Tetrafluoroethylene
TFEP	Tetrafluoroethylene propylene copolymers
THE	Tetrafluoroethylene hexafluoropropylene ethylene copolymers
THV	Tetrafluoroethylene hexafluoropropylene vinylidene fluoride copolymers
TOF	Total organic fluorine
TOP assay	Total oxidizable precursor assay
TrFE	Trifluoroethylene
UK	United Kingdom
UN	United Nations
UNEP	United Nations Environment Programme
US	United States

US EPA	US Environmental Protection Agency
US FDA	US Food & Drug Administration
VDF	Vinylidene fluoride
WWTP	Wastewater treatment plant
X-PAHs	Cl/F-substituted polycyclic aromatic hydrocarbons, X = Cl, F

1 Background, motivation, scope

The Global PFAS Group¹ was created to address Resolution II/5 passed at the second session of the International Conference on Chemicals Management (ICCM 2) in 2009. Resolution II/5 called on various organizations, governments, and additional stakeholders to develop national and international stewardship programs as well as regulatory approaches, with the aim of reducing the presence of certain perfluorinated chemicals in products and, if feasible, eliminate them entirely. This was reaffirmed in Resolution III/3 during the third session of the conference in 2012, which recognized that more work was needed to implement the original resolution. The Global PFAS group brings together experts from OECD members, non-member countries, academia, governments, industry, and NGOs, as well as representatives from other international organisations, with the aim of continually facilitating the exchange of information regarding PFASs and to support a global transition towards safer alternatives. The outputs of the work of the group can be found on the OECD PFAS website².

Developed within the framework of the Global PFAS Group, this report presents recent efforts from September 2023 to June 2025 in collecting and synthesising publicly available scientific and technical information on a subset of per- and polyfluoroalkyl substances (PFASs) that are fluoropolymers. This report aims to provide a comprehensive but not exhaustive overview of the chemical identities of fluoropolymers on the global market and to illustrate their life cycle, including their production, processing, use and end-of-life treatment. In particular, the report considers the environmental releases of fluoropolymers and the presence and releases of other PFASs in commercial products, including those resulting from degradation during processing, use, and end-of-life treatment. The report builds upon a review of peer-reviewed scientific literature, regulatory reports, databases and technical documents. Due to time and resource limitations, the report does not include a thorough examination of safety data sheets, patents, standards, or all possible references. Based on the information considered and the scope addressed, critical knowledge gaps regarding fluoropolymers have been identified. Some gaps are specific to fluoropolymers, while others are not unique to this subset of substances but nevertheless impede a more fulsome understanding.

PFASs represent a class of human-made chemicals characterized by the presence of at least one fully fluorinated methyl or methylene carbon atom (without any hydrogen/chlorine/bromine/iodine atom attached to the carbon atom). In simpler terms, with the few noted exceptions, any chemical featuring at least a perfluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) group is a PFAS (OECD, 2021). They are known for their useful technical properties, including oil- and water-repellency, chemical and thermal stability, electrical insulation, biocompatibility, UV and weather resistance, low permeability, and/or others. The class encompasses a vast array of chemical substances (OECD, 2018; US EPA, n.d.), finding extensive applications in industrial processes and consumer products (Glüge et al., 2020).

While many PFASs have been in production and use since the 1940s (Lyons, 2007; Richter et al., 2018; Wang et al. 2014a,b), concerns about their persistence in the environment, ubiquitous occurrence, and

¹ Previously known as the OECD/UNEP Global Perfluorinated Chemicals (PFC) Group.

² <https://www.oecd.org/en/topics/sub-issues/risk-management-risk-reduction-and-sustainable-chemistry/per-and-poly-fluorinated-chemicals.html>

associated health risks gained prominence in the early 2000s. At the time, attention was focused on two long-chain PFASs, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), prompting a surge in research and risk management measures for a number of PFASs in subsequent years.

Broadly speaking, PFASs encompass both non-polymeric and polymeric substances. The bulk of research concerning identities, life cycles, hazards, occurrences, exposure, and risks has traditionally concentrated on non-polymeric PFASs (Evich et al., 2022). In contrast, public attention to polymeric PFASs, including side-chain fluorinated polymers, fluoropolymers, and perfluoropolyethers (Buck et al., 2011; Fiedler et al., 2021), has been comparatively limited, with research fragmented and dispersed across the public domain. The Global PFAS Group has prioritized understanding of the life cycle of *polymeric* PFASs as a key focus of its endeavours. This report serves as a complementary addition to the preceding *Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle* (OECD, 2022)³ and *Synthesis Report on Understanding Perfluoropolyethers (PFPEs) and Their Life Cycle* (OECD, 2024)⁴.

Fluoropolymers are defined as “carbon-only polymer backbone with F directly attached to backbone C atoms” (Buck et al., 2011).⁵ Fluoropolymers may or may not be PFASs as per the OECD definition of PFASs (OECD, 2021). Fluoropolymers that are PFASs are polymers that contain perfluorinated methylene moieties ($-\text{CF}_2-$) as part of the repeating units such as $-\text{CF}_2\text{CF}_2-$ and $-\text{CF}_2\text{CH}_2-$ in the polymer backbone chain. In contrast, polyvinyl fluoride [PVF, $-(\text{CH}_2\text{CHF})_n-$] polymers are fluoropolymers, but not PFASs (see Figure 1). This report focuses on those fluoropolymers that are PFASs and does not investigate other fluoropolymers that are not PFASs, such as PVF. Moreover, direct fluorination has been utilized to treat commonly used commodity polymers, producing materials where only the surface is fluorinated (~ 0.01 – $10\ \mu\text{m}$) while the bulk of the polymer remains unchanged (Kharitonov et al., 2005; Calleja et al., 2011). Such fluorinated polymers, taken as a whole, are not regarded as fluoropolymers in this report, and thus, are not included, although some aspects such as degradation during high-temperature treatment may share commonalities with fluoropolymers due to their surface-fluorinated layer. Nevertheless, they may warrant further, separate investigation.⁶

Fluoropolymers such as perfluoroalkoxy alkanes (PFA) and fluorinated ionomers including CASRN 111173-25-2⁷ should not be confused with PFPEs. While perfluorinated ether moieties are commonly present, their varied location in the molecules marks the differentiation of the two types of polymeric PFASs. The perfluorinated ether moieties in PFA and fluorinated ionomers are located on the side chains that attach to the polymer backbone chain, whereas for PFPEs, the perfluorinated ether moieties are part of the polymer backbone chain (see Figure 1). Such structural differences result in distinct properties between fluoropolymers and PFPEs. Fluoropolymers such as PFA and fluorinated ionomers are elaborated below, whereas more details on PFPEs can be found in the previous *Synthesis Report on Understanding Perfluoropolyethers (PFPEs) and Their Life Cycle*.

³ The full report is available at <https://doi.org/10.1787/e13559f7-en>.

⁴ The full report is available at <https://doi.org/10.1787/99ee2d3e-en>.

⁵ The full definition provided in Buck et al. (2011) for fluoropolymers is as follows: polymers “made by (co)polymerisation of olefinic monomers, at least one of which contains F bound to one or both of the olefinic C atoms, to form a carbon-only polymer backbone with F atoms directly attached to it, e.g., polytetrafluoroethylene.”

⁶ They have been widely used in industrial and consumer applications such as automotive fuel tanks and vessels for storage of organic liquids including pesticides (Kharitonov et al., 2005). Meanwhile, multiple studies have measured elevated levels of perfluoroalkyl carboxylic acids (PFCAs) with varied carbon chain lengths in such fluorinated polymers (Rand and Mabury, 2011; Whitehead and Peaslee, 2023; US EPA, 2024a). Noticeably, while the US EPA continued to investigate and assess potential impacts on health or the environment, the affected pesticide manufacturer had voluntarily stopped shipment of any products in fluorinated high-density polyethylene (HDPE) containers (US EPA, 2024a).

⁷ Ethanesulfonic acid, 1,1,2,2-tetrafluoro-2-[(1,2,2-trifluoroethenyl)oxy]-, polymer with 1,1,2,2-tetrafluoroethene

In recent years, a significant debate has emerged regarding whether fluoropolymers should be subjected to regulatory scrutiny in conjunction with other PFASs. This relates to the concept of “polymer of low concern.” From 1993 to 2009, expert groups at the OECD engaged in discussions on criteria for identifying polymers of low concern.⁸ No agreed-upon set of criteria at the OECD level was finalised. However, several countries have since implemented their own criteria for reduced regulatory requirements for polymers, drawing on the discussions from the OECD, but tailored to fit their specific regulatory frameworks.⁹ No further work has been conducted at the OECD on polymers of low concern since 2009. It is important to note that life-cycle aspects were not considered during the discussions.

Some have argued that fluoropolymers should be considered “polymers of low concern” (i.e., polymers that are deemed to have low environmental and human health impacts) (Henry et al., 2018; Korzeniowski et al., 2023). Others have argued that it is critical to consider the entire life cycle of fluoropolymers and the associated issues (Lohmann et al., 2020). In other words, it has been argued that not only the characteristics of fluoropolymers themselves should be considered, but also the broad spectrum of emissions and exposure across their entire life cycle, including production, use, and end-of-life treatment. For example, the use of PFOA as a polymerisation aid in fluoropolymer production has been identified as a major source of PFOA in the global environment (Prevedorous et al., 2006; Wang et al., 2014a).

This report does not address the question of whether fluoropolymers are polymers of concern. Instead, it answers a pre-defined set of questions developed for this series of synthesis reports, with the aim of improving understanding of the life cycle of polymeric PFASs to inform future research and action on them. Neither does the report include alternatives to fluoropolymers for their various applications, an important topic that would warrant separate, dedicated assessment(s).

More specifically, the report consists of the following six substantive chapters: Chapter 2 outlines the chemical identities of fluoropolymers on the global market, highlighting challenges and opportunities in their identification and characterization. Chapter 3 details their life cycle, covering synthesis routes, downstream processing, uses, production and use volumes, and end-of-life treatment options. Chapter 4 examines the presence of other PFASs in commercial fluoropolymer products/articles, drawing from theoretical and empirical evidence. Chapter 5 synthesises knowledge on the degradation of fluoropolymers during processing, use and end-of-life treatment, and Chapter 6 reviews the environmental releases of fluoropolymers and other PFASs associated with their life cycle. Chapter 7 provides an overarching summary of key findings and outlines options for future research and policy measures.

⁸ OECD communication on PLC can be found at: https://www.oecd.org/content/dam/oecd/en/topics/policy-sub-issues/risk-management-risk-reduction-and-sustainable-chemistry/polymers-of-low-concern.pdf/jcr_content/renditions/original.media_file.download_attachment.file/polymers-of-low-concern.pdf.

⁹ An overview of the PLC criteria across the world can be found at Table S2 of Groh et al. (2023): <https://www.rsc.org/suppdata/d2/em/d2em00386d/d2em00386d1.xlsx>.

2 Identities of fluoropolymers on the Global Market

Chapter summary:

- Fluoropolymers have been commercially available since the late 1930s, beginning with polychlorotrifluoroethylene (PCTFE) and polytetrafluoroethylene (PTFE). Over time, a wide range of fluoropolymers have been developed, with 131 active Chemical Abstracts Service Registry Numbers (CASRNs) identified in this report as examples.
- Fluoropolymers can be classified into four categories: homopolymers and copolymers commonly known as “fluoroplastics,” copolymers commonly known as “fluorinated ionomers,” and copolymers commonly known as “fluoroelastomers”.
- Homopolymers consist of a single monomer, such as PTFE, PCTFE, and polyvinylidene fluoride (PVDF), with modifications sometimes made to enhance properties.
- Copolymers commonly known as “fluoroplastics,” are copolymers composed of two or more comonomers, including fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA), ethylene tetrafluoroethylene (ETFE), ethylene chlorotrifluoroethylene (ECTFE), and chlorotrifluoroethylene vinylidene fluoride [Poly(CTFE-VDF), or CTFE-VDF copolymers].
- Copolymers commonly known as “fluorinated ionomers,” are typically copolymers of tetrafluoroethylene (TFE) and functionalized perfluoro(alkyl vinyl ethers) (PAVEs).
- Copolymers commonly known as “fluoroelastomers” include vinylidene fluoride (VDF)-based and TFE-based copolymers with two or more comonomers, crosslinked using curing agents.
- In addition to diverse polymer backbones, end groups in fluoropolymers influence their chemical identity and behavior, formed during polymerisation and processing, leading to variations in commercial products.
- Despite a limited number of general structures known as outlined above, due to many possible chain lengths, various end-groups, and other functional modifications, a vast range of fluoropolymer structures are possible and many of them have been commercialized. Many are reported under the same names and CASRNs.
- Identifying and characterizing the chemical identities of individual fluoropolymers presents challenges, while a thorough understanding of these variations is essential for assessing their properties and impacts.
- To confront these critical knowledge and data gaps, it is advisable to engage with manufacturers to more precisely understand existing commercial formulations, including their chemical identities and structural characteristics. Priority may be given to fluoropolymers actively being produced and sold on the global market with high production volumes.
- In addition, developing more comprehensive unique identifiers beyond CASRNs and CAS names may enable a better understanding of the fate and behaviour of individual unique fluoropolymers, along with chemical substances.

A wide range of fluoropolymers has been commercialized by a number of manufacturers since the late 1930s with the synthesis of low-molecular-weight polychlorotrifluoroethylene (PCTFE) and of high-molecular-weight polytetrafluoroethylene (PTFE) (Feiring, 1994).

Building upon the previous compilation and recent updates of existing national and regional chemical inventories (Wang et al., 2020) and the list of commercially available fluoropolymers compiled by Plastics Europe (n.d.), a non-exhaustive list of fluoropolymers on the global market is identified, including 131 active Chemical Abstracts Service Registry Numbers (CASRN). The list of fluoropolymers, and additional information including monomers and registration status in national/regional chemical inventories, can be found in Table S1 in the supporting material file (provided separately).

In addition, as an active CASRN may be assigned to multiple grades¹⁰ of fluoropolymer products with the same general structure (Wang et al. 2021), efforts were made to identify and understand such complexity of fluoropolymer products on the global market by systematically searching for and extracting information from individual manufacturers' websites, including Daikin, Halopolymer, Chemours, Gujarat, AGC, Arkema, 3M/Dyneon and Syensqo.¹¹ An overview of the trade names used by major manufacturers can be found in Table A A.1 of Annex A. For more specific information on specific fluoropolymer products by individual manufacturers, including trade names, fluoropolymer types, series/grades, main applications, and physical forms, refer to Table S2 in the separate supporting material file.

An overview of fluoropolymer types on the global market

Fluoropolymers may be characterized in multiple ways, e.g., homopolymers vs. copolymers,¹² perfluorinated vs. polyfluorinated, linear vs. branched, non-functionalized vs. functionalized,¹³ fluoroplastics vs. fluoroelastomers.¹⁴ Based on commonalities in the monomers and properties, this report groups fluoropolymers into four categories: (1) homopolymers and (2) copolymers that are commonly known as "fluoroplastics," (3) copolymers that are commonly known as "fluorinated ionomers," and (4) copolymers that are commonly known as "fluoroelastomers" (for an illustration of examples, see Figure 1). The general features are comprehensively elaborated below, mainly based on Feiring (1994), Logothetis (1994), and references therein, with further technical details available in Améduri and Sawada (2016a,b), Drobny (2016), Ok et al. (2024a,b), Taguet et al. (2005), and so on. Further details on the synthesis of individual fluoropolymer types are provided in the next chapter.

¹⁰ In the context of commercial fluoropolymer products, "grade" typically does not refer to product quality, but rather to product characteristics, such as the particle size, melt viscosity, mechanical properties, or ratio of different monomers in the case of copolymers.

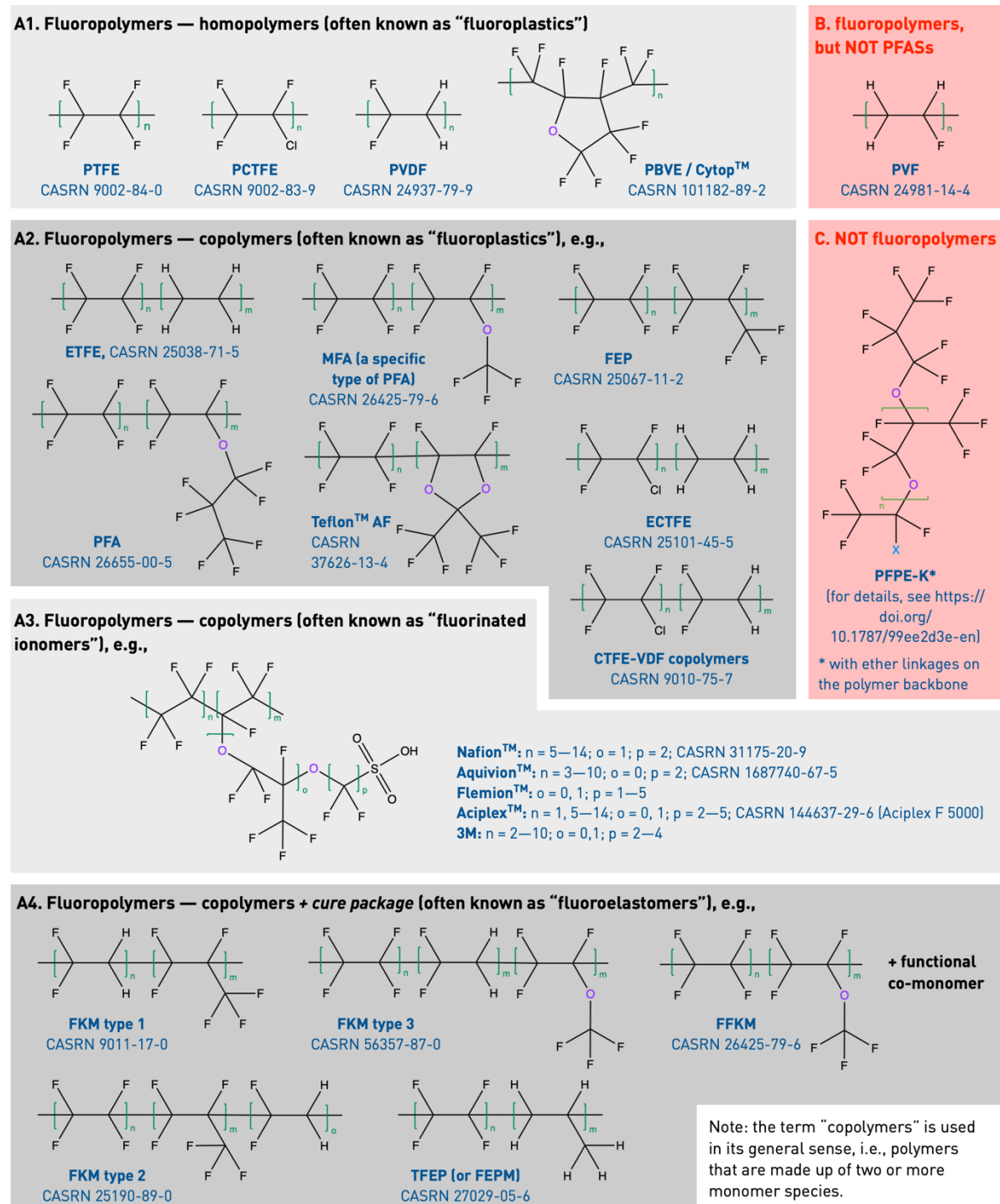
¹¹ This report uses the latest company names at the time of preparation, acknowledging past name changes. For example, Chemours was part of E.I. du Pont de Nemours, AGC was formerly Asahi Glass, Arkema was previously Atofina (formerly Atochem), 3M/Dyneon was formerly Hoechst, and Syensqo was previously Solvay Solexis (formerly Ausimont). For further details, please consult the manufacturers' websites.

¹² In this report, we use the term "copolymers" in its general sense, i.e., a polymer that is made up of two or more monomer species. In the literature or other sources, "copolymers" may also be used in a narrower sense, referring to a polymer that is made up of two monomer species, i.e., "bipolymer," while a polymer that is made up of three monomer species may be referred to as "terpolymer."

¹³ The term "non-functionalized" refers to those fluoropolymers with inert end groups, such as $-\text{CF}_3$ and $-\text{CH}_3$, whereas the term "functionalized" refers to those with end groups that provide specific functionalities, such as carboxylic groups.

¹⁴ Similarly to thermoplastics such as polyethylene (PE) and polypropylene (PP) vs. rubber.

Figure 1. Examples of different types of fluoropolymers



Note: Green colour highlights structural repeating units in the polymer backbone, and purple colour highlights ether linkages. Part “A3” shows copolymers of TFE and functionalized perfluoro(alkyl vinyl ethers) with a functional end group such as sulfonic or carboxylic acid group, where the ether moieties are present on the side chains rather than the polymer backbone, resulting from the polymerisation of $\text{CF}_2=\text{CF}_2$ and $-\text{CF}=\text{CF}_2$ moieties. In contrast, part “C” shows perfluoropolyethers in which the ether moieties are located on the polymer backbone as part of the consecutive repeating units.

Homopolymers¹⁵

These are fluoropolymers that are made up of one monomer species (see Figure 1, A1), with their names typically being “poly” plus the name of the corresponding monomer, namely PTFE made from tetrafluoroethylene (TFE), PCTFE made from chlorotrifluoroethylene (CTFE), and polyvinylidene fluoride (PVDF) made from vinylidene fluoride (VDF). Homopolymers also include Cytop™, made from perfluoro(butenyl vinyl ether) (PBVE). However, it should be noted that a small amount of another monomer species may be added to improve certain properties of specific homopolymers, which may often be referred to as “modified” homopolymers.¹⁶ For example, <1 weight% of perfluoropropyl vinyl ether (PPVE; CASRN 1623-05-8) may be added to produce “modified” PTFE¹⁷ such as Dyneon™ TFM™ PTFE (Feiring, 1994; Hintzer and Schwertfeger, 2014; 3M, 2016; Environment Agency, 2023b).¹⁸ Similarly, Teflon™ PTFE 6C contains about 0.15–0.75 weight% (0.1–0.5 mol%) HFP (Baker Jr. and Kasprzak, 1993). Additionally, (perfluorobutyl)ethylene (PFBE, CASRN 19430-93-4) may be considered as another comonomer¹⁹ (Environment Agency, 2023c), e.g., at the level of up to 0.09 weight% in the production of PTFE polymers processed at high temperature (EFSA CEF Panel, 2011a).

PTFE polymers are typically available in the following four forms with different particle sizes (see Table 1). (1) Granular resin: these are stringy, porous and irregularly shaped particles from a suspension polymerisation, which are dried and ground to different average particle sizes (coarse cut product has better flow properties, while finer cut material gives products with fewer voids). The resin product can be agglomerated to improve flow and billet size, or semi-sintered to improve ram extrusion performance. Finer cut material gives products with fewer voids. A typical resin may have a particle size of 25–800 µm. (2) Fine powder resin: these are PTFE produced via emulsion/dispersion polymerisation, gently coagulated and dried to give small particles with few voids, suitable for paste extrusion. (3) Aqueous dispersion: dispersions used for making fine powder can also be applied in coatings and PTFE fibre production. The raw dispersions are stabilized by adding additional surfactant, concentrated to 50–60% solids. (4) Micronized powder PTFE resin: they are also known as micropowder PTFE, representing low-molecular-weight PTFE powder.

¹⁵ For information derived from Feiring (1994) and the references therein, no additional citations are provided. In contrast, information from other sources is always accompanied by a specific citation.

¹⁶ Legislation in many jurisdictions has adopted the “2% polymer” rule: a polymer is not considered new if it is produced by modifying the existing formulation of a registered polymer through the addition of other registered reactants, provided that none of these added reactants constitutes more than 2 weight% of the resulting polymer; for more details, see Supplementary Information of Groh et al. (2023).

¹⁷ Such modified PTFE may be used for wire coatings, cables and tubing in the semi-conductor industry and cable insulation in the automotive and aerospace industry, for example (Environment Agency, 2023b)

¹⁸ In contrast, Teflon™ PFA 340 contains about 1.3–5.2 weight% PPVE (Baker Jr. and Kasprzak, 1993).

¹⁹ Such modified PTFE may be used for many applications including for wire coatings, cables and tubing in the semi-conductor industry and cable insulation in the automotive and aerospace industry (Environment Agency, 2023c). Other examples include coated cookware, such as coatings on frying pans and articles for oven baking, and moulded articles for industrial use. Cookware and bakeware instructions are to wash before use with hot soapy water. Instructions for food processing machinery indicate rinsing with hot water (EFSA CEF Panel, 2011a).

Table 1. Average particle size and bulk density of the four forms of PTFE (US ITC, 2021). Their molecular weight ranges were not identified during the preparation of this report.

Form of PTFE	Average particle size (micron, μm)		Bulk density (g/L)	
	Minimum	Maximum	Minimum	maximum
Aqueous dispersion	0.05	0.5	1,246	1,520
Granular	20	650	250	930
Fine powder	370	675	460	550
Micropowder	1	20	300	460

PCTFE: The molecular weights of commercial products must be kept sufficiently high for optimum mechanical properties; this can be achieved by proper processing conditions with molecular weights in the range of $1\text{--}10 \times 10^5$ Da where melt processing is still possible. Small amounts (<5%) of VDF may be added in the polymerisation to improve processability with limited effect on polymer properties. In some cases, low-molecular-weight PCTFE may be used, consisting of mainly trimer and tetramer (Cosmetic Ingredient Review, 2018).

PVDF: Although composed of mostly head-to-tail linkages $[-(\text{CF}_2\text{CH}_2)_n-]$, 3–6% of the monomer units in PVDF are reversed (i.e., having units such as $[-(\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2)-]$),²⁰ the number increasing with higher polymerisation temperature. Light-scattering measurements on some fractionated commercial samples showed weight-average molecular weights in the range of 4 to 9.5×10^6 Da. Additionally, the weight-average molecular weight of several Solef™ PVDF (co)polymers are reported to be about 2.4 to 5.7×10^5 Da (Solvay, 2017).

Copolymers that are commonly known as “fluoroplastics”²¹

These fluoropolymers are typically made up of two or more monomer species (see Figure 1, A2). Some are perfluorinated, including fluorinated ethylene propylene (FEP) copolymers made from TFE and HFP, perfluoroalkoxy (PFA) copolymers made from TFE and various perfluoro(alkyl vinyl ethers) (PAVEs; $\text{R}=\text{OCF}=\text{CF}_2$) such as methyl fluoroalkoxy (MFA) copolymers made from TFE and perfluoro(methyl vinyl ether) (PMVE),²² and Teflon™ AF copolymers made from TFE and a cyclic monomer, perfluoro(2,2-dimethyl-1,3-dioxole) (PDD). Others are polyfluorinated, including ethylene tetrafluoroethylene (ETFE) and ethylene chlorotrifluoroethylene (ECTFE) copolymers.

FEP and **PFA/MFA** are random copolymers of TFE with HFP or PAVEs, respectively. In addition to TFE, the comonomer content in FEP is about 3–20 mol%, while only 0.3–5 mol% of the comonomer is required in PFA (3M, 2016). In some cases, PFA may contain more than two comonomers, e.g., Teflon™ PFA (CASRN 26655-00-5) being the copolymer of TFE, PPVE, and perfluoro(ethyl vinyl ether) (PEVE, CASRN 10493-43-3) (RPA, 2023a). **CPT** copolymers are modified PFA, with an additional comonomer of CTFE.

²⁰ Such structural features are important for understanding the byproducts formed during polymerisation and thermal degradation, among others.

²¹ For information derived from Feiring (1994) and the references therein, no additional citations are provided. In contrast, information from other sources is always accompanied by a specific citation.

²² In this report, MFA is considered as a subcategory of PFA, while in some other literature, MFA and PFA may be considered as separate categories of fluoropolymers. MFA has a chemical structure similar to PFA; hence, the basic properties of MFA and PFA are comparable (Kálin et al., 2012).

Available FEP grades include pelletized resins for extrusion and moulding, powders for fluidized bed and electrostatic coating, and aqueous dispersion resins (Kälin et al. 2012).

Teflon™ AF copolymers are made of TFE with PDD (which can homopolymerise or copolymerise with TFE in essentially any ratio). Initial commercial products contain about 65 and 80 mol% PDD.

ETFE copolymers are linear copolymers of TFE and ethylene in a nearly one-to-one molar ratio (though various grades of ETFE can be made with different molar ratios of monomer; Kälin et al., 2012), with the co-monomers having a strong tendency to alternate during polymerisation [i.e., the polymer structure is mainly, $-(CF_2CF_2CH_2CH_2)_n-$]. Commercial ETFE resins may contain small amounts (0.1–10%) of a third monomer which improves their resistance to stress cracking at elevated temperatures; typical ones are perfluoroalkoxy vinyl compounds or perfluoro(alkyl)ethylenes (e.g., PFBE; Environment Agency, 2023c)²³. Their melting point is in the range of 200–300 °C, depending on the TFE/ethylene ratio and degree of alternation; commercial resins have a melting temperature of about 275 °C, corresponding to about 92% alternation.

ECTFE copolymers are copolymers with two monomers in a nearly alternating, one-to-one molar ratio [i.e., the polymer structure is mainly $-(CF_2CFCICH_2CH_2)_n-$]. The commercial polymers contain small amounts of a third comonomer, such as a perfluoro(alkyl)ethylene or 2-trifluoromethyl-3,3,3-trifluoropropene (i.e., hexafluoroisobutylene, HFIB, CASRN 382-10-5; Korzeniowski et al. 2023), to improve the polymer's resistance to catastrophic mechanical failure when stressed at temperatures above 150 °C. Molecular weights of the commercial polymers are in the range of 1 to 5×10^5 Da.

CTFE-VDF copolymers, or Poly(CTFE-VDF), are random copolymers with CTFE and VDF as comonomers. The amount of VDF in the copolymer depends upon the application and processing conditions needed to meet that specific application.

Other examples include copolymers of TFE with isobutylene, of VDF with HFIB, and of HFIB with vinyl acetate, which largely form alternating structures. The VDF-HFIB copolymers are said to be present in limited commercial products. In addition, **THV** copolymers are made of TFE, HFP and VDF, **VT** copolymers are made of VDF and TFE, and **EFEP** copolymers are made of ethylene, TFE and HFP. **FEVE** copolymers are made of alternating fluoroethylene ($CF_2=CFX$) and alkyl vinyl ether [$CH_2=C(H)OR$] monomers, and different functional groups (R) may be selected for functionalities such as transparency, gloss, hardness, flexibility, crosslinkability, pigment compatibility, and adhesiveness.

Copolymers that are commonly known as “fluorinated ionomers”²⁴

These are typically copolymers of TFE and a functionalized PAVE (i.e., PAVE with a functional end group such as a sulfonic or carboxylic group; see Figure 1, A3). A copolymer composition curve shows that random copolymerisation of TFE occurs with functionalized PAVES. Fluorinated ionomers include Nafion™ (made of TFE and perfluorosulfonic acid vinyl ether; CASRNs 31175-20-9 and 66796-30-3), Aquivion™, Flemion™, FORBLUE™, Fumion™, 3M™ Ionomer (made of TFE and perfluorobutanesulfonylfluoride vinyl ether), and Aciplex™. For example, Nafion™ copolymers are manufactured in the USA and sold in various forms such as ion exchange membranes (10^5 – 10^6 Da, molecular weight distribution 1.0–2.4; Henry et al., 2018), reinforced membranes, dispersions (colloidal polymer particles) and resins (in the form of small polymer beads) (RPA, 2023b).

²³ Such modified ETFE may be used in many applications including for wire coatings, cables and tubing in the semiconductor industry and cable insulation.

²⁴ For information derived from Yamabe and Miyake (1994) and the references therein, no additional citations are provided. In contrast, information from other sources is always accompanied by a specific citation. It should also be noted that fluorinated ionomers are intentionally functionalized to improve performance. Copolymers unintentionally modified with a –COOH group, as an unintended consequence of TFE polymerisation, are not fluorinated ionomers.

Copolymers that are commonly known as “fluoroelastomers”²⁵

Fluoroelastomers based on VDF copolymers.²⁶ Most commercially available fluoroelastomers consist of copolymers of VDF with HFP and, optionally, TFE (see Figure 1, A4). In specific applications, other monomers such as PAVEs, CTFE, 1H-pentafluoropropylene (PFP, $\text{CHF}=\text{CFCF}_3$), and 2,3,3,3-tetrafluoropropene (HFO-1234yf, $\text{CH}_2=\text{CFCF}_3$)²⁷ have been copolymerised with VDF to give specialty rubbers. They are also called Fluorine Kautschuk Material (FKM), including Type-1 made of VDF and HFP (typically ca. 66 weight% fluorine content), Type-2 made of VDF, HFP and TFE (typically 67–71 weight% fluorine content)²⁸, Type-3 made of VDF, TFE and PMVE (typically 62–68 weight% fluorine content), Type-4 made of VDF, TFE and propylene (typically ca. 67 weight% fluorine content), and Type-5 made of VDF, HFP, TFE, PMVE and ethylene.

The useful compositional range for elastomeric structures is 20–78 weight% VDF,²⁹ 20–60 weight% HFP, and 0–40 weight% TFE. On a molecular scale, it is important to have about one HFP unit for every 2–4 units of the other monomers present to prevent crystallization.

Fluoroelastomers, like all other thermosetting elastomers, require crosslinking in order to have useful properties. Fluoroelastomers can be cured (vulcanized) by nucleophiles, such as diamines or bisphenols, and with a peroxides/co-agent system³⁰. Diamine curing, originally introduced in the late 1950s, was the predominant way of crosslinking raw fluoroelastomers until the late 1960s, when bisphenol curing was introduced. A most commonly used crosslinking agent is bisphenol AF [2,2-bis(4-hydroxyphenyl)hexafluoropropane, CASRN 1478-61-1]. Others such as hydroquinone, substituted hydroquinones, and bisphenol A also work well, but have been used commercially to a lesser degree due to lower heat resistance, curing speed, compression set, and scorch resistance.

Fluoroelastomers based on TFE–propylene copolymers. In the early 1960s, it was found that TFE readily copolymerises with propylene in a nearly alternating manner to give fluoroelastomers, also known as TFEP or FEPM (see Figure 1, A4). NMR data indicate that nearly 70% of the TFE units are alternating with propylene units. The methyl groups appear to be in a random configuration, which helps to give the polymers an amorphous morphology, in spite of the highly regular alternating structure. The amount of TFE in the monomer feed does not change the polymerisation composition to any great extent but affects the polymerisation rate and the molecular weight of the polymer.

TFE/propylene copolymers are cured by a peroxide/co-agent system. TFE/propylene copolymers may contain small amounts of cure-site monomers, such as an aryloxyalkyl vinyl ether, VDF, and glycidyl vinyl ether. These polymers can be cured either by peroxides or by nucleophiles.

Fluoroelastomers based on TFE–PAVE copolymers.³¹ Since the fluoroelastomers described earlier contain hydrogen, they have limited resistance to very hostile environments. In response, perfluorinated fluoroelastomers were developed, based on copolymers of TFE with 20–40 mol% PAVE, also known as

²⁵ For information derived from Logothetis (1994) and the references therein, no additional citations are provided. In contrast, information from other sources is always accompanied by a specific citation.

²⁶ They are defined by ASTM international standard D1418.

²⁷ This specific comonomer is added according to a response received during the review of this report.

²⁸ The fluorine content is updated according to a response received during the review of this report.

²⁹ The VDF content is updated according to a response received during the review of this report.

³⁰ According to a response received during the review of this report, a third monomer containing iodine or bromine atoms is usually added in small amounts (1 mol%) to make these polymers peroxide-curable. Additionally, co-agents can be triallyl (iso)cyanurate (TAIC or TAC).

³¹ They are defined by ASTM international standard D1418.

FFKM (see Figure 1, A4). The most readily copolymerisable PAVE homologue is PMVE. Certain types of fluoroelastomers by Syensqo may contain up to 45% of PMVE (EFSA CEF Panel, 2015).

A third monomer is usually added in small amounts (1–5 mol%)³² to enable curing of these polymers, including PAVEs carrying functional groups [$\text{CF}_2=\text{CFOR}_\text{F}\text{X}$, $\text{X} = \text{CO}_2\text{R}$, OC_6F_5 , $\text{O}(\text{CF}_2)_n\text{CN}$ or CN], simple substituted fluoroolefins ($\text{R}^1\text{CH}=\text{CR}^2\text{R}^3$, $\text{R}^1, \text{R}^2, \text{R}^3 = \text{H}, \text{Br}, \text{F}, \text{R}_\text{F}, \text{R}_\text{F}\text{Br}$), or perfluoroiodo alkyl and alkynes ($\text{R}_\text{F}\text{I}$ and $\text{IR}_\text{F}\text{I}$). The PAVEs carrying functional groups are the most useful and versatile.

A number of curing systems have been used, e.g., with aromatic or aliphatic diamines and, preferably, the more thermally stable bisphenols, and also with a peroxide/co-agent system.

General understanding of end groups in fluoropolymers³³

Beyond the polymer backbone—characterized by its type and size as described in the previous section—the chemical identity of fluoropolymers is also defined by their end groups. These end groups are formed during polymerisation, influenced by factors such as the initiator, transfer agent, solvent, and potential contaminants. Additionally, they can arise during processing and use of fluoropolymers, due to aging, heating, extrusion, chemical reactions, and so on.

For instance, in PFA, various end groups have been observed, including carboxylic ($-\text{CF}_2-\text{COOH}$),³⁴ amide ($-\text{CF}_2-\text{CONH}_2$),³⁵ acyl fluoride ($-\text{CF}_2-\text{COF}$),³⁶ perfluorovinyl ($-\text{CF}_2-\text{CF}=\text{CF}_2$),³⁷ difluoromethyl ($-\text{CF}_2-\text{CF}_2\text{H}$),³⁸ and ethyl ($-\text{CF}_2-\text{CH}_2\text{CH}_3$)³⁹ groups. Similarly, PVDF may contain end groups such as $-\text{CF}_2-\text{CH}_3$, $-\text{CH}_2-\text{CF}_2\text{H}$,⁴⁰ $-\text{Cl}$, $-\text{CCl}_3$,⁴¹ and $-\text{CF}_2-\text{CH}_2\text{OH}$.⁴²

Fluoropolymers often contain multiple end groups simultaneously, and some end groups may be on side chains.⁴³ For example, a VDF copolymer containing 5–7 mol% of TFE, polymerised using β -hydroxyethyl-tert-butyl peroxide as an initiator, was found to contain $-\text{CH}_3$ (63% of total number of end groups), $-\text{CH}_2-\text{CF}_2\text{H}$ (34%), $-\text{O}-\text{C}(\text{CH}_3)_3$ (2%) and $-\text{O}-\text{CH}_2-\text{CH}_2\text{OH}$ (1%) end groups. The same study also reported about 1.5 side chains per 100 monomer units (despite often being considered a linear polymer).

³² This ratio is updated according to a response received during the review of this report.

³³ For information derived from Pianca et al. (1999) and the references therein, no additional citations are provided. In contrast, information from other sources is always accompanied by a specific citation.

³⁴ Carboxylic groups are generated when a persulfate initiator is used, and they can decompose by thermal treatment and then form acyl fluoride, perfluorovinyl, and difluoromethyl groups.

³⁵ Amide end groups can be generated during the polymerisation step when ammonium salts are used.

³⁶ Acyl fluoride end groups have been observed during industrial extrusions of perfluorinated fluoropolymers by aqueous emulsion polymerisation with $\text{K}_2\text{S}_2\text{O}_8$ as an initiator. In PFA, acyl fluoride end groups can also be generated during polymerisation through radical rearrangement.

³⁷ Perfluorovinyl groups have been observed during press treatment at 380 °C for some minutes.

³⁸ Difluoromethyl groups have been observed when the carboxylic end groups are in ionic form and the polymer is treated with water at 210–250 °C.

³⁹ Ethyl groups may be generated by using ethane as a chain-transfer agent in the emulsion polymerisation of TFE-based fluoropolymers.

⁴⁰ These two groups may be due to hydrogen abstraction from either initiator molecules or PVDF backbone, or both, and their levels in the polymer are strongly dependent on the type and concentration of the initiators.

⁴¹ These two groups may be generated due to CCl_4 present in the polymerisation process.

⁴² This group was always observed in the samples of PVDF or VDF–HFP copolymers synthesised in emulsion using ammonium persulfate as an initiator.

⁴³ Such structural features are important for understanding the byproducts formed during polymerisation and thermal degradation, among others.

Commercial PVDF samples consistently exhibit side chains (Hedhli et al., 2008), including $-\text{CH}_2-\text{CF}_2\text{H}$ and $-\text{CF}_2-\text{CH}_3$ end groups with their molar ratio varying between 1.2 and 4. The total content of the two end groups strongly depends on polymerisation temperature, ranging from 0.05 to 1 per 100 monomer units.

Challenges in the identification and characterisation of individual fluoropolymers

The understanding of specific chemical identities is a challenge for all polymers, and hence, is true for fluoropolymers as well. In order to assess these substances, it is critical to have a comprehensive understanding of specific chemical identities of individual unique polymers, including aspects such as the range of molecular weights, percentage by weight of each monomer present, and type and number of functional end groups (Wang et al., 2021; Groh et al., 2023). Such information can also provide information about potential impurities that may be present in the commercial products (see Chapter 4) and byproducts from thermal degradation (see Chapter 5), among others. Despite a limited number of known general structures, as outlined above, due to many possible chain lengths, various end-groups, and other functional modifications, a vast range of fluoropolymer structures are possible and many of them have been commercialized (for examples of diverse commercial PTFE products, see Table 2). Current technical datasheets and safety data sheets provided by the manufacturers typically provide information on the fluoropolymer type (e.g., PTFE) and general physical properties (e.g., average particle size, bulk density, standard specific gravity, tensile strength), without revealing the structural identities.

This leaves a challenge for assessing the structural identities of individual fluoropolymers on the global market. This lack of structural understanding in the public domain is largely based on two aspects. One is common polymer nomenclature, which tends to be general. Also, detailed information on the polymer identities and structures is often confidential business information or has simply not been made publicly accessible, which applies to all chemical registrations, not only polymers (Wang, 2022).

The current common approaches present significant challenges in accurately and effectively communicating the chemical structural identity of all polymers, including fluoropolymers. For instance, the naming conventions of polymers for public use are generally ambiguous, as they typically refer only to the monomer units or repeating functional group in polymers, making it difficult to infer the complete chemical structure based solely on their names (Wang et al., 2021). Also, while CASRN has been used as a main identifier in this report to look for chemical information, this approach also has inherent limitations—applicable not only to fluoropolymers but to polymers in general.

First, the same CASRNs can be used for different grades of the same fluoropolymer type. For example, Table 2 lists different PTFE products made from different polymerisation methods (indicated by their physical forms as noted above), with different particle sizes, and in some cases, being chemically modified. However, the same CASRN 9002-84-0 was listed in the safety data sheets.

Second, the same CASRNs may also be used for different types of fluoropolymers with the same monomer species. For example, fluoroplastic copolymers THV (made from TFE, HFP and VDF) and FKM type-2 fluoroelastomer copolymers (made from TFE, HFP, VDF and cure package) use the same CASRN 25190-89-0 (Plastic Europe, n.d.; 3M, 2024). Similarly, MFA and FFKM share the same CASRN 26425-79-6 (Plastic Europe, n.d.; CAS Common Chemistry, n.d.), while the former are fluoroplastic copolymers and the latter are fluoroelastomer copolymers.

These possible limitations, which are relevant for all polymers, restricts the understanding of the diversity and complexity of fluoropolymers on the global market, which then impedes specific assessment of their potentially distinct characteristics (Wang et al., 2021; Groh et al., 2023).

Furthermore, for 30 active CASRNs identified in Table S1 in the separate supporting material file, deleted CASRNs are identified, i.e., these CASRNs were replaced by the active CASRNs. Such merge of CASRNs

is generally poorly documented and problematic, as it can pose challenges in tracking information of the substances over time and from different sources (e.g., this report used only the active CASRNs to retrieve chemical information, while certain information may have been associated with the deleted CASRNs only).

Options for better identification of fluoropolymers on the global market

Obtaining comprehensive data about the chemical identities of fluoropolymers, including various structural characteristics such as presence of (minor) comonomers, molecular weights and end-group compositions, remains a challenge. As mentioned, this is not unique to fluoropolymers, but it is relevant for the assessment and management of such substances. To confront these important knowledge and data gaps, it is advisable to engage with manufacturers to understand more precisely existing commercial formulations, including their chemical identities and structural characteristics. Priority may be given to fluoropolymers actively being produced and sold on the global market with high production volumes.

Additionally, CASRNs and CAS names alone are not sufficient in communicating the diversity and complexity of polymers, including fluoropolymers, on the market. Improved naming conventions and novel chemical identifiers are essential to better identify, characterize, and communicate the diversity and complexity of this broad group of chemical substances. Developing more comprehensive unique identifiers beyond CASRNs and CAS names may enable a better understanding of the fate and behaviour of individual unique polymers, including fluoropolymers. Such better understanding may also support the development of predictive models for property estimation, including the addressing of uncertainty and data gaps.

Table 2. Examples of diverse commercial PTFE products with the same CASRN, including varied physical forms, average particle sizes, and recommended, extracted from relevant technical datasheets and safety data sheets provided by Daikin (n.d.) and Halopolymer (n.d.).

(Note: Additional information of a wider range of fluoropolymer products by major manufacturers has also been compiled. To maintain the readability of this table, these details are provided in Table S2 in the separate supporting material file)

Trade name	Listed CASRN	Physical form	Average particle size [µm]	Recommended uses	Notes
Polyflon®					
D-111	9002-84-0	aqueous dispersion	0.30	gland packing seals	
D-210C		aqueous dispersion	0.25	glass cloth impregnation, battery binder and additives for drip prevention	a filler needed for battery binder
D-310		aqueous dispersion	0.25	coatings, cooking appliances and glass cloth impregnated applications that require adhesion, surface smoothness and abrasion resistance	
D-711		aqueous dispersion	0.30	glass impregnation	
E-3705S21R		water-based topcoat ⁴⁴	-		
ED-1939D21R, 3293SW1R		water-based topcoat	-	office automation equipment	
EK-1209BKER, 1209M10R, 1908S21R, 1909S21R, 1959S21R, 1983S21R		water-based primer ⁴⁵	-	cooking appliances and kitchen appliances	
EK-3700C21R, 3707M21R, 3708S21R, 3709M21R, 3709S21R, 3712M21R, 3783S21R, 3793S21R		water-based topcoat	-	cooking appliances and kitchen appliances	
F-104		fine powder	500	for moulding sealing tap, short fiber,	

⁴⁴ Topcoats are the final coats for use over primers or fillers; they are formulated to provide good adherence to the undercoat, the desired appearance (colour, gloss, structure) to the painted unit, additional protection from the weather and aid in other performance requirements (Beckers, 2019).

⁴⁵ Primers are pigmented coatings that are applied to new or old surfaces, prior to the application of undercoats or topcoats (Beckers, 2019).

				pipe, tube, thick wire coating	
F-201		fine powder	530	forming thin tubes and wire coatings	
F-205		fine powder	500	for forming tubes and electric wire coatings	
F-208		fine powder	610	for forming ultrafine tubes and heat-resistant electric wire coatings	
F-302		fine powder	530	for transparent pressure resistant tubing	
L-5		micropowder	5–7	solid lubricant for plastic and grease application	a low-molecular-weight PTFE
L5f		micropowder	3–7	solid lubricant for plastic and grease application	a low-molecular-weight PTFE
M-12		granular, fine cut	58	thin-walled film	
M-18		granular, fine cut	50	medium to large compression moulding products	
M-18F		granular, fine cut	25	compound material with additives (e.g. carbon)	
M-392		granular, free flow	500	compression, automatic and isostatic moulding	
TC-7105GN, 7109BK, 7113LB		solvent-based coating	-	Sliding component	
TC-7400CR,		solvent-based coating	-	-	
TC-7408GY		solvent-based coating	-	-	
TC-7409BK		solvent-based coating	-	-	another unknown fluoropolymer is added in the product
TC-7808GY, 7809BK		solvent-based coating	-	cooking appliances and kitchen appliances	
TD-7139BD		solvent-based coating	-	-	
Fluoroplast-4®					
DE, DL	9002-84-0	aqueous dispersion	400–650	production of pipe liners, unsintered tapes, electrical tapes for wrapped insulations, tapes and beading for sealing applications, etc.; paste extrusion of pipes and rods for chemical, mechanical and electric applications	
DM		fine powder	350–650	fabrication of tubings, pressure hoses, flexible tubings, reinforced hoses, etc.	chemically modified PTFE
FCM-20		granular	10–25	production of articles (rods, pipes, bushings), etc.	
FCM-25		granular	20–30	production of articles (rods, pipes, bushings), etc.	
PN		granular	150±40	production of articles (rods, pipes, bushings, small billets) by compression (direct) and isostatic moulding;	another product of the same grade has a particle size range of 140

				fabricating the end products by moulding such as skived sheets, gaskets, bushings, seals;	– 220 µm.
PN20		granular	14–20	production of articles (rods, pipes, bushings), etc.	
PN25		granular	16–30	thin-skived films, fabricating of gaskets, bridge or pipeline bearing pads, piston rings, diaphragms, compound material with additives, etc.	
PN40		granular	31–40	fabricating of the end products, which include skived film and sheets, gaskets, bridge or pipeline bearing pads, piston rings, diaphragms	another product of the same grade has a particle size range of 22 – 40 µm.
PN60		granular	55–65	fabricating of electrical insulation, insulation and porous, rolled films, tape, and gaskets	
PN90		granular	80–100	fabricating the end products such as skived films, sheets, cylinders, gaskets, valve seats, seals, support slide for heavy loads	another product of the same grade has a particle size range of 100±35 µm.
PN-M1, M2		granular	110±25	Production of articles (rods, pipes, bushings), etc.	modified PTFE
RB		granular	150–250	fabricating the end products such as moulded sheets, small parts, etc.	
RX005, 105		micropowder	1–13	dry lubricant, an additive for plastics and coatings, etc.	max. particle size (d99), 100 µm
RX015, 115		granular	14–24	compound material with additives, production of articles (rods, pipes, bushings), etc.	max. particle size (d99), 140 µm
RX025, 125		granular, fine cut	25 – 34	thin-skived films, compound material with additives, production of articles (rods, pipes, bushings), etc.	max. particle size (d99), 180 µm
RX040, 140		granular	35 – 49	thin-skived films, compound material with additives, production of articles (rods, pipes, bushings) by moulding, etc.	max. particle size (d99), 250 µm
TG		granular, free flow	600 – 800	for manufacturing small rods and thin wall tubes, pipes, tubes, rods of simple shape	

3 The Life Cycle of Fluoropolymers

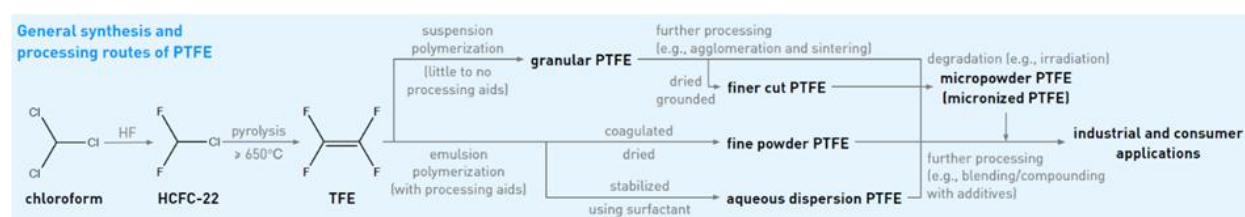
Chapter summary:

This chapter provides an overview of the current state of key life-cycle stages of fluoropolymers.

- **Monomer synthesis:** Distinct synthesis pathways were identified for TFE, HFP, VDF, CTFE and PPVE. During monomer synthesis, undesired byproducts may be formed, including toxic PFIB, HFCs and CFCs. However, byproduct formation data for CTFE and PPVE are lacking.
- **Polymerisation:** PTFE polymers are produced via suspension or emulsion polymerisation, and others following similar or modified processes. Historically, PFOA and PFNA were widely used as polymerisation aids, but have largely been replaced due to environmental concerns. Where PFAS replacements are used, they may pose similar risks. Currently, 50–60% of fluoropolymers are produced without PFAS polymerisation aids, with ongoing efforts to transition further. Additionally, the use of non-fluorinated alternatives may lead to potential trade-offs, including formation of fluorinated byproducts (in the case of PTFE), highlighting a key area for further study.
- **Processing:** Fluoropolymers are available as powders, granules, pellets, or dispersions and require distinct processing methods. PTFE, which does not melt, is processed via compression molding or sintering, while other melt-processable fluoropolymers such as PVDF and PCTFE can be extruded or injection-molded. Fluoropolymers may be compounded with fillers such as glass fiber or carbon to enhance properties. Coating applications involve dispersion mixing, spraying, and heat treatment, while sintering eliminates voids for structural integrity. Fluorinated ionomers are extruded into films, and fluoroelastomers undergo compounding, shaping, and curing. Processing influences final applications, residual PFAS content, and environmental emissions, though control technologies can mitigate these to a good extent.
- **Use/application:** Fluoropolymers are widely used across various industries in three primary ways: as standalone materials, coatings, or additives. They are often present in small amounts within larger products, such as vehicles. Their use spans interconnected industrial applications, with components such as valves, O-rings, and cables appearing across multiple sectors. Different fluoropolymers can sometimes be used interchangeably, though their specific technical requirements may vary. Fully mapping their uses and identifying viable non-fluorinated alternatives remains complex.
- **Production and use volumes:** Global fluoropolymer consumption has risen, with China leading at 37.5%. PTFE remains dominant but declined from 53% in 2018 to 45% in 2022, while PVDF and FEP grew. Major consumers include China, Western Europe, and the United States, driven by industrial demand. Fluoroelastomer use surged from 15 kt in 2001 to over 38 kt in recent years, with China as the top producer (27 kt/year). The automotive sector is the largest consumer of fluoroelastomers, driven by the demand for high-performance engines.
- **End-of-life treatment:** End-of-life treatment for fluoropolymers involves managing post-processing scraps and post-use waste. Around 10–30% of PTFE production results in scraps, with limited data indicating process losses of approximately 20% in the EU—equivalent to 8 kt in 2020, for example. Recycling of post-processing scraps is common, with 50–60% of scraps repurposed through internal or external processes, while 15% is incinerated. Melt-processable fluoropolymers are ground and reintegrated, and PTFE scraps can be reprocessed or degraded into micropowders. Chemical recycling, such as pyrolysis, may recover monomers such as TFE, but its upscaling remains to be seen. Post-use recycling is challenging due to complex product integration, fillers, and coatings. Limited data are available, but for example, most end-of-life fluoropolymer waste is incinerated (84%) or landfilled (13%), and only 3% is recycled, in the EU.

To acquire further information on the life cycle of individual fluoropolymers, several databases, including the US Toxic Substances Control Act Chemical Data Reporting in 2012, 2016 and 2020⁴⁶, SPIN⁴⁷, US FDA FCN,⁴⁸ Glüge et al. (2020)⁴⁹ and J-CHECK databases⁵⁰, were screened for all CASRNs identified in Table S1 in the separate supporting material file, along with a literature review. The life cycle of fluoropolymers encompasses several key stages: monomer synthesis, polymerisation, downstream processing, uses/applications, production and use volumes, and end-of-life treatment (an example of the life-cycle stages of PTFE from monomer synthesis to uses/applications is illustrated in Figure 2). The current state of these key stages is elaborated in detail in the following sections, with a focus on those being implemented by the industry at a fairly large scale, but not those still in the laboratory research and development stage. This overview is intended to be comprehensive but not exhaustive; additional technical details may be found at Ameduri (2009), Ameduri and Sawada (2016a,b), Ameduri and Fomin (2020), Drobný (2016), Ebnesajjad (2021), Gardiner (2014), Smith Jr. et al. (2014), Puts et al. (2019), and so on. Thus, this chapter provides a foundational overview, establishing context for subsequent chapters on the presence of other PFASs in commercial products (Chapter 4), the degradation of fluoropolymers during processing, use, and disposal (Chapter 5), and the environmental releases of both fluoropolymers and other associated PFASs across their life cycle (Chapter 6).

Figure 2. An illustration of the life-cycle stage of PTFE from monomer synthesis to polymerisation and downstream processing and to uses/applications



Note: These life-cycle stages are elaborated in detail in the following sections.

Monomer synthesis⁵¹

This section outlines the general industrial synthesis of key monomers used in fluoropolymer production, including TFE, HFP, VDF, CTFE, and PPVE, while excluding those produced in smaller quantities. Given that yields, including byproduct formation, vary based on manufacturer-specific reaction conditions, precise quantification is not provided.

⁴⁶ Accessed via the US EPA ChemView platform: <https://chemview.epa.gov/chemview/>

⁴⁷ Substances in Products in the Nordic Countries Database: <http://spin2000.net/>

⁴⁸ United States Food and Drug Administration Inventory of Effect Food Contact Substance Notifications: <https://www.cfsanappsexternal.fda.gov/scripts/fdcc/?set=FCN>

⁴⁹ A single sheet version of the PFAS use information from Glüge et al. (2020) can be accessed at <https://www.norman-network.com/nds/SLE/>

⁵⁰ Japan Chemicals Collaborative Knowledge database: <https://www.nite.go.jp/chem/jcheck/top.action>

⁵¹ For information derived from Feiring (1994) and references therein, no additional citations are provided. In contrast, information from other sources is always accompanied by a specific citation.

Industrial synthesis of TFE starts with the fluorination of chloroform (trichloromethane, CHCl_3 , CASRN 67-66-3)⁵² using hydrofluoric acid (HF) to produce chlorodifluoromethane (CHClF_2 , HCFC-22, CASRN 75-45-6)⁵³. The reaction impurities include unreacted chloroform and HF as well as byproducts such as dichlorodifluoromethane (CHCl_2F , HCFC-21, CASRN 75-43-4)⁵⁴ and trifluoromethane (CHF_3 , HFC-23, CASRN 75-46-7)⁵⁵ (PBL and TNO, 2021). Subsequent processing involves various separation processes to remove/recover byproducts and to purify the HCFC-22 product.

In a next step, HCFC-22 goes through a noncatalytic gas-phase pyrolysis at 600–900 °C and (sub-)atmospheric pressures to produce TFE. The reaction gives yields as high as 95%. Apart from the main reaction, minor side reactions, mostly originating with the action of HCl, lead to the formation of numerous byproducts (ECETOC, 2003), including HFP, perfluoroisobutylene (PFIB, CASRN 382-21-8),⁵⁶ octafluorocyclobutane ($\text{c-C}_4\text{F}_8$, PFC-318, CASRN 115-25-3),⁵⁷ and saturated chlorofluoroalkanes (CFCs)⁵⁸. As TFE used for fluoropolymers needs to be extremely pure,⁵⁹ usually containing only 1–10 ppm (1–10 mg/kg w/w) impurities (ECETOC, 2003; Guts et al., 2019), impurities such as byproducts are typically removed by a complex distillation process, and unreacted HCFC-22 may be recovered (for details, see PBL and TNO, 2021).

HFP is produced in two ways. As mentioned above, it is a co-product in the synthesis of TFE from the pyrolysis of HCFC-22. HFP yield can be increased, in lieu of TFE production, by altering the reaction conditions such as reduction in the pyrolysis temperature and use of steam as a diluent of the reactants. In addition, it can be prepared by heating TFE (together with HFC-23) to 700–900 °C under reduced pressure. Significant quantities of byproducts, including PFIB, are formed during the pyrolysis process (ECETOC, 2005a). After this pyrolysis process, the output gas stream passes through similar separation steps such as distillation as described above, where unreacted TFE and HFC-23⁶⁰ may be recycled (PBL

⁵² According to the IPCC Sixth Assessment Report, it has a 100-year time horizon global warming potential (GWP) value of 20.6, i.e., on a 100-year time horizon, 1 kg of chloroform has the same GWP as 20.6 kg of CO_2 (Greenhouse Gas Protocol, 2024).

⁵³ According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 1 960, i.e., on a 100-year time horizon, 1 kg of HCFC-22 has the same GWP as 1 960 kg of CO_2 (Greenhouse Gas Protocol, 2024). Additionally, HCFC-22 is listed in Annex C, Group I of the Montreal Protocol, with an ozone-depleting potential of 0.055 (UNEP Ozone Secretariat, 2020). However, its use as a feedstock in the manufacture of other chemicals is excluded from the legal obligation under the Protocol (Andersen et al., 2021; EIA, 2024). About 97% of HCFC-22 feedstock is used to produce TFE and HFP, part of which is used to produce fluoropolymers, while other portions are used for producing other chemicals such as HFCs and HFOs (TEAP, 2023).

⁵⁴ According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 160, i.e., on a 100-year time horizon, 1 kg of HCFC-21 has the same GWP as 160 kg of CO_2 (Greenhouse Gas Protocol, 2024). Additionally, HCFC-21 is listed in Annex C, Group I of the Montreal Protocol, with an ozone-depleting potential of 0.04 (UNEP Ozone Secretariat, 2020).

⁵⁵ According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 14 600, i.e., on a 100-year time horizon, 1 kg of HFC-23 has the same GWP as 14 600 kg of CO_2 (Greenhouse Gas Protocol, 2024).

⁵⁶ It is highly toxic, listed as a Schedule 2 substance of the Chemical Weapons Convention, i.e., chemicals that are feasible to use as chemical weapons and which have small-scale applications outside of chemical warfare and so can be legitimately manufactured in small quantities (OPCW, n.d.).

⁵⁷ According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 10 200, i.e., on a 100-year time horizon, 1 kg of PFC-318 has the same GWP as 10 200 kg of CO_2 (Greenhouse Gas Protocol, 2024).

⁵⁸ According to the IPCC Sixth Assessment Report, many chlorofluoroalkanes may have high 100-year time horizon GWP values (Greenhouse Gas Protocol, 2024). More information on the identities of the chlorofluoroalkane byproducts is not identified during the preparation of the report.

⁵⁹ These impurities may impact TFE solubility and reactivity, or act as chain transfer agents, adversely affecting reaction rate, product yield, molecular weight, and the final product's thermal stability (Guts et al., 2019).

⁶⁰ For Chemours, a closed-loop system of HFC-23 is operating in the monomers plant (PBL and TNO, 2021).

and TNO, 2021), and other byproducts may be either incinerated directly, or collected and transported for incineration at a remote facility (ECETOC, 2005a). HFP is very stable and does not autopolymerise and can be stored in a liquid phase without using an inhibitor (PBL and TNO, 2021).

VDF is most typically prepared by elimination of HCl from 1-chloro-1,1-difluoroethane (CH_3CClF_2 , HCFC-142b, CASRN 75-68-3)⁶¹ at temperatures of 700–900 °C⁶² in the gas phase, typically in a continuous closed reactor (ECETOC, 2005b). It can also be produced by elimination of HF from 1,1,1-trifluoroethane (CH_3CF_3 , HFC-143a, CASRN 420-46-2)⁶³, by dechlorination of 1,2-dichloro-1,1-difluoroethane ($\text{CClF}_2\text{CH}_2\text{Cl}$, HCFC-132b, CASRN 1649-08-7), and from other intermediates.

CTFE is prepared from 1,1,2-trichloro-1,2,2-trifluoroethane ($\text{CCl}_2\text{FCClF}_2$, CFC-113, CASRN 76-13-1)⁶⁴ by dehalogenation using zinc in methanol, or in the vapor phase using aluminum fluoride-nickel phosphate or metal oxide catalysts in the presence of hydrogen. No information on byproducts was identified during the preparation of this report.

PPVE is prepared from HFP in three steps. HFP is converted to hexafluoropropylene epoxide (HFPO) by reaction with oxygen, by electrochemical oxidation, or by reaction with hypochlorites or hydrogen peroxide in alkaline media. The fluorinated epoxide undergoes a rearrangement and dimerization using a catalyst (e.g., an alkali metal fluoride) to yield the acid fluoride $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COF}$, which is then pyrolyzed over an alkali metal carbonate or phosphate at 75–300 °C to form PPVE. No information on byproducts was identified during the preparation of this report.

Polymerisation

This section begins with an overview of the general polymerisation processes for synthesising various fluoropolymer types, followed by an in-depth analysis of the use of fluorinated and non-fluorinated polymerisation aids in these processes. Supporting information on the production history of several major fluoropolymers, including production capacity information, can be found in Annex B, and supporting information on fluoropolymer manufacturing sites is provided in Annex C.

⁶¹ HCFC-142b is typically produced from 1,1,1-trichloroethane through its reaction with HF and VDF, i.e., $\text{CH}_3\text{CCl}_3 + \text{HF} + \text{CH}_2=\text{CF}_2 \rightarrow \text{CCl}_2\text{FCH}_3$ (HCFC-141b) + CH_3CClF_2 (HCFC-142b) + CH_3CF_3 (HFC-143a) + byproducts; with the presence of catalysts, HCFC-142b and HFC-143a are the main products (Andersen et al., 2021). According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 2 300, i.e., on a 100-year time horizon, 1 kg of HCFC-142b has the same GWP as 2 300 kg of CO_2 (Greenhouse Gas Protocol, 2024). Also, 1,1,1-trichloroethane is listed in the Annex B, Group III of the Montreal Protocol with an ozone-depleting potential of 0.1, and HCFC-141b and HCFC-142b are listed in the Annex C, Group I of the Montreal Protocol with an ozone-depleting potential of 0.11 and 0.065, respectively (UNEP Ozone Secretariat, 2020).

⁶² The reaction can be run at higher temperatures in the presence of copper catalysts, or at lower temperatures in the presence of steam.

⁶³ According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 5 810, i.e., on a 100-year time horizon, 1 kg of HFC-143a has the same GWP as 5 810 kg of CO_2 (Greenhouse Gas Protocol, 2024).

⁶⁴ CFC-113 is typically produced from perchloroethylene (PCE) reacting to HF and Cl_2 at 240–375 °C (Andersen et al., 2021). According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 6 520, i.e., on a 100-year time horizon, 1 kg of CFC-113 has the same GWP as 6 520 kg of CO_2 (Greenhouse Gas Protocol, 2024). Also, CFC-113 is listed in the Annex A, Group I of the Montreal Protocol, with an ozone-depleting potential of 0.8 (UNEP Ozone Secretariat, 2020).

General Processes⁶⁵

In general, monomers are converted to fluoropolymers by conventional free-radical addition polymerisation techniques similar to those used for producing conventional polymers such as polystyrene; however, each fluoropolymer requires different formulation procedures (Kälin et al., 2012).

PTFE polymers are made by polymerisation of TFE, typically conducted at 70–120 °C, with two distinct processes used: suspension and emulsion polymerisations. The chemical structure of the polymer from both processes is identical, but the particle size and subsequent processing steps vary greatly.

A suspension polymerisation process is used to produce granular PTFE, using little (2–200 ppm) or no dispersing agent (Kälin et al., 2012; Guts et al., 2019): TFE vapor is fed to a heated reactor containing a weak acid, surfactants, deionized water and a free-radical initiator. Vigorous agitation is used in place of a dispersing agent to produce a precipitated resin. After several hours, the TFE feed is stopped, the reactor is vented and purged with nitrogen and the remaining reactor contents are discharged through a screen to remove dislodged polymer adhesions or coagulum and into a cooling vessel. The agglomerates of resin are dried and subjected to additional finishing operations to convert the polymer into four types of granular products: coarse, finely ground, agglomerated and presintered resins, with each type having a different shape and particle size.

In the emulsion polymerisation process (J.G. Drobny and S Ebnesajjad, 2023, Kälin et al., 2012, US ITC, 2021), two types of PTFE, Fine Powder Resins and Aqueous Dispersions are produced. TFE vapor is fed to a heated reactor containing a weak acid, surfactants (also known as emulsifying agents or polymerisation aids), paraffin wax and deionized water after removing oxygen. A free-radical initiator solution is added to initiate the polymerisation. Then, gentle agitation with the presence of surfactants is used to give a stable aqueous dispersion of small polymer particles (0.1 – 0.3 µm). For fine powder resin, the polymerised dispersion is followed by coagulation by adding a coagulating agent (or acid). The coagulated wet polymer is washed with deionized water and dried. For aqueous dispersion, hydrocarbon surfactant is added to the polymerised dispersion and gently heated for concentration into a solids content of 60% and 65 %. After further formulation with hydrocarbon surfactant and additives, the commercial product is sold with a polymer content of 60 % by weight.

Hence, a number of chemicals are used in the suspension/emulsion polymerisation of TFE, and Table 3 lists known ingredients used in the polymerisation and post-polymerisation, many of which are PFASs. Among them, prior to the phase-out of CFCs, Vydax™ was used as a dispersion of solid PTFE in CFC-113, which was often further diluted by the end user to meet individual process requirements; later, E.I. du Pont de Nemours (now Chemours) began supplying Vydax™ in dispersions of isopropyl alcohol and water (Grenfell, 1999). Furthermore, surfactants used as dispersing/emulsifying agents in the suspension/emulsion polymerisation, collectively known as polymerisation aids, are separately examined in greater detail in the following section.

Micropowder PTFE can be manufactured by direct emulsion polymerisation (approximately 15%), or it can be produced by thermal or irradiation degradation of high-molecular-weight PTFE resin (approximately 85%; for more details see below for end of life treatment), both virgin and recycled, by randomly cleaving the original polymers into smaller entities (Danish EPA, 2024).

⁶⁵ For information derived from Feiring (1994) and references therein, no additional citations are provided. In contrast, information from other sources is always accompanied by a specific citation.

Table 3. Non-exhaustive list of ingredients used in the polymerisation of TFE and post polymerisation

Function	Chemical Name
Coagulating agent	acetone, methanol
Coagulation aid	potassium nitrate, nitric acid
Initiator ⁶⁶	ammonium carbonate, ammonium persulfate, ammonium sulfite, barium peroxide, borax, disuccinic peroxide, hydrogen peroxide, lithium persulfate, potassium permanganate, sodium bisulfite, sodium hydrosulfite, succinic acid, zinc peroxide, bis(pentafluoropropionyl) peroxide (CASRN 356-45-6), bis(2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-1-oxopropyl) peroxide (CASRN 56347-79-6), bis(3-chloro-2,2,3,3-tetrafluoropropionyl) peroxide (CASRN 88505-66-2), bis(trifluoromethyl) peroxide (CASRN 927-84-4), bis(trichloroacetyl) peroxide (CASRN 2629-78-9), oxygen difluoride (CASRN 7783-41-7), lead(IV) tetrakis(trifluoroacetate) (CASRN 16656-82-9), sulfur chloride pentafluoride (CASRN 13780-57-9), silver(II) difluoride, chromic fluoride, lead tetrafluoride, hydrogen peroxide, tert-butyl 2,2-dimethylperoxypropanoate, <i>tert</i> -Amyl peroxy-2-ethylhexanoate, <i>tert</i> -Amyl peroxy-pivalate, <i>tert</i> -butyl peroxy-pivalate, etc.
pH adjuster	ammonium hydroxide, hydrochloric acid, nitric acid, sodium hydroxide
Removes monomer inhibitor	silica gel
Solvents/carriers ⁶⁷	purified deionized water, CFC-113, HFC-4310mee (1,1,1,2,2,3,4,5,5,5-decafluoropentane, CASRN 138495-42-8), ⁶⁸ HCFC-22, perfluoro-1,2-dimethylcyclobutane (CASRN 28677-00-1), perfluorohexane, perfluoro-1,3-dimethylcyclohexane (CASRN 335-27-3), perfluorodecalin, perfluoro- <i>N</i> -methylmorpholine (CASRN 382-28-5), bis(perfluoro- <i>n</i> -butyl)sulfide, arsenic trifluoride (CASRN 7784-35-2), isopropyl alcohol, water
Stabilizer	nitrogen, paraffin wax
Chain transfer agents ⁶⁹	HFC-32 (difluoromethane, CASRN 75-10-5) ⁷⁰ , HFC-23, HFC-152a (1,1-difluoroethane, CASRN 75-37-6) ⁷¹ , H ₂ , hydrocarbons, citric acid

⁶⁶ These are ingredients to generate free radicals to initiate the polymerisation. The commercially preferred class of fluorinated initiators are the oligo(hexafluoropropylene oxide) peroxides such as bis(2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-1-oxopropyl) peroxide (CASRN 56347-79-6), and bis(pentafluoropropionyl) peroxide (CASRN 356-45-6) is also widely used in commercial polymerisation (Guts et al., 2019). Bis(perfluoroacyl) peroxides are employed extensively in industry because they generate stable end-groups, thus reducing the need to treat the polymer with fluorine in the postprocessing step (Guts et al., 2019).

⁶⁷ Polymerisation also needs an electron source that can be the solvent, or better, carrier, the choice of which is, among other aspects, linked to the initiator (ETC/WMGE, 2021). In the case of PTFE, the term “carrier”, rather than “solvent,” should be used because PTFE does not dissolve in anything (Puts et al., 2019). Further, due to the strong electron-withdrawing effects of fluorine, fluorinated radicals are highly electrophilic and readily undergo proton transfer with conventional polymerisation solvents, rendering hydrocarbon solvents unsuitable for synthesising high-molecular-weight perfluorinated polymers via free-radical mechanisms, with water being the only conventional solvent inert to these radicals (Puts et al., 2019).

⁶⁸ According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 1 600, i.e., on a 100-year time horizon, 1 kg HFC-4310mee has the same GWP as 1 600 kg CO₂ (Greenhouse Gas Protocol, 2024).

⁶⁹ Chain transfer agents (CTAs) cause problems in the reaction since they terminate the polymer chain, but they are sometimes needed because without them, macroradicals can be trapped in the polymer matrix, resulting in lower thermal stability. Further, they prevent the product from sticking to the walls (ETC/WMGE, 2021).

⁷⁰ According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 771, i.e., on a 100-year time horizon, 1 kg HFC-32 has the same GWP as 771 kg CO₂ (Greenhouse Gas Protocol, 2024).

⁷¹ According to the IPCC Sixth Assessment Report, it has a 100-year time horizon GWP value of 164, i.e., on a 100-year time horizon, 1 kg HFC-152a has the same GWP as 164 kg CO₂ (Greenhouse Gas Protocol, 2024).

Surfactant/dispersing agents/dispersant/emulsifying agents	Various acids and related discussion see Figure 3 below, perfluoro(methylcyclohexane) (CASRN 355-02-2), 1,2-dichlorohexafluorocyclobutane (CASRN 356-18-3), 1-chloro-6-hydroperfluorohexane (CASRN 307-22-2), 1,2-dichlorotetrafluoroethane (CASRN 76-14-2), perfluorokerosene, perfluoro- <i>n</i> -pentane sulfonic acid (CASRN 2706-90-3), 3-ketopimelic acid (CASRN 1608-78-2), chlorendic acid (CASRN 115-28-6)
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Note: This list is based on PTFE patents and publicly available information (Henry et al., 2018; Puts et al., 2019; ETC/MMGE, 2021). Note that no single PTFE polymerisation process uses all of these.

PCTFE polymers are made by the free-radical polymerisation of CTFE in bulk, aqueous suspension or emulsion. Fluorinated surfactants have been used in emulsion polymerisation. Some producers make PCTFE by suspension polymerisation without any fluorinated or non-fluorinated surfactants as polymerisation aids.

PVDF polymers are synthesised through free-radical initiated polymerisation under a variety of conditions. Generally, aqueous suspension or emulsion processes are used, using a free-radical initiator. Fluorinated surfactants have been used in emulsion polymerisations but have been replaced with non-fluorinated surfactants by many producers. Molecular-weight control is achieved by the use of chain-transfer agents, such as acetone, chloroform, or trichlorofluoromethane. Nonaqueous polymerisations employing liquid chlorofluoroalkane solvents and fluorinated acyl peroxide initiators are also known. The polymer particles obtained are washed and spray-dried and are sold as powder or are converted into pellets (Kálin et al., 2012).

Cytop® polymers are prepared by cyclopolymerisation of linear perfluorodienes such as perfluoro-3-butenyl-vinyl ether (PBVE). The polymerisation process of Cytop® can be run in either aqueous or nonaqueous media.

Copolymerisation of HFP or PAVE with TFE to produce **FEP** or **PFA/MFA** can take place in aqueous or nonaqueous media, or mixed aqueous-nonaqueous media. Aqueous processes are similar to the dispersion polymerisation of TFE using a dispersing agent. Nonaqueous polymerisations tend to be run at slightly lower temperatures (30–60 °C) in a fluorinated solvent using a soluble organic initiator such as perfluoropropionyl peroxide. FEP has generally been produced commercially by an aqueous process, while both aqueous and nonaqueous processes have been used for PFA. Molecular-weight control is achieved by the use of chain-transfer agents. Stabilisation processes include heating the polymer in the presence of steam, or reacting with methanol, ammonia, or amines to convert the end groups to more stable ester, amide, or difluoromethyl groups. Treatment of PFA with elemental fluorine provides a finished polymer with stable –CF₃ end groups and a very low level of ionic contamination, which is of special importance to the semiconductor industry.

The polymerisation process of **Teflon™ AF** can be run in either aqueous or nonaqueous media.

ETFE copolymers are produced by free-radical, suspension polymerisation of the monomers in aqueous, nonaqueous (e.g., 1-hydroperfluorohexane or 1H-PFHx;⁷² Environment Agency, 2023a), or mixed systems, under conditions where TFE, but not ethylene, will homopolymerise. Emulsion polymerisation, using fluorinated polymerisation aids, may also be employed.

ECTFE copolymers are prepared by the free-radical copolymerisation of the monomers in aqueous, organic, or mixed media.

⁷² It may also be named as HFC 52-13p. The tropospheric lifetime of 1H-PFHx through reaction with hydroxyl radicals was estimated to be 31 years (Environment Agency, 2023a). It has a 100-year time horizon GWP value of 2 000, i.e., on a 100-year time horizon, 1 kg 1H-PFHx has the same GWP as 2 000 kg CO₂ (UNEP Ozone Secretariat, 2022).

FEVE copolymers are prepared by solution polymerisation of fluorinated olefins (e.g., CTFE) and alkyl vinyl ethers (e.g., in xylene; Zhang et al., 2023).

CTFE-VDF copolymers, or poly(CTFE-VDF), are prepared by suspension polymerisation of the monomers in water using an inorganic redox catalyst system without any fluorinated or non-fluorinated surfactant as polymerisation aids.

Fluorinated ionomers are polymerised in the presence of radical initiators, and in an aqueous medium or an inert organic solvent. No surfactant is used in Nafion™ production (RPA, 2023b).

Fluoroelastomers based on VDF copolymers, TFE–propylene copolymers and TFE–PAVE copolymers are usually prepared in aqueous emulsion, with free-radical initiators and emulsifying agents, which might be fluorinated or non-fluorinated surfactants. Free-radical solution polymerisations are also possible, but chain transfer from the solvent keeps the molecular weights low.

Little information was identified on the polymerisation of the **other fluoropolymers** during the preparation of this report. It is further noted that copolymers comprising TFE, HFP, and VDF—suited for an elastomer application—can be polymerised without any emulsifier (Hintzer and Schwertfeger, 2014).

Fluorinated and non-fluorinated polymerisation aids

As stated above, the polymerisation process of many fluoropolymers has used fluorinated/PFAS surfactants as polymerisation aids (e.g., dispersing agents in suspension polymerisation, or emulsifying agents in emulsion polymerisation). These include the suspension and emulsion polymerisation of PTFE,⁷³ emulsion polymerisation of PVDF (Wang et al., 2014a), polymerisation of THV, ETFE, THE (made of TFE, HFP and ethylene, CASRN 35560-16-8), and fluoroelastomers such as CASRNs 9011-17-0 (made of VDF and HFP), 25190-89-0 (made of TFE, HFP and VDF), 54675-89-7 (made of TFE, VDF and propylene), 27029-05-6 (made of TFE and propylene), 26425-79-6 (made of TFE and PPVE), 9010-75-7 (made of CTFE and VDF), and 26425-79-6 (made of TFE and PMVE) (Duncan, 2003). Here is an overview of fluorinated/PFAS polymerisation aids and their replacements. Residuals of fluorinated/PFAS polymerisation aids and other associated impurities in fluoropolymer products and associated environmental releases are further elaborated in Chapters 4 and 6, respectively.

In the past, PFOA (typically in the form of its ammonium or sodium salts, APFO/NaPFO)⁷⁴ was used in most cases except for the emulsion polymerisation of PVDF,⁷⁵ where some manufacturers used a perfluorononanoic acid (PFNA)-based polymerisation aid—Surflon™ S-111 (Buck et al., 2011; Wang et al., 2014a).

Wang et al. (2014a) reviewed patents on the suspension and emulsion polymerisation of PTFE to deduce PFOA use rates, noting that the use rates are generally reported in a large range over several orders of magnitude. For the suspension polymerisation of PTFE, Wang et al. (2014a) estimated 0.00075% and 0.11% by weight of PTFE formed, as a lower and higher scenario for the historical use of APFO/NaPFO. This is in line with the use of 0.0002–0.02% reported in Guts et al. (2019). For the emulsion polymerisation

⁷³ In the past, no or little APFO/NaPFO was used as a polymerisation aid in suspension polymerisation, whereas <1 wt% APFO/NaPFO was used in the emulsion polymerisation (Carlson and Schmiegel, 2000). In practice, E.I. du Pont de Nemours (now Chemours) added APFO at the Washington Works in Parkersburg, WV, in the emulsion polymerisation since 1951, whereas APFO was not used in the suspension polymerisation until 1965 (Paustenbach et al., 2007). Similarly, the then ICI and Hoechst also used APFO/NaPFO in the suspension polymerisation (van Battum et al. 1979).

⁷⁴ In practice, fluorinated polymerisation aids are typically used in their salt form. For simplicity, this report generally refers to them by their acid form.

⁷⁵ Notably, in the suspension polymerisation of PVDF (approximately 25% of past annual production), no fluorinated or PFAS polymerisation aid was used, see S1.2.1 in the Supplementary Material of Wang et al. (2014a).

of PTFE, Wang et al. (2014a) estimated 0.23% and 0.8% by weight of PTFE formed, as a lower and higher scenario for the historical use of PFOA. From the three patents identified that reported the use of PFOA quantitatively, Wang et al. (2014a) estimated that the historical polymerisation regime and conditions for FEP and PFA resemble those used to produce PTFE by emulsion polymerisation. For the emulsion polymerisation of PVDF, Wang et al. (2014a) estimated the use rate of Surflon™ S-111 to be 0.5% to 1% by weight of PVDF formed between 1975 and 1994 and to be 0.1% to 0.5% by weight of PVDF formed after 1994.

Given the concern about the hazards and risks of PFOA and its longer-chain homologues, US EPA and eight major global fluoropolymer manufacturers agreed on the global 2010/2015 PFOA Stewardship Program in 2006, with the aim to: (1) achieve a 95% reduction by 2010, in comparison to a year 2000 baseline, in both facility emissions and product content levels of PFOA, PFOA precursors and related higher homologue chemicals, and (2) virtually eliminate these chemicals from emissions and products by 2015 (US EPA, 2024b). This has stimulated action by many fluoropolymer manufacturers to find replacements for PFOA and PFNA, while some other manufacturers in China continue their use of PFOA.⁷⁶ For example, in 2008, 3M/Dyneon introduced its replacement ADONA and reported 2009 was the first full year of PFOA-free operation. Similarly, in June 2010, E.I. du Pont de Nemours (now Chemours) announced the GenX technology, including HFPO-DA (hexafluoropropylene oxide dimer acid), in its fluoropolymer manufacturing (RIVM, 2016; Ebnesajjad, 2021). An overview of currently used fluorinated/PFAS polymerisation aids in the polymerisation of fluoropolymers is provided in Figure 3. Supporting information on some of the fluorinated replacements, including their usage in polymerisation, their physicochemical characteristics, and residual levels in final products, can be found in Annex D.

Meanwhile, recent research shows that these fluorinated replacements pose similar hazards to the environment and human health as their predecessors (Wang et al., 2015). For example, the EU listed HFPO-DA as a substance of very high concern⁷⁷ in 2019 (ECHA, 2019).

Therefore, some fluoropolymer manufacturers have worked towards phasing out fluorinated/PFAS polymerisation aids in fluoropolymer production (for an overview, see Table 4). For example, Syensqo discontinued the use of fluorinated/PFAS polymerisation aids in the United States and announced that by 2026, it will manufacture nearly 100% of its fluoropolymers without fluorinated/PFAS polymerisation aids at its site in Italy (Solvay, 2022). Overall, about 50–60% of fluoropolymers are currently manufactured without fluorinated/PFAS polymerisation aids (Korzeniowski et al., 2023; Baua et al., 2023) with much progress to be closely followed in the next years.

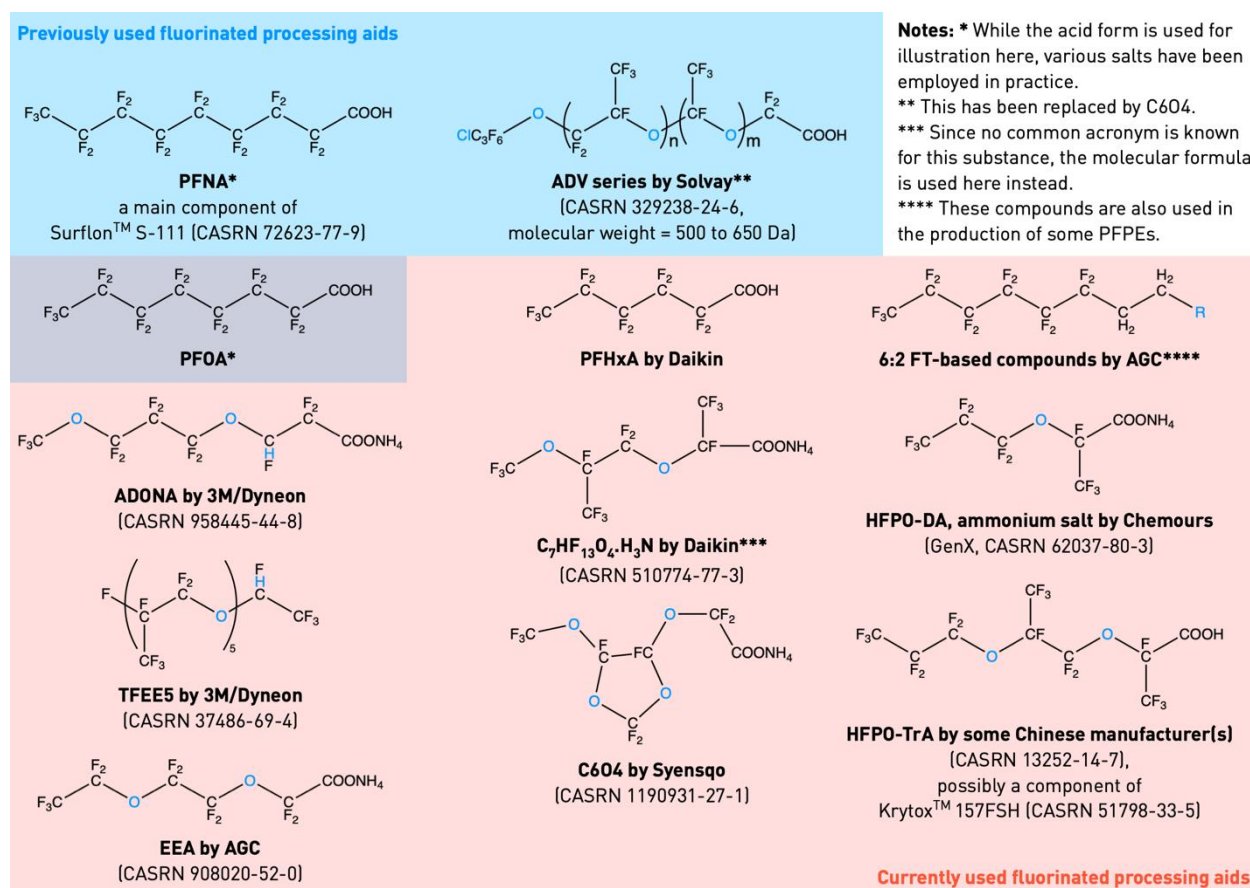
Meanwhile, the use of non-fluorinated polymerisation aids may involve trade-offs. Recent studies indicate that in PTFE production, non-fluorinated polymerisation aids may react with fluorocarbon radicals during polymerisation, leading to lower-quality polymers and the generation of a broader range of unintended fluorinated byproducts compared to fluorinated aids (Guts et al., 2019; Chemours, 2023a; Sworen et al., 2024); for more details on unintended fluorinated byproducts, see Chapter 4 “Polymerisation aids, along with their degradation products, impurities, and related byproducts”. Chemours (2023a) also noted that the

⁷⁶ Wang et al. (2013) noted that one Chinese manufacturer has replaced PFOA with another functionalized PFPE, but its structure and CASRN remains unrevealed, and that another Chinese manufacturer may have used 6:2 FTCA ($C_6F_{13}CH_2COOH$, CASRN 53826-12-3) as an alternative polymerisation aid, but this has not been confirmed.

⁷⁷ ECHA (2019) notes: The combined intrinsic properties justifying the inclusion for the Member State Committee as a substance for which there is scientific evidence of probable serious effects to human health and the environment which give rise to an equivalent level of concern are the following: Persistence, mobility, potential for long-range transport, observed adverse effects (at least the following probable effects for human health: effects on the liver, the kidney, and the haematological and immune systems and effects on development; at least the following probable effects for the environment: population relevant effects on birds and mammals); as well as low adsorption potential and high water solubility rendering the substance fully bioavailable for uptake via (drinking) water. Together, these elements lead to a very high potential for irreversible effects.

types of unintended fluorinated byproducts can vary depending on the polymerisation aid, monomers, recipe, manufacturing process, and resulting polymers. In contrast, AGC has recently announced that its new technology “makes it possible to manufacture fluoropolymers having the same type of high-performance properties as those produced by conventional methods with an extremely low generation of fluorinated byproducts, without using any surfactants” (AGC, 2024). However, specific technical details were not disclosed, including which fluoropolymer types the technology is applicable to. Therefore, future research is needed to better understand the formation and release of fluorinated byproducts when using non-fluorinated polymerisation aids, especially leveraging the advancements of suspect and non-targeted screening using high-resolution mass spectrometry (Chemours, 2023a; Sworen et al., 2024). Additionally, Chemours (2023a) recommended implementing strict manufacturing standards and advanced emission control technologies to manage risks associated with both fluorinated and non-fluorinated polymerisation aids, including those arising during processing and from final products.

Figure 3. An overview of previously and currently used fluorinated polymerisation aids in the polymerisation of fluoropolymers (the substances are named after their common acronyms).



Note: Blue highlights atoms that are neither carbon nor fluorine on the fluorinated carbon chains.

Source: EFSA CEF Panel (2009, 2010, 2011b, 2011c, 2012, 2014); Wang et al. (2013); Dams and Hintzer, 2017; AGC (2020a, 2020b); Daikin (2020)

Table 4. Availability of non-fluorinated polymerisation aids

	Availability of non-fluorinated polymerisation aids	Manufacturers offering products made using non-fluorinated polymerisation aids*
PTFE	Yes	Gujarat (since 2022) ⁷⁸
PCTFE	Yes	
PVDF	Yes	Gujarat ⁷⁹ , Arkema (since 2008) ⁸⁰ , Syensqo (since 2021) ⁸¹
FEP	No	
PFA/MFA	Yes	Gujarat (since 2023) ⁸²
ETFE	No	
ECTFE	Yes	
THV	No	
FKM	Yes	Gujarat (since 2022) ⁸³ , Syensqo (since 2021) ⁸⁴ , Chemours (since 2020) ⁸⁵ , Daikin (aiming for the end of 2025) ⁸⁶

Notes:

* AGC (2024) announced new technologies for producing fluoropolymers without using any surfactants; however, specific technical details—including the applicable fluoropolymer types—were not disclosed.

Please note that different polymerisation techniques may be applied depending on the fluoropolymer type; some require the use of (fluorinated) surfactants, while others do not. Additionally, individual polymer grades may vary in processing and performance requirements. Therefore, the availability of non-fluorinated polymerisation aids listed here does not guarantee their suitability for all grades of a given fluoropolymer. This table also does not account for potential trade-offs, which are discussed in the text. For detailed and product-specific information, it is recommended to consult the respective manufacturers.

Source: Chemservice, 2022, with recent updates

Processing

After polymerisation, fluoropolymers are typically available in the form of powders, granules, pellets, or aqueous dispersions before being processed into final, application-ready products (see Table A A.1 in Annex A). Due to variations in their molecular structures and properties, different fluoropolymers require distinct processing methods. For instance, PTFE polymers do not melt into a liquid state, but into a gel-like phase (maintaining its shape unless mechanically deformed), and cannot be melt-extruded, whereas many

⁷⁸ <https://www.gfl.co.in/assets/pdf/Announcement-9th-March-2022.pdf>

⁷⁹ <https://www.gfl.co.in/assets/pdf/GFL%20Announcement%2030.11.22.docx>

⁸⁰ <https://www.arkema.com/global/en/media/newslist/news/global/products/2008/20081202-arkema-welcomes-yl/>. It is further reported that Arkema's two largest PVDF production plants made the transition before 2023, while the last plant was to achieve its transition to the non-fluorinated surfactants by the end of 2024 (Arkema, 2023).

⁸¹ <https://www.syensqo.com/en/innovation/pfas;> <https://www.syensqo.com/en/article/eliminating-pfas;> <https://www.solvay.com/en/press-release/solvay-launches-non-fluorosurfactant-technologies-in-us>

⁸² <https://www.gfl.co.in/assets/pdf/GFL%20Announcement%2030.11.22.docx>

⁸³ <https://www.gfl.co.in/assets/pdf/Announcement-on-NFPA-technology-FKM-27-Aug-2022.pdf>

⁸⁴ <https://www.syensqo.com/en/innovation/pfas;> <https://www.syensqo.com/en/article/eliminating-pfas;> <https://www.solvay.com/en/press-release/solvay-launches-non-fluorosurfactant-technologies-in-us>

⁸⁵ <https://www.chemours.com/en/news-media-center/3bl-news?mid=379606&pgno=46&fdpgno=1>

⁸⁶ <https://www.daikinchemicals.com/sustainability/pfas.html>

other fluoropolymers, such as PCTFE and PVDF, are melt-processable (SPI, 2005). Additionally, fluoroelastomers require specialized processing due to their cross-linking nature. Processing temperatures vary depending on the molecular structure of the fluoropolymer; an overview of their melting points, continuous use temperatures, and processing temperatures⁸⁷ is provided in Table 5.

The processing methods of fluoropolymers not only determine their final applications but also influence residual byproducts including other PFASs present in products (Chapter 4), degradation of fluoropolymers during processing, use, and end-of-life (Chapter 5), and environmental releases (Chapter 6). For example, techniques such as extrusion and injection moulding can lead to air and water emissions containing fluorinated residues (Chemours, 2023b). However, these emissions can often be effectively managed using standard emission control technologies (Chemours, 2023b). Further details regarding these implications are provided in the relevant chapters that follow.

Compounding involves mixing fluoropolymers with additives such as fillers and pigments for desired characteristics. For example, PTFE may be compounded with materials including, but not limited to, carbon, graphite, glass fibre, stainless steel, or bronze to enhance the mechanical properties such as abrasion resistance (US ITC, 2021)⁸⁸. Among these, glass fibre is the most commonly used filler, usually sold in compounds with 15–25% glass fibre by weight (US ITC, 2021). Similarly, fillers such as carbon black, titanium dioxide, or silica have been used in amounts which vary in the range of 10–30 parts per hundred of raw FFKM (Feiring, 1994). The standard ingredients used for fluoroelastomers include fillers, processing aids, metal oxides (acid scavengers), activators (hydroxides), a cure system (cross-linker and accelerator), and pigments in case of coloured formulations (Drobny, 2016).

Shaping techniques resemble those used for conventional plastics, such as extrusion or moulding. The choice of technique depends on the fluoropolymer type and application requirements. For example, granular PTFE polymers are usually processed through compression or isostatic moulding followed by sintering, or ram extrusion with inline sintering. Compression-moulded products are often fabricated into basic shapes such as cylinders and cubes, which are then machined into seals, bearings, bushings, piston rings, and diaphragms (US ITC, 2021). Fine powder PTFE, having the same high melting point and viscosity as granular PTFE, may be processed into a finished product via paste extrusion due to their small particle size (US ITC, 2021). Additionally, PVDF can be functionalized to allow for extruded composite structures with polyolefins, nylons, PVCs, and other polymers and is routinely processed on equipment used to extrude PVC and polyolefins (Kälin et al., 2012). Similarly, EFEP (ethylene, TFE and HFP) copolymers can be co-extruded with conventional plastics such as polyamide, ethylene vinyl alcohol (EVOH), and modified polyethylene, due to their low processing temperature (Korzeniowski et al., 2023).

Coating⁸⁹ with fluoropolymer dispersions typically involves the following processing steps: mixing of dispersions with other ingredients, applying the formulated dispersion onto surfaces, fabrics or yarns by spraying or immersion in a dispersion bath, followed by drying, baking, or sintering. Spraying may generate a mist that might be an additional exposure risk. During drying, baking, and sintering, water and other volatile ingredients (or their degradation products) are removed from the coated products (SPI, 2005).

Sintering is a common technique for some fluoropolymers such as PTFE and PCTFE. It involves heating the polymer to a temperature that causes the polymer particles to melt and fuse together, eliminating voids

⁸⁷ For ECTFE, processing stability may be improved through the addition of stabilizers such as polyhydric phenol phosphites, zinc alkanoates, and other commercially available options (Feiring, 1994).

⁸⁸ The additive content may range between 2% and 60%, depending on the application, and additives may offer several key benefits, including: enhanced wear resistance (e.g., carbon and graphite), increased thermal conductivity, improved mechanical properties (e.g., bronze), improved hardness and stiffness (e.g., molybdenum disulfide), and stabilisation of chemical, thermal, and electrical properties (e.g., glass fibre) (Odochian et al., 2011).

⁸⁹ Powder and dispersion grades of PVDF (e.g., 44% in dimethyl phthalate and diisobutyl ketone) are available for coatings (Kälin et al., 2012).

that may result in weak points or flaws in the polymer structure. This process, also referred to as heat treating or “coalescence” in PTFE processing, is analogous to sintering in metallurgy (SPI, 2005). For PTFE, sintering temperature range between 360°C and 380°C, exceeding their melting point (Inoflon, n.d.).

As noted above, several processing steps may be combined to achieve the final products. For example, fluorinated ionomers are often fabricated into films (typically 100–250 µm thick) using conventional extrusion techniques. Films with different ion-exchange capacities or functional groups can be laminated. These films are generally reinforced with PTFE cloth or mixed with small amounts of fibrous materials. They are converted into ion-exchange membranes via alkaline hydrolysis, allowing for functionalisation with sulfonic or carboxylic acid groups.

Fluoroelastomers are available in three forms: raw gum (requiring compounding with additives), precompounded material (containing curatives and accelerators, requiring only the addition of fillers, pigments, or processing aids), and full compounded material (containing the wide range of additives according to specific performance requirements). The compounding process prepares the material for specific processing methods, which include mixing (on a mill or in an internal mixer), shaping (extrusion, calendaring), and curing. Curing methods involve heating the shaped semi-finished product in an autoclave with hot air or steam at approximately 170°C (338°F). Alternative processing methods include moulding, which combines shaping and curing in one step through compression moulding, transfer molding, or injection moulding. Fluoroelastomers can also be processed using latex technology, where elastomer particles are dispersed in water and applied through dipping, coating, or casting, followed by drying and curing.

Table 5. Typical melting points, continuous use and processing temperatures of fluoropolymers

	Typical melting point [°C]	Typical maximum continuous use service temperature [°C]	Typical processing temperature** [°C]
PTFE	330***	260	380
PCTFE	215	120	265
PVDF	170	150	232
PVDF copolymer****	115–170	100–150	232–249
FEP	260	205	360
PFA	305	260	380
MFA	280	249	360
ETFE****	220–270	150	310
ECTFE	230	140–150	280–310
THV****	120–230	70–130	171–310
EFEP****	158–195	100–150	220–260
HFP-TFE-ethylene (HTE) copolymer****	160–210	105–150	200–290

Notes :

** Note that the processing temperatures in this table are actual polymer temperatures, not oven or equipment temperatures, which may be significantly higher. Processing and continuous use temperatures depend on use, environment and processing history.

*** Gel point (when the polymer forms a clear coalescible gel).

**** Product families include different products with different continuous use temperatures and different processing temperatures.

Source: SPI, 2005; SPI, 2019; Plastics Europe, 2021. When values are available in both SPI (2005) and Plastics Europe (2021), data from Plastics Europe (2021) are used in the table.

Uses/Applications

Fluoropolymers are used and are reported to have been used in a variety of industrial sectors and applications. Table 6 provides a comprehensive but not exhaustive overview of these uses.⁹⁰ Tables S2 and S3 in the separate supporting material file present supporting details on the use of the commercial fluoropolymer products from manufacturers' websites and the use information associated with the 131 CASRNs identified in this report, respectively.

As shown in Table 6, fluoropolymers are used across numerous industrial sectors and applications⁹¹ for various functionalities, highlighting their diversity and complexity. Nevertheless, four general observations can be made.

First, fluoropolymers are generally used in three main ways: (1) as standalone materials (e.g., O-rings, wires, tubes, membranes, films, etc.), (2) as coatings on other materials, or (3) as additives in other materials and products (e.g., as processing aids in conventional plastics, in paints and inks, in lubricants and greases). They are often present in the form of small components and in small amounts within larger products—for example, an estimated 350–800 g per vehicle (Ameduri, 2020; Baua et al., 2023) including on average 330 g of fluoroelastomers per internal combustion engine (ICE) vehicle (Daikin, 2020).

Second, fluoropolymer use exhibits complex interconnectivity across industrial sectors and applications. Many industrial applications, such as valves, O-rings, seals, fittings, pumps, pipes, packaging, filters and vessels, are commonly used across industry sectors. Additionally, fluoropolymers are often embedded in products that become components of other products (e.g., seals, lubricants, cabling), creating complex, interlinked value chains.

Third, different fluoropolymers can be used in the same applications. In some cases, they meet distinct technical requirements, while in others, they may be used interchangeably.

Fourth, fully mapping the applications, functionalities, and relevant sectors of fluoropolymers remains challenging due to diversity and complexity. Meanwhile, some reports suggest that fluoropolymers may compete with other alternative materials in certain markets (e.g., Kálin et al., 2012). Further research is needed to assess which fluoropolymer uses are technically essential/critical and where performant non-fluorinated alternatives are available.

⁹⁰ This report draws on the categorisation of industrial sectors and applications outlined in the *PFAS Technical and Regulatory Guidance Document* by the US Interstate Technology Regulatory Council (US ITRC, 2023), with several additional sectors and applications. This approach is used for reference purposes only and is not intended to suggest that it is the sole or definitive method for categorizing industrial sectors and applications.

⁹¹ Chemours reports offering various fluoropolymers in multiple grades for over 1 400 applications across more than 30 industries in the Europe, the Middle East and Africa region (Chemours, 2023b).

Table 6. Sample use of fluoropolymers in various industrial sectors and applications

Industrial sectors / Application*	Documented use examples of fluoropolymers ⁹²
Agriculture	ETFE is used in agricultural film for greenhouses [3].
Aviation and aerospace	Mechanical components made of fluoropolymers (such as PTFE and PFA tubing, piping, seals, gaskets, cables, and insulators) are widely used [1, 3]. Fluoroelastomers are used in: O-ring seals in fuel, lubrication, and hydraulic systems; manifold gaskets; fuel tank bladders; firewall seals; engine lube siphon hoses; clips for jet engines; electrical connectors; shaft seals; traps for hot engine lubricants; tire valve stem seals; and heat-sealable tubing for wire and cable insulation [4]. PTFE strips are used to improve the wear resistance of moving parts as well as miscellaneous fixation of parts for internal and external hull [4]. In aerospace turbine engines, PTFE fibres in fan blade wear strips enhance low friction performance [4]. Adhesive PTFE-based tapes serve as a substitute for paints, e.g., for marking of aircraft [4]. Low-molecular-weight PCTFE polymers (primarily oligomers with 3–4 monomer units) have been used as a hydraulic fluid for aircraft [20]. ETFE copolymers are used as non-plenum wire and cable insulation (e.g., military aircraft, missile hookup wires, and space vehicles), while smaller amounts of FEP, PVDF, ECTFE and PFA are used in aircraft wire [3]. FEP copolymers are used as a release film liner by the airplane industry in the bagging layup of reinforced epoxy parts for composite tail and wing sections and other applications such as frames and lavatories, and as a primary insulation material for wiring in military and other aircraft (including wiring for ground-support equipment) [3]. A significant amount of FEP is laminated to polyimide film for use in aircraft wire and cable insulation, as well as in making advanced composites for use in commercial and military aircraft and aerospace applications such as fuselages, wing skins and engine nacelles [3]. CTFE-VDF copolymers are used in aerospace applications such as antistatic packaging for satellites, telescope, cameras and electronics [3]. THV copolymers are used as a barrier layer in fuel hoses [14]. FFKM copolymers are used in numerous gas turbine engines for aircraft to allow the use of high thermal stability oils, which in turn allow for higher engine temperatures lowering fuel emissions [4].
Automotive and road transport	Mechanical components made of fluoropolymers (such as PTFE), including bushings, wiring and cable, fuel delivery tubing, seals, bearings, gaskets, piston rings and lubricants [1, 2, 3, 4]. Fluoroelastomers are used in: shaft seals; valve stem and valve seals; fuel injector O-rings; fuel

⁹² A high-level overview of the uses, properties, and functionalities of individual fluoropolymer types across major industrial sectors and applications is provided in Tables 1 and 2 of Korzeniowski et al. (2023). In addition, high-level illustrations of the use of fluoropolymers in the chemical industry, semiconductor industry, energy industry, automotive industry (including electric vehicles), and medical products are provided in Chemours (2023b), see Graphics 2, 3, 5, 6a, 6b, and 8.

	hoses and fuel hose liners; in-tank and quick-connect fuel system seals; gaskets (valve and manifold); balls for check valves; heat-sealable tubing for wire insulation; bellows for turbocharger lubricating systems; lathe cut gaskets; and engine head gaskets [4]. PTFE-based seals are commonly used in the industry for radiators, transmissions and air conditioners [3]. Additional uses of PTFE include “push-pull” cables for throttles, transmissions, clutches and brakes, automotive hoses for the transport of various fluids (such as reformulated fuels), oxygen sensor cables for engines [3]. PTFE can also be found in car polish products [4], and in internally lubricated engineering thermoplastic compounds for steering wheel sensors, throttle body gears, gas pedal and clutch systems, gearbox and under-the-hood components, interior and lighting gears, actuators and sliders, sensor systems, and others [5]. PVDF polymers are used in automotive transmission wire, railcar, and mass transit applications [3]. ETFE wires and cables are used in automotive wire, lighting and instrument wiring in mass transit vehicles [3]. ETFE copolymers are also used in low-permeability multilayer tubing for direct fuel handling applications [3]. ETFE copolymers are used as an anti-graffiti overlay for traffic signage [4]. PTFE, ETFE or PFA (co)polymers are used for lubrication-free bearings to achieve a low friction, low stiffness, and high temperature resistance, e.g., in ball joints, belt tensioners, decoupled pulleys, dual mass flywheels, solenoid valves, clutch release, steering torque sensors, seat height adjustment, pedal work, seat folding mechanism, headrest height adjustment and centre console lid [4]. THV copolymers are used in low-oxygen-permeation automotive fuel lines [3]. FEPM used in lightweight, high-voltage automotive cables and motor cables for Japanese high-speed bullet trains [14]. FKM fluoroelastomers are used as sealants in turbocharger hoses [15].
Biotechnology	Polymers used for reaction vessels, stirrers, and other components, filtration, and moisture barrier [1]
Building and construction	Fluoropolymer membranes and coatings such as PTFE and PVDF in architectural materials (like fabrics, roofing membranes, metals, stone, tiles, concrete, radomes); adhesives, seals, caulks; additives in paints (for example, low- and no-VOC latex paints), varnishes, dyes, stains, sealants; surface treatment agents and laminates for conserving landmarks [1]. For example, filled PTFE polymers are used as bearing pads for high-rise buildings and bridges [3]. PTFE-coated fiberglass is used as a dome covering for large buildings such as sports stadiums [3]. PTFE polymers are also used in skidways for construction projects, and PTFE tapes are used for professional applications such as drinking water, compressed air systems, and installation of windows and doors [4]. PVDF polymers are used in weather-resistant exterior architectural coatings [3]. For architectural coatings, PVDF polymers are typically sold as a dispersed powder with pigments and solvents included for application to metals such as aluminum, aluminized steel and galvanized steel for use on exterior surfaces in industrial construction, for commercial construction such as warehouses, power plants, monument-type structures (e.g., landmark office towers) and light commercial buildings, and, to a lesser extent, for residential roofing and siding for houses, apartments and condominiums, as well as in dry, powder form for melt-applied powder coating of steel coil for the manufacture of steel roofing, siding and other products [3]. ECTFE copolymers are used in anticorrosion applications such as coatings or in self-supporting construction (pipes) and architectural films [14].

	THV copolymers are used in the bonding layer in multilayer construction [14].
Cable and wiring	Coatings and jacketing made of fluoropolymers (such as PTFE and PVDF) for weathering, flame, and soil resistance, with cables used in many applications, including communication facilities, antennae, and computer networks [1, 3]. ECTFE copolymers are used in film and in non-plenum wire and cable applications across sectors including automotive, aircraft, mass transit, military, and nuclear power plants [3]. FEP elastomers are used in high-performance wire and cable applications as insulating materials with high heat resistance [14].
Chemical industry	Fluoropolymers (such as PTFE) used to coat chemical tanks and pipes to enhance corrosion and high temperature resistance (e.g., chemical transfer and heat exchangers), as sealing and gasket materials for chemical processing, and for filtration media used in chemical manufacturing processes and emissions controls [1, 3]. Fluoropolymer fibres are also used in reinforced materials for chlor alkali ion exchange membranes [13]. Skived sheets made from PTFE are used for cladding chemical processing equipment [3]. FEP copolymers are used in chemical processing applications including linings for fittings, pumps and tubing, as well as uses in bellows and valve components [3]. ETFE copolymers are used in chemical processing applications including tank, pump, valve and pipe linings and moulded items such as tower packaging, valve seats, mist eliminators, fittings, and pipes and tubes [3]. ECTFE copolymers are used in solid and lined pipelines, fittings, pump and valve components, fitting housings, components for wet-process stations and tanks and tank linings [3]. PCTFE polymers are used in the manufacture of seals and seats for petrochemical and chemical processing equipment, aiding in the safe transfer of liquefied natural gas, liquid nitrogen and liquefied propane from ship to shore and vice versa [3]. Nafion™ resins in the form of small polymer beads are used as non-electrochemical ion exchange materials in the chemical, pharmaceutical, and several other industries [16].
Cosmetics and personal care products ⁹³	Dental floss, toothpaste, dental creams, tooth powders, throat lozenges, chewing gums, sunscreens, cosmetics, and micro powders used in creams and lotions [1]. PTFE polymers are used as bulking agents and slip modifiers in cosmetics [4, 20]. The results from a 2017 use survey indicated that PTFE polymers were being used at concentrations up to 13% in leave-on products (mascara), at concentrations up to 2.4% in rinse-off products (hair bleaches), at maximum use concentrations ranging from 0.5% to 3% in face powders, and at maximum use concentrations up to 0.44% in oral hygiene products [20]. FEP copolymers are used as film formers, skin-conditioning agents (emollient), and slip modifiers in cosmetics [20].

⁹³ It should be noted that under the European Cosmetics Regulation (Regulation (EC) No 1223/2009) chewing gum, throat lozenges and dental floss are not considered cosmetics/personal care products.

	PCTFE polymers are used as film formers and skin-conditioning agents (occlusive) in cosmetics [20].
Electrical and electronics	Fluoropolymers (such as PVDF and PTFE) are used in insulators, solder sleeves, printed circuit boards, cell phones, computers, speakers, and transducers [1, 3]. For example, a major use of granular PTFE polymers is for the fabrication of electrical components such as cable connectors, circuit breakers and stand-off insulators [3]. Unfilled granular PTFE polymers are also used in the fabrication of coaxial cores, ribbon cable, and skived electrical insulating tapes (used to wrap cables or coated with adhesives for pressure-sensitive tapes) [3]. Some granular PTFE grades are used in printed circuit boards, particularly for specialized microwave applications [3]. Fine powder PTFE polymers are used in the manufacture of tape, tubing and wire insulation in the sector [3]. PTFE polymers are also used in spaghetti tubing that is made to slip over bare wire as an electrical insulation material [3]. Small amounts of FEP, PVDF, ECTFE and PFA are used in computer wiring [3]. Moreover, PTFE polymers are used as sound-permeable membrane for mobile phones and digital cameras [4]. FEP copolymers are used for plenum cable, as primary insulation and as a jacketing material, e.g., in the data transmission segment of the plenum wire market, e.g., Local Area Network (LAN) cabling [3, 4]. FEP copolymers are also used as a jacketing material for PTFE-coated wire in certain applications, as well as in heat trace cable, computer back-panel wiring, coaxial cable cores and insulation, round and flat radio frequency transmission lines, downhold cable, and thermocouple wires [3]. PVDF materials are used as cable jacketing for fibre optic, data and phone cables, and industrial speciality cables, in nonplenum wire applications for copper wire and optical cable jacketing, and in electric heat trace cable, industrial control wire, computer back-panel wire, leak trace cable, anode lead wire and cable ties [3]. ETFE wires and cables are used in computer back panels and heat trace cables [3]. ETFE copolymers are also used in heat-shrink tubing, wire tie wraps and injection-moulded parts such as coil forms, sockets, connectors, switch components, insulators, lithium battery cases, and fasteners [3]. ECTFE plenum wires and cables are used in telecommunications, data transmission, and fire alarm [3]. MFA copolymers are suitable for primary insulation of hook-up wire and telecommunication cables [3]. PFA/MFA copolymers are used in heat trace cable, as well as in appliance, computer and aerospace wire, as well as for electrical parts such as connector inserts, standoff insulators and insulating bushings [3]. CTFE-VDF copolymers are used in pressure-sensitive tapes in various electrical/electronic applications, and in bonding materials for laminates (e.g., for circuit boards) [3]. CTFE-VDF copolymers are also used in electroluminescent displays, including in electroluminescent lamps, cockpit lighting systems, aircraft cabin lighting systems, formation lighting (in navigational lighting for approach-and-landing guidance lighting systems), wing tip lights, and military cockpits, with CTFE-VDF films acting as a moisture barrier and an electrical insulation material [3].
Energy ⁹⁴	Fluoropolymers such as FEP and PVDF are used to cover solar panel collectors, in electrolyte fuel cells and in alkaline water electrolysis

⁹⁴ More details on the functionality of individual fluoropolymer types in specific battery types and potential alternatives can be found in BAJ (2023). More details on the use of individual fluoropolymer types in specific parts in the power transmission applications can be found in VDMA (2023). More details on the use and functionality of

	(technology for large-scale hydrogen production), as PTFE expansion joint materials for power plants, and in filtration of fly ash from stack emissions [1, 2, 3], as well as paints and coatings for wind turbines and coating for wires and cables [2]. Fluoropolymers are also used in heat exchangers, tubing and filters in coal-based power plants [4]. PTFE materials are used as lubricants for wind turbines [4], and in the module parts of lithium-ion batteries [9]. PFA copolymers are used in gaskets of lithium-ion batteries [9] PTFE and TFE-PP polymers (poly(propylene-co-tetrafluoroethylene), CASRN 27029-05-6) are used as positive electrode binder for nickel metal hydride battery and nickel cadmium battery, and powders of fluoropolymers such as PTFE, FEP and PFA are used for the negative electrode surfaces of nickel metal hydride battery and nickel cadmium battery [9]. PTFE, ETFE and FEP are used as positive electrode binder for lithium primary batteries (CR/BR type, cylindrical and coin shapes), and PTFE materials are used as a positive electrode binder for lithium primary batteries (ER type) [9]. PTFE, ETFE, FEP and PVDF are used as positive electrode binders for coin-shaped lithium rechargeable battery, and PFA copolymers are used in gaskets for coin-shaped lithium rechargeable battery [9]. PVDF materials are used as a separator and binder in lithium-ion batteries, and back sheets for solar cells [3]. PVDF polymers are also used polymer electrolytes [9]. PTFE materials are used in the positive electrode binder of alkaline button battery (LR and SR) [9]. FEVE/ETFE copolymers are used as release film for wind turbines and in wind blade protection coating (to prevent moisture in the air from affecting curing process) [4]. THV copolymers are used in solar panels [3]. Perfluorinated sulfonyl fluoride ionomers act as a binder and proton conductor in the catalyst layers in fuel cells, while PTFE materials are part of the gas diffusion layer and controls the hydrophobicity of the components, which in turn regulates the water management of a fuel cell [4]. Nafion™ materials are sold as dispersions in water, colloidal mixtures of microscopic particles of solid ionomers suspended in water, which are generally used alongside ion-exchange membranes as functional binding agents for adhering catalysts to the membrane, as well as multiple other electrochemical applications [16].
Explosives, propellants, guns and ammunition	Fluoropolymers (PTFE, PVDF, or fluoroelastomers such as Viton®) are applied to guns for lubrication and protection against degradation during long-term storage, tungsten-iron-fluoropolymer shot alloys (as a replacement for lead in hunting waterfowl and coots), in visual flares, warheads, incendiaries, and others applications, such as in processes as surface coating in direct contact with pyrotechnic compositions [1, 10].
Firefighting / safety	Fluoropolymers used in firefighting equipment and protective clothing (such as those woven with PTFE). [1]
Food processing	Fluoropolymers such as PTFE and PVDF are used in the fabrication of food-processing and food-contact materials such as liners for trays, ovens, grills, conveyor belts, industrial bakeware moulds [1, 4]. Other uses include piping and tubing for drinking water applications; filters to capture

Nafion™ ion-exchange membrane applications in polymer electrolyte membrane fuel cells (PEMFCs), polymer electrolyte membrane water electrolyzers (PEMWEs), and redox flow batteries, as well as chloralkali process, can be found in RPA (2023b).

		contaminants, such as those from steam filtration in food processing; seals, O-rings, gaskets, tubing and pipes, expansion joints; valves and fittings, chutes, guiding rails, rollers, funnels and sliding plates, tanks, linings, knife and scissor blades, springs, filter membranes, and sensor covers [4]. Fluoroelastomers are used as US FDA approved seals in food handling processes [4]. PTFE impregnated glass cloth is commonly used in food-contact applications as a release agent [4]. PTFE-coated elastomers are often used as seals in pressure bearing equipment [4]. Cans, especially beverage cans, are often coated with PTFE wax or micropowder PTFE to reduce friction and facilitate easy sliding of cans on production lines [4]. PVDF materials are used in the fabrication of industrial cookware equipment [4].
Household products	and cleaning	Nonstick coatings (fluoropolymers such as PTFE) for cookware and bakeware, including electrical cooking appliances such as toastie makers and grills, sewing machine presser feet, and glass [1, 2, 4]. Fluoropolymers may also be used in dishwashers [4]. Certain solid, non-sintered fluoropolymers are used to produce items such as films (which may be used to wrap meat, cheese, or vegetables, or for food heating in the microwave), bags (which may be used for storing food in the freezers), and sheets (which may be used in contact with butter, cheese and milk) [19]. PTFE sprays for lubrication of doors, locks, bike chains, motorcycles, etc. [4]. A major use of FEP films is as a release film in vacuum bagging [3]. ETFE films are used in kitchens for lamination on stove tops and walls [3]. PFA polymers are used in coating resins for captive use on cookware (in combination with PTFE) [3].
Lubricants ⁹⁵		Typically, low-molecular-weight powders and dispersions are produced by chain scission (i.e., irradiation) of high-molecular-weight PTFE and some FEP. Among them, lubricants made from virgin PTFE are used in applications such as composites, coil coatings, paints, waxes, finishes, inks, greases, textile applications, mould releases, and rubber and plastics, including for mechanical joints and contact points in mechanisms, whereas lubricants from scrap PTFE are often used in printing inks [3]. (Micropowder) PTFE may also be used to thicken other lubricants based on, e.g., fluorosilicone oils and perfluoropolyethers (PFPEs), as well as used as a solid additive in non-PFAS-based low viscosity lubricants and greases and dry-film lubrication⁹⁶/external release agents [4]. The use of PTFE in engine oils is rather limited due to its inherent instability in oil, the risk of oil filter clogging, and difficulties with recycling [17].

⁹⁵ More details on the use of fluoropolymer-based lubricants in individual industrial sectors and applications can be found in Table A.59 of Baua et al. (2023). More detailed elaboration of individual categories of lubricants, and examples of lubricant products that contain fluoropolymers (Table 7), can be found in Danish EPA (2024).

⁹⁶ Examples of dry-film lubrication include glass cloth for automotive (bushings for car door hinges, trunk lids, seats and wipers), electronics (bushings for office machines), hydraulics (cylindrical bushings for hydraulic machinery), industrial machinery (thrust washers for conveyor belts), food processing (industrial, retail or quick service restaurants) and consumer uses (bike chain and waterproof zippers) (Baua et al., 2023).

	Lower-molecular-weight oils and greases based on PCTFE are used as inert sealants and lubricants in severely oxidative or corrosive environments [3], which can be thickened with silica, micropowder PTFE and/or high-molecular-weight PCTFE [4].
Machineries / mechanical applications ⁹⁷	Filled PTFE grades are used as machine bearings and in the fabrication of bushings, seals, bearing surfaces and piston rings in compressors and other industrial mechanical applications [3]. For heavy machinery, PTFE waxes are used to coat parts which need a high abrasion resistance (e.g., containers, excavators) [4]. ETFE copolymers are used in seal glands, pipe plugs, corrugated tubing, fasteners and pump vanes [3].
Medical products ⁹⁸	Fluoropolymers (such as PTFE) used in surgical patches, cardiovascular grafts, synthetic knee ligaments, jaw implants, raw materials for human body implants (such as catheters, stents, sutures, device surface coatings, needles, and other) given biocompatibility and extremely low coefficient of friction, dialysis membranes, anesthesia, packaging of operating tools, and machine components (O-rings, filters, tubing, and others) [1, 2, 3]. Fluoropolymers, especially PTFE, are applied in, e.g., sealant (tape or monofilament/cord) and in devices such as breathing air devices, medical ventilators and oxygen supply systems [4]. Fluoropolymers are also used in making rigid gas permeable contact lenses, together with other materials [4], and orthodontic wires for aligning teeth [22]. Fluoroelastomers allow for protein-resistant and sterile filters, tubings, O-rings, seals and gaskets for kidney dialysis machines and immune-diagnostic instruments [4]. Fluorinated ionomers are used in dry or humidified breath for anaesthesia and respiratory care as well as for biomedical inserts [22]. Porous membranes containing expanded PTFE (ePTFE) or PVDF are used as mesh material or patches, because they reduce adhesion, one of the possible complications in hernia reinforcement [4]. Catheter tubes are usually made of ePTFE because this provides a very smooth surface and minimizes the need to use force, but also FEP polymers are sometimes used [4]. PTFE materials are also used as internally lubricated thermoplastic compounds for medical devices such as drug delivery auto-injectors for diabetes and emergency anaphylaxis response, surgical tools for laparoscopic surgeries, and robotic surgical equipment [7]. PVDF materials are applied in connection devices for catheters, for instance with peritoneal catheters [4], and also used as coating for packaging and hoses and seals, as well as membranes in cochlear implants [4]. PFA or FEP copolymers are used to coat aluminum-metered dose inhalers to prevent interaction of the medical ingredient with the casing [4]. PTFE/PFA polymers are used as coating in guide wires, catheters, stone catchers, polypectomy snares, anti-adhesive coating, handles, speculums, and obturator bars, as well as used in multi-lumen catheter, high-purity transfer line, working channel in flexible endoscopes, seals, heat shrink tube, and insulation of wires, cables and complex electronic components [4]. PCTFE materials are used as connectors for kidney dialysis machines and fittings for syringes and blood analyzers [3]. UV sterilisation of medical devices may also be performed in the presence of PCTFE without concern for degradation [3]. PCTFE is also generally used in <i>in vitro</i> diagnostics

⁹⁷ Examples of Kalrez® perfluoroelastomer parts and Vespel® parts and shapes, including details on their uses in different industrial sectors and associated functionalities, can be found in EPPA (2023).

⁹⁸ More details on the use of fluoropolymers in specific medical products can be found in Tables A.99 and A.103 of Baua et al. (2023).

	(IVD) reagents and instruments [22]. ECTFE materials are used as coating in electrosurgery / monopolar and bipolar high-frequency surgery, biopsy forceps with high-frequency connection, coagulation probes, and papillotomes for use in high-frequency surgery [4]. ETFE materials are used in biomedical and labware equipment, including oxygen respirator components, blood analyser valves, evaporating dishes, and centrifuge tubes [22].
Nuclear industry	Lubricants used for valves and centrifugal bearings in enrichment processes [1]. PTFE materials are used as gasket materials in closed vessels in a nuclear power plant [4]. ETFE wires and cables are used in the nuclear power plant control room floor modules [3].
Oil and gas industry ⁹⁹	Fluoropolymers are used in the sector, including lining of gas pipes and insulation of cable and wire during drilling, in flexible risers and flowlines, liners in the high-pressure lines used in offshore choke and kill systems, seals used in downhole drilling operations, valve bodies, valve packing, valve seals, O-rings, pipe gaskets, in capacitive sensors and their connecting cables, ball valves, in fluid transfer equipment, flexible pipes, vibration dampers, packer elements, pneumatic actuators, pneumatic regulating devices, blow-out preventors, stators and “mud motors”, pump liners, packaging vents, dispensers, nozzles, compressors, subsea hydraulic couplers, and heat exchangers, and membranes for filtration [1, 4]. PVDF materials are used in oil extraction at offshore sites [3]. Fluoropolymers such as FEP and ETFE are used as sheathing materials for permanent downhole cables in the oil and gas industry [15]. Fluoroelastomers are widely used to produce components (e.g., seals, liners, valves, O-rings, gaskets and packer elements) [4].
Pharmaceutical industry ¹⁰⁰	Fluoropolymers (such as PTFE and PVDF) are used for reaction vessels, stirrers, and other components, filtration, and moisture barriers [1, 3]. PTFE materials are used in ophthalmic solutions packaging, acting as hydrophobic membrane to allow the venting of air while retaining fluid within the container and preventing leakage [4]. PFA/MFA copolymers are often used for lining large-capacity storage tanks and high-pressure processing vessels [3]. ECTFE materials are used in solid and lined pipelines, fittings, pump and valve components, fitting housings, components for wet-process stations and tanks and tank linings [3]. CTFE-VDF films are used as packaging for pharmaceutical products such as rigid and semirigid push-through blister packages, unit dosage packs and aseptic peel packs (e.g., as a temporary packaging material for newly developed pharmaceutical products until those products can be demonstrated to have an adequate shelf life using less-expensive packaging film) [3]. PCTFE materials are also used in blister packs for drugs that require oxygen-free storage, acting as an oxygen-barrier [3].

⁹⁹ More details on the use of individual fluoropolymer types in specific applications in the sector can be found in API (2023).

¹⁰⁰ Examples of the use of fluoropolymers in the pharmaceutical industry, including in chemical synthesis plants, bioprocessing facilities and aseptic processing, are illustrated in ISPE and EFPIA (n.d.).

		Nafion™ resins in the form of small polymer beads are used as non-electrochemical ion exchange materials in the chemical, pharmaceutical, and several other industries [16].
Photolithography semiconductor	&	Equipment raw materials (such as PFA) for moulded wafer baskets to handle corrosive liquids and gases [1, 3]. PVDF grades from suspension polymerisation are used in the sector in pipes/fittings and fibre for ultrapure water treatment [3]. PFA materials are extensively used for wafer carriers (boats, trays and baskets), pumps, pipe and fittings, filtration systems, and tubing [3]. Solid PFA pipes and tubes are used to transport high-purity chemicals (including deionized water) for use in the manufacture of semiconductors [3]. In semiconductor production, ECTFE materials are used as fire-safe plastic sheeting in clean rooms, powder coatings, and as a replacement for PVDF in sheet linings for ultrapure water systems [3].
Plastics and rubber		Fluoropolymers (such as PTFE, VDF-HFP—CASRN 9011-17-0) are used as processing aids, as a raw material in plastics (e.g., polyethylene, polypropylene, polyimides, polysulfones, polyphenylene sulfide resins, among others) and rubber production, and as an intermediate material. They are used in moulded material production to enable easy release and reduce imperfections, polymer processing aids [1, 3, 11]. According to stakeholders, the concentrations of fluoropolymer-based processing aids normally range between 500 and 1000 ppm [4, 11]. PTFE materials are used as an anti-drip additive in flame retardant polycarbonate resins used in thin-wall (thickness <1.0 mm) consumer electronics applications [6]. Since the 1960s, internally lubricated engineering thermoplastic compounds comprise a base thermoplastic polymer and a fully or partially fluorinated polymer such as PTFE (typically in the range of 5–20 weight%), which serves the purpose of providing lubrication in the final moulded part to reduce wear and friction between moving components [8]. Uncured FKM materials are used as a polymer processing additive or polymer extrusion aids in small amounts (50–2000 ppm) dispersed in polyolefins such as high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) [14]. Fluoropolymers with the comonomers TFE, 2,3,3,4,4,5,5-heptafluoro-1-pentene (CASRN 1547-26-8) and ethylene are intended to be used as polymeric processing agents at up to 0.2 weight% in a wide range of plastics [18].
Recreational and musical equipment		Stringed sports equipment (for example, tennis racquets) and stringed instruments; fishing rods and reels; lubricants; piano keys [1]. PVDF materials are used for monofilament such as fishing line and strings of musical instruments [3].
Textiles (upholstery, leather, and apparel)	carpets,	Fluoropolymers (such as PTFE) are used in the construction of outdoor gear, clothing, and housewares [1]. This includes breathable, membrane-lined drysuits used in water sports; water-resistant but breathable boots, socks, and gloves; medical applications such as surgical drapes and gowns; military gear such as overwater flight suits; chemical-proof clothing; and professional uniforms and protective clothing for outdoor work. They are also used in space suits and cleanroom garments [3]. ePTFE materials are used in some face masks, up to 1.9 weight% [4]. Fluoroelastomers are used in safety clothing and gloves [4]. For example, CTFE-VDF copolymers are used in fabric treatments (e.g., for protective clothing) [3].
Wood industry		Polymeric PFAS fabrics are used during the bleaching process and in the clear coating of wood substrates [1].

Miscellaneous	Fluoropolymers are used as corrosion inhibitor on steel. For this purpose, cationic and amphoteric fluorinated surfactants are used to impart a positive charge to fluoropolymer particles, which facilitates the electroplating of the fluoropolymer [4]. Fluoropolymer fibres are used as liquid or gas solid filtration separation, including in the flue gas filtration at thermal power plants, waste incineration plants, cement plants, non-ferrous metal metallurgy plants, and in the filtration and purification of strong acid/alkali liquid or chemical solvents in the chemical industry, pharmaceutical industry and semiconductor industry [13]. Granular PTFE grades are used in making laboratory apparatus [3]. Fine powder PTFE grades are used for incinerator filter bags to capture dioxin generated at incinerators [3]. ePTFE membranes are laminated to a wide variety of substrates such as polyester needle felts and woven glass fibre to be made into filter bags, and pleatable materials such as polyester and cellulose for filter cartridges and elements [4]. PTFE materials are also used in internally lubricated thermoplastic compounds for drinking water and water management applications such as water meter impellers, water meter housings, faucet components, water purification components, and impellers for industrial and household pumps (e.g. for pool and spa, drainage and irrigation, fish tanks and ponds, caravan and RV/camper, coffee machines, and faucets and shower heads) [8]. PTFE materials are used as a geomembrane (lining material) in pits used for landfilling to prevent contamination of groundwater through leachates emitted from hazardous waste [12]. FEP materials are used to make heat-shrinkable roll coverings for use in industries such as paper manufacturing, chemical processing, textile manufacturing, food processing, and packaging, to make tubing used in government water sampling programs, and to make monofilament [3]. PVDF materials are used in anticorrosion coatings and linings for items such as tanks, vessels, pumps, heat exchangers, pipeline valves and fittings, laboratory materials, instrumentation and medical accessories, as well as in extruded film, filter cloth (also known as “screen” for paper manufacturing), tower packaging, monofilament, mist eliminators, and nozzles [3]. PVDF materials are also used in water treatment membranes [3].
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Note: Some uses described in one category may also be listed under other specific industrial sectors or applications in this table; such duplications have not been removed.

Source: [1] US ITRC (2023), [2] Wood (2022), [3] Kálin et al. (2012), [4] Baua et al. (2023), [5] SABIC (2023a), [6] SABIC (2023b), [7] SABIC (2023c), [8] SABIC (2023d), [9] BAJ (2023), [10] GICAT (2023), [11] FPE (2023), [12] Tippet and Goard (2023), [13] Changzhou XCF and Xingchen (2023), [14] Korzeniowski et al. (2023), [15] Chemours (2023a), [16] RPA (2023b), [17] JRC (2016), [18] EFSA CEF Panel (2016), [19] EFSA CEF Panel (2012), [20] Cosmetic Ingredient Review (2018), [21] Jones et al. (1991), [22] FPS Economy and FPS Public Health (2023).

Historical and ongoing Production and Use Volumes

Information in the public domain regarding production and use volumes is scattered, and generally at a high level.¹⁰¹ The latest global and regional volumes are summarized here, with supporting data available in Annex E. Additionally, interested readers may find more detailed production volumes of PTFE, FEP, PFA, and PVDF from between the late 1940s and 2012, broken down on an annual and regional/national basis, in the *Supplementary Material* of Wang et al. (2014a).

On a global scale, the consumption of fluoroplastics (both homopolymers and copolymers) was about 216 kt in 2012 (Dams and Hintzer, 2017), increasing in 2018 to ca. 320 kt, reaching 68.4% of the total global production capacities.¹⁰² The proportion of fluoropolymer types consumed include 53% PTFE, 16% PVDF, 10% FEP, 1% PFA, 1% ETFE and 17% of others; and with a geographical distribution, ca. 37.5% in China (120.1 kt), 21.5% in the US, 15.9% in Western Europe, 5.7% in Japan, and 19.4% in other parts of the world (Plastics Insight, 2019). Detailed estimates of the fluoroplastic consumption in the EU in 2015 and 2020 can be found in Tables A E.2 and A E.3 in Annex E.

Focusing on PTFE consumption in 2018, China purchased the most, 40.5%, followed by Western Europe (19.7%), the United States (15.9%), Japan (5.3%) and others (18.6%) (Plastics Insight, 2019). In Western Europe, Germany, with its strong automotive and chemical industries, and Italy, with its domestic appliance and compounding industries, were the largest consumers of PTFE (37% and 28% respectively of total consumption) (Plastics Insight, 2019). The largest demand in Western Europe, broken down by industry, came from the chemical process technology (41%), followed by the mechanical and plant engineering (19%), the electrical/electronics industry (16%) and the automotive industry (9%) (Plastics Insight, 2019).

In 2018, China was also the largest consumer of PVDF (24.3 kt), ahead of the United States (12.4 kt) and Western Europe (10.8 kt) (Plastics Insight, 2019). The most important drivers for further market development are architectural coatings (especially in China) and new applications such as lithium-ion batteries, photovoltaic modules, water filtration systems and special films for architectural and automotive glazing (Plastics Insight, 2019).

In 2022, while the total consumption volumes were not identified, it is noted that the market share of PTFE to the total consumption decreased to about 45% (in comparison to 53% in 2018), whereas the market share of PVDF and FEP increased to about 22% and 12% (in comparison to 16% and 10%), respectively (S&P, 2022a). In addition, China remains the dominant consumer of fluoroplastics in the world, representing 37% of PTFE consumption and nearly 48% of other fluoroplastics consumption in 2022 (S&P, 2022a).

Data on the production and use volumes of fluoroelastomers remain limited. Globally, consumption was at about 15 kt in 2001 (ECETOC, 2005b), rising to about 20 kt in 2009 (Dams and Hintzer, 2017), about 24 kt in 2014 (Drobny, 2016) and >38 kt in recent years (IHS Markit, 2020). FKMs dominate the market, accounting for over 90%, followed by fluorosilicone elastomers (ca. 8%)¹⁰³ and FFKM (ca. 1%) (IHS, 2020). China has the largest production capacity (ca. 27 kt per year), followed by Western Europe, the United States and Japan.

¹⁰¹ Multiple market research reports are available to offer such data commercially. However, due to the high price of such reports, these sources could not be considered here.

¹⁰² The distribution of the production capacities in 2018: Asahi/AGC 4%, Arkema 7%, Chemours 12%, Daikin 11%, 3M/Dyneon 5%, Shandong Dongyue Group 13%, Solvay 8%, others 40% (Plastics Insight, 2019)

¹⁰³ This specific type of elastomers is captured in the previous *Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle*; see Chapter 5 in OECD (2022).

In 2018, approximately 64% of FKM was used in the automotive industry, 11% used in the chemical and oil and gas industries, and 9% in aerospace (IHS Markit, 2020). The global fluoroelastomers market has been driven largely by China's rapid automotive industry growth over the past decade (S&P, 2022b). Future market growth is expected to be driven by new product developments in sealing applications (better performance), further tightening of emissions standards in many of the industrialized countries, and the expansion and resurgence in automobile production (S&P, 2022b).

In the EU, approximately 8,900 tonnes of fluoroelastomers are produced annually (Daikin, 2020). The automotive sector accounts for about 70% of their use, driven by stricter environmental regulations and the need for high-performance engines. Another 20% is used in the chemical industry, primarily for seals and O-rings that ensure safe containment of hazardous and corrosive chemicals. Additionally, fluoroelastomer seals and O-rings are used in machinery (7%) and industries using valves, such as oil and gas, pharmaceuticals, semiconductors, and aerospace (3%). These materials are used in high-temperature environments (150°C or higher) or applications involving direct contact with corrosive fluids.

End-of-life treatment

End-of-life treatment for fluoropolymers can be categorized into two main areas: the treatment of post-processing fluoropolymer scraps and the management of post-use (or post-consumer) products containing fluoropolymers.

Post-Processing Fluoropolymer Scraps

A significant portion of fluoropolymer production results in scrap materials, such as PTFE shavings and chips, which constitute approximately 10–30% of total PTFE production (Kálin et al., 2012; PBL and TNO, 2021). Similarly, PFA processing can lead to the generation of up to 30% waste (Améduri and Hori, 2023). Most clean and unfilled scraps from machining processes are either returned or sold for recycling. Limited data are available for individual regions. For example, in the EU (Conversio, 2022), fluoropolymer product manufacturers have process loss of around 20% (roughly 8 kt in 2020). About 20–25% of fluoropolymer manufacturers have internal recycling processes for these losses, while 30–35% send their waste to external recycling companies. Around 15% export their waste to other EU companies, and 5–10% outside the EU, primarily to Asia. Approximately 15% of fluoropolymer processing losses are not recycled and are instead incinerated as hazardous waste (Conversio, 2022).

For melt-processable fluoropolymer scraps, recycling typically involves collection, grinding, and reintegration into the manufacturing cycle, similar to the mechanical recycling of conventional plastics. When properly collected, cleaned, and processed, these recycled materials can be used in high-end applications (ETC/WMGE, 2021; Korzeniowski et al., 2023). Due to its ability to be processed and reused for up to five times, it is reported to be common that up to 20% reprocessed PVDF is used in the production of injection-moulded and extruded products (Améduri and Hori, 2023). Companies in the United States and Europe have successfully implemented PVDF recycling, with at least one major fluoropolymer manufacturer introducing a range of PVDF products based on recycled materials (ETC/WMGE, 2021). Similarly, despite observing a decrease in viscosity and yellowing of the samples, likely due to degradation of the polymer chains, the addition of up to 10 weight% recycled PFA was found to be an effective approach for reusing PFA residues through mechanical recycling (Améduri and Hori, 2023).

For PTFE, various treatment techniques exist. Production scraps can be ground into fine powder and reprocessed through compression moulding or ram extrusion. Prior to grinding, the scrap is shredded and heated to eliminate volatile contaminants. The ground powder is then treated with acids to dissolve inorganic substances and subsequently washed (ETC/WMGE, 2021). Recycled PTFE materials, also known as reprocessed or mechanical grade PTFE, have different structures than virgin PTFE

(ETC/WMGE, 2021; Chemours, 2023b). They are often blended with virgin PTFE for cost-driven applications where high purity is not required, such as in rods, tubing, and tapes in non-critical chemical, electrical and mechanical applications (ETC/WMGE, 2021; Chemours, 2023b).

Another approach involves irradiation degradation or thermal degradation at approximately 500°C, reducing the molecular chain length to about 1% of its original state. This process produces micropowder PTFE, as described in the polymerisation section above, which can be used in specific applications (ETC/WMGE, 2021; PBL and TNO, 2021; Korzeniowski et al., 2023; Chemours, 2023b; Danish EPA, 2024). In 2010, the global market for micropowder PTFE made from irradiation alone was estimated to be approximately 7 000–10 000 tonnes per year (Danish EPA, 2024).

For these aforementioned recycling schemes, treatments can be undertaken onsite by the manufacturers of fluoropolymers themselves, or at a larger scale by specialist recycling companies (Korzeniowski et al., 2023). The presence of fillers, colorants, and other materials in the composition of the final products can be a limiting factor (Korzeniowski et al., 2023).

Furthermore, chemical recycling of several fluoropolymers has been developed. Fluoropolymers are ground and decomposed into their monomers at temperatures exceeding 600°C via pyrolysis. The recovered monomers, such as TFE, are purified and reused for manufacturing new fluoropolymers (Korzeniowski et al., 2023). In 2015, 3M/Dyneon commissioned the world's first fluorinated polymer chemical recycling pilot facility in Germany, capable of treating 500 tonnes of PTFE, PFA and/or FEP waste per year (ETC/WMGE, 2021; Korzeniowski et al., 2023).¹⁰⁴ This process has a reported recovery rate of 90–95% for monomers such as TFE and HFP (ETC/WMGE, 2021; Korzeniowski et al., 2023), with substantial savings in raw material consumption and CO₂ emissions (Dams and Hintzer, 2017). As it was announced that 3M will exit all PFAS manufacturing by the end of 2025, the commercial feasibility of chemical recycling of fluoropolymers should be further investigated.

Post-Use Fluoropolymer Product Waste

As is true for all complex, multi-material products, recycling post-use fluoropolymer products is challenging due to their integration into complex, multi-material products. Also, fluoropolymers are commonly found in coatings, fabrics, mechanical components, and other embedded applications, making separation difficult (Korzeniowski et al., 2023). In addition, the overall share of fluoropolymers is too low to establish any sorting and recycling approach (Conversio, 2022). The presence of fillers, colorants, and other additives further complicates recycling efforts (Korzeniowski et al., 2023).

In some cases, low-temperature heating methods are used to remove fluoropolymer coatings from metal surfaces or lithium-ion batteries for metal recovery. However, studies have not confirmed whether these processes effectively capture volatile emissions, including PFASs (ETC/WMGE, 2021).

Hence, the majority of end-of-life fluoropolymers are either landfilled, incinerated¹⁰⁵, or processed in blast furnaces for energy recovery. Limited data are available for a comprehensive global picture. As an example, data from the EU indicate that approximately 23.5 kt of fluoropolymer waste was collected in 2020, primarily through mixed waste streams or partially source-separated fractions. Around 84% of fluoropolymer waste was incinerated, either for energy recovery (72%) or as part of metal recycling processes (12%). Roughly 13% was landfilled, while only 3% was recycled through electronic waste collection or industrial reprocessing (Conversio, 2022).

¹⁰⁴ Initial discussions related to this pilot plant can be traced back to as early as 1998 (Simon and Kaminsky, 1998).

¹⁰⁵ Standard incinerators have limitations on the quantity of fluoropolymers they can process due to the formation of highly corrosive hydrofluoric acid during combustion (Hintzer and Schwertfeger, 2014).

4

Presence of other PFASs in commercial products¹⁰⁶

Chapter summary:

This chapter provides an in-depth analysis of the introduction and persistence of other PFASs in fluoropolymer products throughout their life cycle, from synthesis to end-of-life treatment. Impurities can originate from several sources, including unreacted starting materials, impurities within these materials, reaction intermediates, byproducts and degradation products. These PFAS impurities are highly persistent and can remain in products or be released during various life-cycle stages, posing potential environmental and health risks. However, comprehensive data on which specific PFASs are present in commercial products and their levels remain scarce, hindering a full understanding of, and ability to assess, their impacts, noting that an industrial transition is underway, partly driven by regulations.

- **Monomer Synthesis:** During this life-cycle stage, byproducts may remain as trace impurities, carried over into the polymerisation process. However, the exact conditions under which these impurities form and their concentrations are not well understood.
- **Polymerisation:** PFASs can be introduced as unreacted co-monomers, impurities, intermediates, or byproducts (e.g., oligomers). Both fluorinated and non-fluorinated polymerisation aids can introduce PFASs into fluoropolymer products. Fluorinated aids such as PFOA are highly stable and can persist in the final product, with some products (such as PTFE emulsions) containing high levels of residual low-molecular-weight PFASs. Non-fluorinated polymerisation aids can also lead to the formation of PFAS byproducts, such as polyfluorinated residuals, through reactions with fluorocarbon radicals during polymerisation.
- **Other Ingredients and Byproducts:** Some fluoropolymer formulations include other fluorinated ingredients, such as PFPEs, or undergo high-temperature processes that may result in degradation products such as PFIB. These degradation products, including perfluorinated acids, can accumulate in stored products, posing risks if ventilation is inadequate.
- **End-of-Life treatment:** During irradiation or thermal decomposition of PTFE to produce micropowders, PFAS degradation products such as PFHxA and PFOA can be generated. The presence of both short- and long-chain PFCAs (perfluoroalkyl carboxylic acids) in PTFE micropowder has been noted, with specific PFCAs detected at varying concentrations.
- **Unidentified Origins:** Some PFAS contamination, such as the presence of PFHxA in ETFE manufacturing, remains unexplained, pointing to potential unknown sources of PFASs in fluoropolymer production.

There is a need for further research to identify and mitigate PFAS contamination throughout the fluoropolymer life cycle. This includes better understanding the specific types and quantities of PFASs introduced at each stage and the impacts of these substances. Enhanced monitoring and stricter process controls are necessary to minimize PFAS contamination, especially during polymerisation, processing, and at the end-of-life treatment.

¹⁰⁶ Subject to the specific context, commercial products may refer to polymers produced by primary manufacturers of fluoropolymers (e.g., granular resin, fine powder resin, aqueous dispersions), compounded fluoropolymers for subsequent processing, or articles containing fluoropolymers. For the sake of simplicity, they are all referred to as “commercial products” in this report.

Similar to other polymers such as side-chain fluorinated polymers and PFPEs (OECD, 2022, 2024), impurities might be introduced into commercial formulations and products from a number of different origins, including (1) unreacted starting materials used in the synthesis, (2) impurities from the starting materials, (3) reaction intermediates and byproducts, and (4) degradation products of the unreacted starting materials, reaction intermediates, byproducts, and fluoropolymers themselves. Existing information shows evidence of the presence of other PFASs from (some of) these origins, while also noting that an industrial transition is underway driven in part by current and anticipated regulations such as those under the Stockholm Convention on Persistent Organic Pollutants¹⁰⁷ and the EU REACH regulation. However, a comprehensive overview of which other PFASs may be present in different commercial formulations and at what levels remains generally missing. In addition, no established testing protocols exist to generate such an overview, hampering a comprehensive understanding of the environmental releases and degradation pathways of such PFASs.

Nevertheless, the following sub-sections examine existing evidence on the introduction of other PFASs at each key life cycle stage into fluoropolymer products from different (potential) origins and their fate in the subsequent life-cycle stages (if available). Furthermore, PFASs are inherently highly persistent, either in their original form or through transformation into other persistent PFAS compounds. Once introduced into a product, they may partially remain within it, while a portion is released over time, unless removed and safely disposed of, depending on their specific properties and the conditions of the processes involved. Therefore, reported environmental releases may provide additional information on potential PFASs that may be present in fluoropolymer products; the releases are elaborated in detail in Chapter 6. Supporting information on studies detecting individual PFASs in commercial fluoropolymer products can be found in Table S4 in the separate supporting material file.

Introduced during monomer synthesis

As stated above, during the synthesis of TFE, various byproducts—such as HFP, PFIB, c-C4F8, and several CFCs—may be generated. Most of these byproducts are removed through distillation; however, trace impurities (1–10 ppm) may persist in TFE and carry over into subsequent life-cycle stages such as polymerisation (ECETOC, 2003). This could potentially explain the presence of PFIB and HFP in the finished products (SPI, 2005). However, the same document noted that the conditions under which these compounds form, and in what quantities, had not yet been investigated.

Similarly, an analysis of another comonomer, 2,3,3,4,4,5,5-heptafluoro-1-pentene (CASRN 1547-26-8), identified 17 impurities, 12 of which remain unknown. Among the five identified impurities, two were structurally related alkenes, while the remaining three were structurally similar but saturated compounds (EFSA CEF Panel, 2016). According to EFSA CEF Panel (2016), these alkenes are expected to be incorporated into the copolymer chain, while the non-reactive impurities—both identified and unidentified—are expected to volatilize under (polymerisation) processing conditions.

No further information was identified during the preparation of this report. Consequently, the precise identities of impurities in these monomers and others and their fate during later life-cycle stages such as polymerisation and processing—including how newer technologies have impacted their formation and fate—remain uncertain, underscoring the need for further research.

¹⁰⁷ The list of new POPs, including many PFASs, can be found at: <https://www.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx>

Introduced during polymerisation

At this life-cycle stage, a wide range of substances may be introduced, including (co)monomers, fluorinated and non-fluorinated polymerisation aids (see Figure 3 and Table 4), and other ingredients—some of which may be PFASs (see Table 3). Consequently, PFASs may be introduced and remain in the polymers, as unreacted starting materials, impurities from the starting materials, reaction intermediates and byproducts (e.g., oligomers), and degradation products of these substances. The following sub-sections provide an overview of these different origins, along with relevant examples.

Unreacted co-monomers and their impurities

Existing evidence supports that during polymerisation, some (co)monomers remain unreacted and can be present in fluoropolymers. While most unreacted monomers are released or removed during drying and high-temperature processing such as shaping and sintering, trace amounts—often below detectable levels—may remain in the final products,¹⁰⁸ although the frequency of such occurrences remains unclear. For example, less than 1 ppm of unreacted monomer has been reported in VDF-based polymers (ECETOC, 2005b), while low levels of unreacted HFP have been detected in HFP-based polymers (ECETOC, 2003a). Specifically, two solid FKM products were found to contain 3 ppm of HFP (Korzeniowski et al., 2023).

Additionally, the residual level of PFBE (a comonomer used in the production of some PTFE and ETFE) was measured in both an unsintered PTFE powder and a sintered finished tape material. Detected levels were 31 µg/kg in the polymer powder and below the detection limit of 5 µg/kg in the finished material. This suggests that the polymerisation process results in only low residual levels of PFBE, which are further reduced to non-detectable levels during sintering due to its high volatility (EFSA CEF Panel, 2011a; Environment Agency, 2023c).

There are limited data on the global presence of unreacted (co)monomers in fluoropolymer products. In the EU, the quantity of unreacted PPVE in fluoropolymer products is estimated to be below 100 kg per year, based on concentration data provided by the manufacturer and the maximum theoretical supply level corresponding to the current REACH-registered tonnage band of 999 tonnes per year (Environment Agency, 2023b). Similarly, one manufacturer estimated that the total quantity of PFBE present in ETFE products supplied to all customers globally would be less than 0.5 kg per year, based on a mass balance calculation and extrapolation from estimated process solvent levels in the final polymer (Environment Agency, 2023c). As mentioned earlier, the fate of impurities within (co)monomers during polymerisation and processing remains poorly understood.

Regardless of their exact origins, SPI (2005) noted that trace amounts of residual gases such as PFIB, HFP, and TFE may be present in fluoropolymer resins and finished products and be gradually released¹⁰⁹. In unventilated spaces—such as closed storage rooms or trucks—these gases can accumulate to potentially hazardous levels, particularly when large quantities of fluoropolymer materials and products are

¹⁰⁸ Henry et al. (2018) and Korzeniowski et al. (2023) analysed the levels of unreacted (co)monomers in a commercial solid PTFE product, as well as in specific commercial solid products of ten types of fluoroplastics, including PVDF, VDF-HFP copolymer, ECTFE, an ECTFE terpolymer, PCTFE, FEVE, EFEP, CPT, THV, and a perfluoro(alkenyl vinyl) ether polymer (CASRN 37626-13-4). Additionally, they examined three commercial fluoroelastomer (FEP, FKM, and FFKM) products and a commercial fluorinated ionomer product. Their findings indicated no detectable residual monomers in any of these products, except for 3 ppm of HFP found in two solid FKM products (Korzeniowski et al., 2023).

¹⁰⁹ As a separate note, in the context of food contact materials, the EU has set specific migration limits for the following (co)monomers and their impurities (EC, 2023): HCFC-22 (6 mg/kg food; FCM No. 134), CTFE (ND; FCM No. 148), TFE (0.05 mg/kg food; FCM No. 281), HFP (ND; FCM No. 282), PMVE (0.05 mg/kg food; FCM No. 391), PPVE (0.05 mg/kg food; FCM No. 423), and (perfluorobutyl)ethylene (CASRN 19430-93-4; permitted only as a co-monomer up to 0.1 weight% in the polymerisation of fluoropolymers sintered at high temperatures; FCM No. 973).

stored. As a precaution, proper ventilation of these areas is recommended before personnel entry and safe handling practices should be followed (Fluoropolymers Product Group of Plastics Europe, 2025).

Polymerisation aids, along with their degradation products, impurities, and related byproducts

Polymerisation aids can be categorized into fluorinated and non-fluorinated types, each affecting the PFASs present in fluoropolymer products through different mechanisms.

Legacy fluorinated polymerisation aids based on PFOA and PFNA are highly stable and remain intact during polymerisation. Their fate in fluoropolymers depends on how the fluoropolymers are subsequently recovered and processed. This is in line with existing evidence of residual PFOA in commercial products. Major manufacturers reported the substantial decrease of PFOA in their dispersion products over time, due to extra treatment, replacement of PFOA with alternative polymerisation aids, or a combination of both (for supporting data, see Annex F).

After polymerisation, granular and fine powder products are recovered and dried, during which most of the PFOA polymerisation aids are washed out and volatilized as exhaust gases (Paustenbach et al., 2007; Henry et al., 2018), though a small amount may remain in the products. Several early industry studies measured trace levels of PFOA in granular and fine powder products, typically on the order of 1–10 ppm (Pinchot, 2004; Cope, 2004, 2005), while a study from 1979 reported a higher level of PFOA (94 ppm) in a Hostaflon™ TF 2026 granular resin product (Cavanaugh, 1985). It is likely that the levels in granular and fine powder products have been further reduced, at least in many parts of the world, due to additional treatment methods, as described in more detail below.

Commercial fluoropolymer products may also be available in dispersion/emulsion forms. Dispersion products of PTFE, for example, contain a rather large amount of PFOA residuals, ranging from 400 ppm up to 7000 ppm, with typical levels below 2000 ppm (Baar et al., 2005). In addition, 100–200 ppm of APFN was estimated to remain in some PVDF dispersion products as residuals (Prevedouros et al., 2006). More recently, a study showed a similar level of PFOA (1100 ppm) in a PTFE emulsion and of HFPO-TrA (trimer homologue of HFPO-DA; 830 ppm) in another PTFE emulsion from China (Meng et al., 2021), although a comprehensive picture of residual levels across products and regions remains unclear.

PFAS polymerisation aids in dispersions may be partially removed during some processes (e.g., up-concentration) and stabilisation with nonionic, nonfluorinated emulsifiers. However, these steps cannot completely remove the PFAS polymerisation aids, even if applied multiple times (Hintzer and Schwertfeger, 2014). To fully remove these PFAS polymerisation aids, the stabilized fluoropolymer dispersion needs to be treated with a strong basic anion exchanger, such as Amberlite™ IRA 402, in an anion exchange process (Hintzer and Schwertfeger, 2014). However, the extent to which this additional cleaning process is applied to commercial fluoropolymers remains unclear.

As mentioned in Chapter 3, granular, fine powder or aqueous dispersion fluoropolymers products may undergo further processing at high temperatures, such as shaping and/or sintering, to produce the final products. During these processes, most of the PFAS polymerisation aids may be released or removed, leaving only trace amounts remaining in products. This is supported by the findings that trace levels of PFOA, in the range of a few ppm or less, have been detected in a number of fluoropolymer articles from China (Meng et al., 2021, 2024). Even lower levels can be achieved, driven by regulatory requirements. For example, in the EU, the POPs Regulation¹¹⁰ sets the unintentional trace contaminant (UTC) limit at 25 ppb for PFOA and 1 ppm for PFOA-related substances.

The fate of fluorinated replacements to PFOA is more complex. These replacements can be divided into two categories: PFHxA and its 6:2 fluorotelomer precursors, and perfluoroalkylether carboxylic acids

¹¹⁰ Regulation (EU) 2019/1021, <http://data.europa.eu/eli/reg/2019/1021/2024-10-17>

(PFECAs). While the insertion of ether linkage (–O–) in the fluorinated carbons has no impacts on the persistence under natural conditions (Wang Z. et al., 2015), it does make PFECAs more susceptible to degradation during high-temperature processing (see Table A D.1 in Annex D). These two categories are separately discussed below.

PFHxA is as stable as PFOA throughout the polymerisation and processing processes, while its precursors may degrade into PFHxA. Therefore, the fate of PFHxA and its precursors during polymerisation and processing is likely similar to that of PFOA. However, PFHxA may be present in higher concentrations in products compared to PFOA (which may also be the same for the levels of releases during polymerisation and processing). During the public consultations of the PFHxA restriction proposal in the EU, two manufacturers who use PFHxA or its precursors as polymerisation aids indicated that achieving the proposed 150 ppm threshold in their fluoropolymer products was not feasible (AGC, 2020a, 2020b; Daikin, 2020). One manufacturer has measured PFHxA levels in their products, but this information has been claimed confidential. In a recent study conducted in the United States watch bands marketed as containing fluoroelastomers were tested, and PFHxA was the most frequently detected compound (found in 41% of the 22 watch bands tested), with a median concentration of about 0.8 ppm and a maximum of approximately 17 ppm (Wicks et al., 2025).

For PFECAs and their replacements, it is important to note that several of these compounds may degrade at temperatures higher than the polymerisation conditions but lower than the processing conditions, resulting in volatile transformation products, such as decarboxylated substances (see Table A D.1 in Annex D). Therefore, these replacements are expected to remain stable during polymerisation. After the polymerisation process, a portion of these compounds will be released or removed, while some will remain in the granular, fine powder, or aqueous dispersion products, with the levels depending on the desired physical form of the product. Following processing, depending on their degradation temperature, either the replacements themselves, or their degradation products, may be partially released or removed, while some may persist in the final products.

For example, 3.3 ppm of ADONA was detected in an unsintered fluoropolymer micropowder (EFSA CEF Panel, 2011b), while 0.4 ppm of TFEE5 and its longer-chain homologue was found in a product processed at 300°C for approximately 10 minutes—below its decomposition temperature, which starts at 370°C (EFSA CEF Panel, 2012). In contrast, decarboxylated products of Krytox™ 157FSH and C₇HF₁₃O₄.H₃N were detected in several baking trays and one coating, but no or only limited parent acids were present (Wolf et al., 2024).

Impurities in PFAS polymerisation aids generally include homologues (Wang et al., 2014a; EFSA CEF Panel, 2012), such as PFCA homologues including ultra-short-chain ones in PFOA, as well as other side products (EFSA CEF Panel, 2014). These homologues are expected to follow a similar fate during polymerisation and processing as the primary compound, and thus may be present in fluoropolymer products, albeit at lower levels than the primary compounds, as demonstrated in several recent studies (Meng et al., 2021, 2024; Joudan et al., 2024; Wicks et al., 2025). However, for other types of impurities, limited to no information is found regarding their chemical identities, making it challenging to determine their fate during polymerisation and processing.

Non-fluorinated polymerisation aids have been introduced to the market. They address the direct introduction of other PFASs into fluoropolymer products, as elaborated above. However, recent studies indicate that during polymerisation, non-fluorinated polymerisation aids may react with fluorocarbon radicals, leading to formation of PFAS byproducts. For example, Sworen et al. (2024) reported the presence of multiple homologous series of polyfluorinated residuals in a PTFE dispersion using dioctyl sodium sulfosuccinate (DOSS) as a polymerisation aid. These residuals were formed through the addition of TFE to DOSS, resulting in compounds such as DOSS–C₈H₁₆ + –(CF₂)_n– and DOSS–2H + –(CF₂)_n–. The total concentration of these fluorinated byproducts was found to be approximately 100 ppm. The authors also investigated potential mechanisms underlying the formation of these byproducts.

One overall key lesson learned is the importance of complementing targeted analytical methods with non-targeted analytical approaches to comprehensively assess process chemistries. This includes, but is not limited to, consideration of processes involving non-fluorinated polymerisation aids, as well as the formation and fate of various impurities, such as fluorinated byproducts, as emphasized by Sworen et al. (2024). More importantly, all impurities should be reduced to insignificant levels, both in terms of their release into the environment and their presence in final products (Ameduri et al., 2023).

Other fluorinated ingredients and associated substances

Limited relevant information was identified during the preparation of this report, highlighting a potential need for further research in this area.

As noted, some PTFE products are supplied as dispersions, with Vydax™ used as a dispersion of solid PTFE in CFC-113, which was then replaced by IPA and water due to concerns over CFCs (Grenfell, 1999). Additionally, during ETFE production using 1H-PFHx as a solvent, 1H-PFHx is recovered and distilled for reuse, though small amounts may remain as impurities in final products or be released to wastewater and air during processing. Based on mass balance estimates, it is estimated that less than 0.1 tonnes of 1H-PFHx are present annually in fluoropolymer products supplied by one manufacturer to customers (Environment Agency, 2023a).

Reaction byproducts including oligomers

Oligomers are inherent intermediates in the polymerisation process. For example, Sworen et al. (2024) detailed the formation mechanisms of multiple homologue series of oligomers in a PTFE dispersion, including $\text{H}(\text{CF}_2)_n\text{COOH}$, $\text{HOOC}(\text{CF}_2)_n\text{COOH}$, $\text{CH}_3(\text{CF}_2)_n\text{COOH}$, and $\text{H}(\text{CF}_2)_n\text{SO}_3\text{H}$, which were collectively present at approximately 60 ppm. This dispersion was produced using DOSS as a polymerisation aid and a redox initiation system based on t-butyl hydroperoxide (TBHP) and ascorbic acid. The study also explored the formation pathways of oligomers when persulfate was used as an alternative initiator (Sworen et al., 2024). At present, a comprehensive understanding of the presence and variability of oligomers across different types of fluoropolymers, produced using various methods, remains lacking.

While they cannot be entirely eliminated, their presence can be reduced by adjusting reaction ingredients and conditions. Following polymerisation, oligomers may partially remain in the final products, while some are released during post-polymerisation processing.

For example, using solid-state NMR, Harris et al. (n.d.) detected weak signals indicating impurities that contain $-\text{CH}_2\text{CF}_2\text{H}$ end groups in PVDF samples. Similarly, EFSA CEF Panel (2016) reported an oligomeric fraction below 1 500 Da at 27 ppm of in a representative fluoropolymer sample composed of TFE, heptafluoropentene and ethylene after grinding and a four-hour extraction using isooctane.

In contrast, Korzeniowski et al. (2023) noted no detectable level of low-molecular-weight components (<1000 Da) in specific commercial solid products of ten types of fluoroplastics, three types of fluoroelastomers (FEP, FKM, and FFKM), and one type of fluorinated ionomer. However, this absence can be attributed to post-polymerisation processing steps that remove water-soluble residuals and drive off volatile compounds (Henry et al., 2018). For example, a series of nine polyfluorinated carboxylic acids, each differing by a $-\text{CF}_2\text{CH}_2-$ unit, was identified downstream of manufacturing facilities near Decatur, Alabama, US, where PVDF $[-(\text{CF}_2\text{CH}_2)_n-]$ is produced (Newton et al., 2017).

Therefore, future studies are warranted to measure oligomer levels and other potential byproducts in aqueous dispersion products and in the environment close to polymerisation and processing facilities.

Unknown origins

Limited information was identified during the preparation of this report. A report indicated that ETFE manufacturing can result in the presence of PFHxA as a residual contaminant, with a maximum working concentration of 0.4 ppm as reported by one respondent during stakeholder engagement (Danish EPA, 2024). However, the source of this contamination was not identified.

Introduced during processing

The introduction of other PFASs into fluoropolymer products can occur both intentionally and unintentionally. For example, in some commercial fluoropolymer products, other PFASs are deliberately added as active ingredients. For example, a discontinued product Fomblin™ Grease RT 15¹¹¹ is a mixture of PTFE and some PFPEs (CASRN 69991-67-9). Similarly, Polyflon™ TC-7409BK is composed of PTFE and another unidentified fluoropolymer (see Table 1). Additionally, lubricating greases containing PTFE can be prepared using a fluorinated surfactant as a dispersant, ensuring equal distribution of PTFE within the grease matrix (AGC, 2020b).

In contrast, processing,¹¹² particularly those high-temperature ones such as melt extrusion, inevitably leads to some degree of polymer degradation and thus, unintentional introduction of other PFASs into the products (SPI, 2005, 2019). For example, during the processing of FEP, heat-induced degradation results in lower-molecular-weight polymers, as well as formation of PFIB and other reactive byproducts (SPI, 2005, 2019). PFIB may be trapped in the molten polymer and gradually be released, which may pose a hazard if substantial quantities of coated wires are stored in poorly ventilated areas (SPI, 2005, 2019). Moreover, some processing techniques require even higher temperatures than those typically recommended in Table 5 (e.g., certain nonstick coating processes for fluoropolymer dispersions), to achieve certain technical effects (SPI, 2005, 2019). Because the formation of hazardous degradation products is accelerated under such conditions, necessitating strict process control measures to mitigate releases and associated risks (SPI, 2005, 2019). For more detailed information on degradation and degradation products during processing and relevant treatment, please refer to Chapter 5.

Currently, a comprehensive understanding of the presence and variability of other PFASs introduced during different processing steps are lacking.

Introduced during use

At this stage of the life cycle, additional PFASs are primarily introduced as degradation products of fluoropolymers and other PFASs present in the products, as detailed in Chapter 5.

Introduced during end-of-life treatment / PTFE micropowders

This section focuses on the introduction of additional PFASs into secondary micropowder PTFE. As noted in Chapter 3, such micropowder is typically produced through the degradation of PTFE via irradiation or thermal decomposition at approximately 500°C. Both processes generate fluorocarbon radicals, which can react with oxygen to form per- and polyfluorinated acyl fluorides (Wolf et al., 2024). As a result, upon contact with water or water vapor, both treatment processes can generate a variety of PFAS acids,

¹¹¹ According to a response received during the preparation of this report, this grade has been obsolete since 2015.

¹¹² Information on the end-of-life treatment to produce PTFE micropowders is provided in Section 4.5 below.

including PFHxA (AGC, 2020a, 2020b), PFOA (Danish EPA, 2024), and C₉–C₁₄ PFCAs (Chemours, 2023b; Danish EPA, 2024).¹¹³

Wolf et al. (2024) detected of ca. 1 ppm C₅–C₂₇ PFCAs in a PTFE micropowder following thermal extraction at 250°C for 30 minutes. The study also noted that PFCAs with odd-numbered carbon chains were present at higher concentrations, while even-numbered PFCAs appeared in lower amounts, with the strongest signal observed for C₁₉ PFCA.

The presence of both shorter- and longer-chain PFCAs in the micropowder is also likely. Among others, previous studies have reported the formation of trifluoroacetic acid (TFA) from PTFE thermolysis at 500°C, with reported yields of 7.8% (Ellis et al., 2001) and 1.2% (Cui et al., 2019). Given the complexity of PFAS byproducts generated during the irradiation or thermal treatment of PTFE waste, further research is needed to fully characterize these compounds.

Others

Meng et al. (2021) noted that in all of their samples manufactured without PFOA, PFOA was detected, ranging from 9-15 ppm. The authors hypothesized that this may be due to the transfer of historical residues from tools, reactors, and pipes used in polymerisation, or from contact with other media during transportation. Such likely cross-contamination related to the broader production, processing, and end-of-life treatment systems throughout the fluoropolymer life cycle may warrant further investigation.

¹¹³ It should be noted that PFOA, C₉–C₁₄ PFCAs, and their related substances have now been listed under the Stockholm Convention.

5

Degradation of fluoropolymers during their life cycle

Chapter summary:

Fluoropolymers are generally expected to be stable under natural conditions however they may remain susceptible to degradation under extreme conditions.

- **Degradation during processing:** Limited information exists, but industry sources acknowledge that high-temperature during melt extrusion can cause thermal breakdown—producing various degradation products such as PFIB and lower-molecular-weight polymers—depending on factors such as temperature, oxygen availability, resin composition, and processing conditions.
- **Degradation during use:** Fluoropolymers are typically used because of their resistance to degradation; however, some fluoropolymers may degrade under specific and extreme use conditions, impacting performance and contributing to PFAS exposure. This report presents three examples, acknowledging that further work is needed for a comprehensive understanding across varied uses, as many studies on the degradation of various fluoropolymers under different conditions have been identified but were not included in this report.

Physical wear: PTFE-coated magnetic stirring bars can shed particles under mild conditions, potentially leading to widespread contamination and raising concerns about microplastic release, with filler additives improving durability but complicating end-of-life treatment. It highlights the need for further investigation into physical wear of fluoropolymers across their lifecycle.

Chemical reaction: While fluoropolymers are generally chemically resistant, different types such as PTFE and PVDF exhibit distinct degradation behaviors under specific conditions. PTFE can degrade under prolonged exposure to strong acids or reactive metals at elevated temperatures, while PVDF is more chemically reactive, undergoing degradation in the presence of certain acids, bases, solvents, and reactive battery materials. It highlights the importance of understanding polymer-specific degradation mechanisms for safe and effective use across various applications.

In applications like fuel cells, Nafion™ membranes, though effective, undergo degradation over time, producing PFAS degradation products such as perfluoro(2-methyl-3-oxa-5-sulfonic pentanoic) acid and perfluoro(4-sulfonic butanoic) acid.

- **Degradation during end-of-life treatment:** Significant regional disparities in waste treatment capacity exist. A substantial portion of fluoropolymers may end up in the environment and persist, while another portion may undergo open burning or high-temperature incineration.

The thermal degradation of fluoropolymers varies widely depending on polymer type, temperature, oxygen levels, and additives. Greater understanding of polymer compositions and advanced analytical methods are needed to better assess degradation pathways and environmental impacts during high-temperature treatment. Nevertheless, open burning poses significant environmental risks due to uncontrolled emissions.

High-temperature incineration (≥ 850 °C) with strict operational controls and flue gas treatment significantly improves fluoropolymer degradation compared to open burning. But despite some evidence of low atmospheric PFAS emissions at these conditions, the formation, fate, and environmental release of diverse and often unmonitored fluorinated degradation products—including those in flue gas, bottom ash, and fly ash—remain incompletely understood, especially given variable incinerator performance worldwide.

Reprocessing PTFE into micropowder through irradiation or thermal degradation at around 500 °C can generate various degradation products, some of which may remain in the micropowder or be released during processing or use, with their full fate still unclear.

This analysis underscores the need for further research and action on fluoropolymer degradation throughout their life cycle, associated PFAS formation, and related environmental impacts.

Fluoropolymers are generally expected to be stable under natural conditions due to their (relatively) large molecular size and high degree of fluorination, particularly for those perfluorinated or perhalogenated ones. However, they may remain susceptible to degradation under extreme conditions, particularly high temperatures and other harsh environments encountered during processing, use, and disposal, as outlined below. Additional supporting information from existing studies is provided in Table S5 in the separate supporting material file.

Degradation during processing

Limited information is available regarding the degradation of fluoropolymers during processing, including physical degradation, which may warrant further investigation. Degradation during processing in typical conditions is extremely limited (Hougham et al., 1999), however, industry sources broadly acknowledge that high-temperature processes, such as melt extrusion, may inevitably cause some degree of polymer breakdown, particularly above their recommended processing temperatures (for a comprehensive overview of the thermal degradation of fluoropolymers, see the following section).

Thermal degradation may result in the formation of a wide range of degradation products, including lower-molecular-weight polymers, as well as PFIB and other reactive byproducts, with the rate of formation increasing with temperature (SPI, 2005, 2019; Plastics Europe, 2021). For example, during the processing of PCTFE at 275–300°C, thermal degradation, including the generation of a mixture of monomers and low-molecular-weight oils, has been observed, necessitating the use of corrosion-resistant parts (Feiring, 1994). The degradation products of fluoropolymer resins are influenced by several factors, including temperature, oxygen availability, the physical form of the article, and the duration of exposure to elevated temperatures. Additionally, the presence of some monomers or additives in the resin can also affect the nature of degradation products (SPI, 2005, 2019; Plastics Europe, 2021; for further details, see Section 5.3 below). For example, in the effluent gases from an extruder die¹¹⁴ operated at a melt temperature of 390 to 410 °C, HFP and PFIB are observed, but no COF₂, likely due to the anaerobic conditions within the extruder (SPI, 2005, 2019).

Thermal degradation products may be partially released at the site of formation, while a portion may remain trapped within the molten polymer, leading to subsequent releases over time (SPI, 2005, 2019). As a result, manufacturers typically recommend the use of local exhaust ventilation, a common operating procedure in the thermoplastic processing industry, during processing to minimize potential exposure (SPI, 2005, 2019).

Degradation during use

Fluoropolymers are known for excellent thermal stability, UV resistance, and chemical inertness, and are typically used because of their resistance to degradation (Saleh et al., 2022; Ebnesajjad, 2013; Hougham et al., 1999). For instance, PTFE hollow fibre membranes immersed for months in n-heptane, 1-decene, benzene, and toluene (representing heavy hydrofluorocarbons) showed no change in characteristics, demonstrating their robustness for CO₂ removal in membrane contactor systems (Saleh et al., 2021). Similarly, certain PVDF-based architectural coatings have shown minimal gloss and colour changes after 30 years of continuous South 45° exposure in South Florida, although achieving this level of durability requires careful selection of all formulation components, including co-resins, pigments, and solvents (Wood et al., 2000).

¹¹⁴ Extrusion dies are thick, circular steel disks containing one or more openings through which the material is forced. As it passes through the die, the material acquires the shape of the die opening.

Nevertheless, some fluoropolymers may undergo degradation under specific and extreme use conditions, affecting their performance and lifespan. Understanding the degradation mechanisms and the factors influencing them is crucial for understanding exposure to PFASs and other chemicals associated with fluoropolymer use and for optimizing the use of fluoropolymers in different applications. A large number of studies on the degradation of various fluoropolymers under different conditions has been identified during the preparation of this report; however, it is not possible to capture all of this work here. This section describes three examples of degradation at certain conditions, while acknowledging that further work is needed to comprehensively understand fluoropolymer degradation across the wide range of possible use conditions.

Physical wear

Pham et al. (2011) reported that PTFE-coated magnetic stirring bars can shed PTFE particles (0.04–0.08 weight%) under mild conditions (20–60 °C for up to 4 hours), likely due to friction with slurried solids or the glass vessel. Such contamination was observed in samples from two independent laboratories, suggesting the issue may be widespread (Pham et al., 2011). This is attributed to PTFE's relatively low mechanical strength and high susceptibility to wear, particularly under abrasive conditions (Saisnith and Fridrici, 2021). Addition of fillers (e.g., glass fibres, carbon fibres, bronze, graphite, metals, and inorganic compounds) reduces wear rates by up to two orders of magnitude compared to pure PTFE (Saisnith and Fridrici, 2021). However, the inclusion of fillers may also complicate end-of-life treatment. The physical wear of fluoropolymers, including the release of micro- and nanoplastics (Améduri and Hori, 2023), may warrant further investigation, not only during the use phase but also during end-of-life treatment and after their release into the environment.

Chemical degradation

Fluoropolymers are generally resistant to chemical degradation, but different fluoropolymers may act distinctly under different conditions. For example, PTFE material is known for its chemical inertness, including in boiling sulfuric, nitric, hydrofluoric, or hydrochloric acids, as well as in boiling solutions of aqueous bases (Puts et al., 2019). However, two studies have shown that under aggravated conditions—specifically, exposure to a strong acidic solution (approximately pH 1, composed of sulfamic, hydrochloric and hydrofluoric acids¹¹⁵) at elevated temperatures between 70 and 80°C for a duration of two months—PTFE gaskets may undergo accelerated aging. These conditions, which simulate the acid-cleaning processing used in tire mould maintenance, have been shown to induce varying degrees of hydroxylation and defluorination in PTFE samples across samples from different manufacturers (Fragassa et al., 2016; Giorgini et al., 2016). Furthermore, nascent alkali and alkaline earth metals along with certain other metals and metal oxides, such as mixtures containing aluminium and magnesium, are known to attack PTFE materials below their thermal decomposition temperature, resulting in the formation of metal fluorides and carbon (Puts et al., 2019).

In contrast to more inert PTFE, PVDF can undergo chemical reactions with common reagents under relatively milder conditions than PTFE. For instance, PVDF materials are susceptible to degradation in the presence of a combination of strong acids such as fuming sulfuric acid (H₂SO₄) and nitric acid (HNO₃) at room temperature, or a mixture of acetic acid (CH₃COOH) and 98% sulfuric acid at approximately 100 °C. However, exposure to hydrochloric (HCl), humic (HA) and sulfuric (H₂SO₄) acids in various concentrations has been reported to result in no significant reaction with PVDF (Marshall et al., 2021).

¹¹⁵ When the samples were exposed only to the mixture of sulfamic and hydrochloric acids, no signs of degradation were observed. This suggests a possible synergistic effect among sulfamic, hydrochloric, and hydrofluoric acids in promoting the accelerated aging of PTFE.

PVDF can also be affected by a range of organic solvents, including acetone, acetophenone, dimethylformamide, and methyl ethyl ketone, at ambient temperature (Nguyen, 1985), as well as by certain strong bases (Marshall et al., 2021). For example, under strongly alkaline conditions ($\text{pH} \geq 11$), PVDF can readily undergo dehydrofluorination via an E2 mechanism, resulting in the elimination of HF and the formation of carbon–carbon double bonds ($\text{C}=\text{C}$) or crosslinking between chains, similar to the effects observed during thermal degradation. These newly formed double bonds enhance the susceptibility of adjacent groups to further dehydrofluorination, thereby facilitating additional chemical reactions (Marshall et al., 2021). Additionally, in KOH-isopropanol solution, PVDF materials degrade to yield products containing carbon–carbon triple bonds ($\text{C}\equiv\text{C}$), $\text{C}=\text{C}$ and carbonyl groups ($\text{C}=\text{O}$) (Nguyen, 1985). The reactivity and degradation sensitivity of PVDF are influenced not only by the strength of the base but also by the specific cation present. For example, PVDF can react with both low (<1 weight%) and high (>30 weight%) concentrations of NaOH, whereas similar reactions with potassium hydroxide (KOH) typically require higher concentrations, e.g., >30 weight% (Marshall et al., 2021). Additionally, the reaction of PVDF with bases can be catalysed by organic solvents such as tetrabutylammonium bromide (TBAB) (Marshall et al., 2021).

Furthermore, a 2018 study indicates that while PVDF materials remain stable when used as a binder in graphite electrodes, they undergo degradation in the presence of silicon (Marshall et al., 2021). For example, lithium silicides such as Li_7Si_3 and $\text{Li}_{12}\text{Si}_7$ —formed during solid electrolyte interphase (SEI) formation between the silicon-based anode and the liquid electrolyte in the initial cycles of a lithium-ion battery, are highly reactive. These species can attack the lower-energy C–C and C–H bonds within the PVDF polymer chain, leading to PVDF binder degradation in the electrode structure (Marshall et al., 2021). In addition to lithium silicides, lithium oxides have also been shown to contribute to PVDF degradation in lithium-ion batteries (Marshall et al., 2021). The precise degradation mechanisms and their impacts remain largely unexplored, which may be particularly important for industries such as batteries and fuel cells, where PVDF materials are commonly used as a binder in electrodes and in the synthesis of membranes (Marshall et al., 2021).

It is currently unclear whether such chemical degradation during use results in the formation of non-polymeric PFASs and other fluorinated degradation products, as well as how degradation may occur for other polyfluorinated fluoropolymers.

Degradation during use of fuel cells

Although Nafion™ ionomers have shown high effectiveness and stable performance in applications, evidence of polymer degradation has been observed after several hours of operational working conditions. Membrane degradation is principally brought about by chemical attacks on the polymers (Okonkwo et al. 2021). Degradation may result in degradation products such as perfluoro(2-methyl-3-oxa-5-sulfonic pentanoic) acid (in the case of Nafion™) and perfluoro(4-sulfonic butanoic) acid (in the case 3M™ Ionomers) (Zatoń et al., 2017). Gas diffusion layers degradation such as carbon corrosion and PTFE loss has also been reported in many long-term experiments to cause a decrease in mass transport, water management ability and conductivity (Pan et al., 2021).

Degradation during end-of-life treatment

According to UNEP (2024), 38 per cent of global municipal solid waste¹¹⁶ generated in 2020 was unmanaged—either dumped or openly burned—while the remaining waste was managed through

¹¹⁶ Fluoropolymers can be present in both industrial and municipal solid waste. Industrial waste management practices vary widely across countries—some use high-temperature incineration, while others treat industrial waste alongside municipal waste. This report does not separately address industrial waste management, except in the context of post-

landfilling (30%), incineration (13%), or recycling (19%). The level of controlled municipal solid waste management varies widely across regions: Sub-Saharan Africa and Central and South Asia have the lowest rates, whereas nearly all municipal solid waste in North America and Western Europe is properly managed. Regional differences also exist in treatment methods—North America primarily relies on sanitary landfills, while Western Europe emphasizes recycling and incineration solutions. Looking ahead, the fastest growth in municipal solid waste generation is expected in rapidly developing economies, where waste production is already outpacing management capacity.

Applying such context to the end-of-life treatment of fluoropolymers, it suggests that most fluoropolymer-containing waste may be dumped, landfilled, openly burned, or incinerated, while some may be recycled as outlined in Chapter 3. Given the general high stability of fluoropolymers, particularly perfluorinated and perhalogenated types, those landfilled or dumped are likely to remain largely unchanged over time. However, studies on certain low-molecular-weight PFASs containing non-fluorinated methylene ($-\text{CH}_2-$) moieties, such as $\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ and $\text{C}_4\text{F}_9\text{CH}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, show that their non-fluorinated segments may undergo (bio)degradation, forming short-chain PFCAs (Peng and Hung, 2012; Coope et al., 2014). This raises questions about the potential degradability of fluoropolymers containing non-fluorinated moieties, such as PVDF and ETFE, under natural conditions, particularly with exposure to weathering. Although such degradation is likely to be slow, both in the environment and in landfills, the fate of landfilled and dumped fluoropolymer waste may warrant further investigation.

The following subsections provide a more in-depth analysis of the fate of fluoropolymer waste during high-temperature end-of-life treatments, including open burning and incineration. The discussion starts with a general overview of the thermal degradation of fluoropolymers, followed by a focused analysis of specific incineration cases, distinguished from open burning by higher temperatures and the additional step of flue gas treatment. The final subsection briefly revisits the degradation associated with irradiation and thermal treatment of post-processing PTFE scraps into micropowder PTFE, as outlined in Chapter 3. Additional supporting information of existing studies can be found in Table S5 of the separate supporting material file.

General overview of the thermal degradation of fluoropolymers

The thermal degradation of various fluoropolymers has been extensively studied in the literature, including their degradation temperature ranges, associated degradation products, and the influence of oxygen availability and additives on the degradation behaviour of individual fluoropolymer types (for examples, see Table 7 and Table S5 in the separate supporting material file). Although the overall picture remains complex and many details are yet to be fully understood, several general observations can nevertheless be made.

(1) The temperatures at which thermal degradation of fluoropolymers occurs span a continuum, with degradation rates exponentially increasing as the temperature rises; for examples, see Figure 5 in Cox et al. (1964), Figure 3 in Baker Jr. and Kasprzak (1993), and Figure 5 in Giannetti (2001). For example, the thermal degradation of PTFE begins gradually around 260 °C, initially very slow but with the degradation rate increasing significantly above 400 °C (Améduri and Hori, 2023).

(2) Degradation generally occurs more rapidly in air or steam environments than in nitrogen or vacuum conditions. This is because, in the absence of oxygen, pyrolysis is driven by internal molecular decomposition, typically initiated at the least stable functional group. Specifically, during pyrolysis of perfluorinated fluoropolymers, cleavage of the C–C bond is dominant in initial reactions, forming perfluorocarbon radicals (Jiang et al., 1986; Baker Jr. and Kasprzak, 1993; Wang J. et al., 2022). In contrast, the presence of oxygen allows additional reactions to occur between oxygen and reactive groups

processing waste used to produce micropowders. However, general insights into municipal waste treatment may also apply to industrial waste, while recognizing potential differences, such as higher incineration temperatures for industrial waste treatment.

in the molecule (Baker Jr. and Kasprzak, 1993; Wang J. et al., 2022). More significant differences have been observed for FEP (Cox et al., 1964; Baker Jr. and Kasprzak, 1993), PVDF, and several VDF copolymers (Cox et al., 1964; Nguyen, 1985), among others. Interestingly, unlike most fluoropolymers, PCTFE materials do not show significantly increased degradation in oxygen but may degrade slightly more slowly in oxygen than in vacuum (Cox et al., 1964).

(3) Perfluorinated fluoropolymers tend to be more thermally stable than polyfluorinated ones. For example, Baker Jr. and Kasprzak (1993) compared the thermal degradation of six commercial fluoropolymers in air and found that at 350 °C, Tefzel™ 200 (a copolymer of TFE with 48% ethylene and 0.5–2% perfluorobutyl-ethylene) exhibited significantly lower thermal stability, with a 6.8% weight loss over one hour, compared to the more stable perfluorinated polymers—PTFE, PFA, and FEP, which showed less than 0.22% weight loss over the same period. Similarly, Cox et al. (1964) observed that PTFE and FEP exhibited higher thermal stability than PVDF, VDF copolymers, and PCTFE, both in vacuum and in oxygen. This is because the partial replacement of fluorine atoms with hydrogen or chlorine facilitates the elimination of HF or HCl and promotes chain scission, thereby making degradation significantly easier. Moreover, since HCl is more readily eliminated than HF, this may help explain the greater thermal stability of PVDF compared to PCTFE (Cox et al., 1964; Jiang et al., 1986). Interestingly, Nguyen (1985) reported that during pyrolysis in vacuum, the thermal degradation of PVDF stabilized at around 460 °C after 67% weight loss, with only an additional 4% loss occurring at higher temperatures tested. This stabilisation was attributed to the formation of substantial double bonds and cross-links within the polymer chain (Nguyen, 1985; Marshall et al., 2021).

(4) Thermal stability generally decreases with an increasing number of side chains. For example, among the commercial fluoropolymers tested by Baker Jr. and Kasprzak (1993), a PTFE polymer was the most thermally stable, followed by two PFA copolymers containing 0.5–2% PPVE side chains. The FEP polymer containing 5–10% –CF₃ branching showed the lowest thermal stability among the perfluorinated fluoropolymers tested. This aligns with the findings of Cox et al. (1964), which showed that PTFE materials were more stable than FEP, especially in the presence of oxygen.

(5) Fluoropolymers with stable –CF₃ end groups exhibit greater thermal stability than the same polymers with other end groups. For example, among the commercial fluoropolymers tested by Baker Jr. and Kasprzak (1993), the PFA with fully fluorinated –CF₃ end groups exhibited greater stability than the one without. Giannetti (2001) reported the relative thermal stability of various fluoropolymers based on the temperature at which 5% weight loss occurs in nitrogen, as determined by thermogravimetric analysis (heating rate: 10 °C per minute). The resulting stability sequence—consistent with considerations (3), (4), and (5)—is as follows: PTFE > PFA ≈ MFA > FEP >> ETFE > PVDF > ECTFE > PCTFE.

(6) Certain additives can significantly increase the degradability of fluoropolymers. For example, Puts and Crouse (2014) observed that CuSO₄ and AlF₃ accelerate the thermal degradation of PTFE, lowering the degradation onset temperature by 50 °C and 30 °C, respectively. In contrast, the sulfates of Al, Zn, Ni, Co, Fe, and Mn, as well as the fluorides of Zn, Cu, Ni, Co, Fe, and Mn, showed minimal to no impact on PTFE thermal degradation. Additionally, beyond fillers such as montmorillonite, silica and zeolites (Marshall et al., 2021), Rehwoldt et al. (2022) found that the oxides of Al, Ti, and Cu can also enhance the thermal degradation of PVDF, whereas the oxides of Si, Mg, and Bi may delay the onset of its decomposition, along with boron-doped graphene and magnetite (Marshall et al., 2021). Moreover, Samms et al. (1996) found that platinum does not substantially affect the overall stability of Nafion™ membranes. Overall, the effects of various co-existing substances on the thermal degradation of fluoropolymers remain underexplored.

Existing studies further show that the thermal degradation of fluoropolymers can yield a wide range of degradation products including many PFASs, ranging from volatile low-molecular-weight gases to solid oligomers (for examples, see Table 7). Among them, the commonly studied thermal degradation products are various fluorinated gases, including many per- and polyfluoroalkanes such as CF₄, C₂F₆, C₃F₈, c-C₄F₈ and C₃F₅Cl as well as per- and polyfluoroalkenes such as TFE/C₂F₄, HFP/C₃F₆, CF₂=CH₂, and PFIB, often

being the major degradation products (Lewis and Naylor, 1947; Simon and Kaminsky, 1998; Ellis et al., 2001, 2003; García et al., 2007; Odochian et al., 2011, 2013; Puts et al., 2014). Similarly, the formation of chloropentafluoropropene was observed during the thermolysis of PCTFE at 500 °C (Ellis et al., 2003). Based on the design and implementation of their thermolysis experiment, much of the PFOA observed by Ellis et al., 2001 can be attributed to hot-air stripping of residual ammonium perfluorooctanoate (APFO) polymerisation aid typically present in PTFE at that time.

Some studies have also qualitatively shown that measurable amounts of TFA, PFOA and other PFCA homologues can be generated during the thermolysis of non-functionalized PTFE (Ellis et al., 2001, 2003; Schlummer, 2015), FEP (Baker Jr. and Kasprzak, 1993), PCTFE, ECTFE, PFA (or a TFE-PPVE elastomer) (Ellis et al., 2003), fluorinated ionomers (Feng et al., 2015), and VDF-HFP and VDF-CTFE copolymers (Cui et al., 2019) at temperatures between 250 °C and 700 °C (see Table 7). The exact mechanisms for the formation of PFCAs have not been fully understood yet. However, it has been postulated that the thermolysis of some fluoropolymers such as PTFE materials generate radicals including $\cdot\text{CF}_2(\text{CF}_2)_n\text{CF}_2\cdot$ and carbene as $:\text{CF}_2$ (Ellis et al., 2001; Odochian et al., 2011, 2013; Puts et al., 2014; Feng et al., 2015), which can further react with other radicals and water vapour to generate PFCAs (Ellis et al., 2001; Young and Mabury, 2010; Feng et al., 2015).

Additionally, many other types of fluorinated chemicals including PFASs may be generated during thermal degradation. For example, Myers et al. (2014) noted the formation of perchlorofluoroalkanoic acids (PXCAs, X = Cl, F) during thermal decomposition of PCTFE at 400 °C, which was also observed in Ellis et al. (2003), and of Cl/F-substituted polycyclic aromatic hydrocarbons (X-PAHs, X = Cl, F) during thermal decomposition of PCTFE at 800 °C. The authors noted that the fluorine to chlorine ratio increased as the unsaturation increased, indicating that chlorine is lost faster in the formation of double bonds. Thus, it may be interesting to further study how such formation may occur to other fluoropolymers during thermal degradation, particularly with regard to possible formation of X-PAHs.

Furthermore, secondary degradation products can form through reactions between the thermal degradation products of fluoropolymers and their surrounding environment. For example, during the thermal degradation of PTFE in the presence of glass or quartz, compounds such as SiF_4 , CO, CO_2 , and water are formed due to secondary reactions between PTFE degradation products and silicon dioxide (Simon and Kaminsky, 1998). However, most studies have focused on specific groups of degradation products, rather than providing a comprehensive analysis of all possible degradation products. Direct comparisons across studies are also challenging due to (1) the use of qualitative versus quantitative approaches, and (2) variations in experimental conditions, instruments, and methodologies—even when examining similar degradation products from the same types of fluoropolymers (though likely not identical samples)¹¹⁷. For example, Cui et al. (2019) noted that the differences in trifluoroacetic acid (TFA) yields from the thermal degradation of the same types of fluoropolymers, compared to those reported by Ellis et al. (2001), were likely due to differences in instrumental settings. Nevertheless, the following general observations may be drawn.

Different types of fluoropolymers produce distinct mixtures of degradation products, reflecting variations in their chemical structures (see Table 7). Studies, including those by Jiang et al. (1986), Ellis et al. (2001), and Ellis et al. (2003), have tested several types of fluoropolymers under identical conditions. While some common degradation products are observed likely due to shared substructures within the polymer chains, many degradation products are unique to specific types of fluoropolymers.

Adding to the diversity and complexity of thermal degradation, even the same type of fluoropolymer can produce substantially different degradation products depending on factors such as temperature, oxygen availability, and the presence of additional substances—and these factors may influence different fluoropolymers in distinct ways.

¹¹⁷ For further details, see Section *Challenges in the identification and characterisation of individual fluoropolymers*.

Temperature: For example, Baker Jr. and Kasprzak (1993) observed that during thermal degradation in air, FEP materials begin to produce PFIB at 380 °C, but not at 350 °C. In contrast, PTFE materials generate PFIB at 525 °C, but not at 400 °C. Generally, temperatures higher than 850 degrees are expected to result in fewer degradation products, smaller absolute quantities, and lower molecular masses (RIVM, 2021).

Oxygen presence: Pyrolysis typically leads to the formation of more per- and polyfluoroalkanes and per- and polyfluoroalkenes, as chain cleavage is the dominant degradation mechanism (Jiang et al., 1986). The presence of oxygen not only facilitates direct reactions with the polymer chain but also promotes secondary reactions with the degradation products. For example, García et al. (2007) observed that during the thermal degradation of PTFE, increasing oxygen levels led to the disappearance of C₂F₄, a decrease in C₃F₆ levels, and an increase in CF₄ and C₂F₆. These findings suggest that the presence of oxygen in the atmosphere, combined with the high temperature of the reactor, promotes combustion reactions of the pyrolytic products, including further reactions of C₂F₄ with oxygen to form CF₄ and CO₂ (Améduri and Hori, 2023). Puts et al. (2019) further noted that during the thermal degradation of PTFE, oxygen may lead to the formation of CF₂O from initial degradation products; CF₂O can subsequently react further to form CO₂, CO, and CF₄, or HF in the presence of moisture.

Presence of additional substances: For example, Puts and Crouse (2014) observed that during the pyrolysis of PTFE, the presence of Al₂(SO₄)₃ and NiSO₄ increased the yield of hexafluoropropylene (HFP), while the presence of AlF₃ led to the exclusive formation of HFP and C₂F₆. Similarly, Al₂O₃, TiO₂, and CuO have been shown to enhance the release of HF during the pyrolysis of PVDF, while SiO₂, MgO, and Bi₂O₃ suppress HF release (Rehwoldt et al., 2022). Notably, the presence of Al₂O₃ also led to the formation of trifluorobenzene, a byproduct not observed with the other tested metal oxides.

In summary, the thermal degradation of fluoropolymers and the resulting degradation products are highly diverse and complex, influenced by many known factors. Current knowledge on the thermal degradation of fluoropolymers, including its complexity, may carry the following three key implications, among others.

First, despite the diversity and complexity, it can nevertheless be concluded that high-temperature treatment will generate a wide range of degradation products from fluoropolymers. This is particularly concerning in cases of open burning (typically 200–600 °C), where many of these degradation products—including various PFASs—may be directly released into the environment, via air, water and solid residues, without any form of control. As noted at the beginning of this section, open burning remains a significant method of waste treatment in many parts of the world. For more controlled high-temperature incineration, different considerations may apply, as further elaborated in the following subsection.

Second, future studies on thermal degradation of fluoropolymers should aim to analyse a broader range of potential degradation products across different media, potentially leveraging advances in suspect and non-targeted screening techniques using high-resolution mass spectrometry. Ideally, a mass-balance analysis should be considered, though it is important to acknowledge the analytical challenges involved—including the lack of validated methods capable of capturing all possible degradation products and analytical standards (Horst et al., 2020; Trier et al., 2025). While testing, sampling, and analytical methods continue to evolve, researchers may additionally consider comparing quantifiable compounds alongside advanced tools such as total organic fluorine (TOF) analysis, extractable and adsorbable organofluorine (EOF/AOF) analysis, and the total oxidizable precursor (TOP) assay (Horst et al., 2020). Such approaches could contribute to a more comprehensive understanding of the full scope of degradation outcomes.

Third, this complexity further underscores the importance of identifying the chemical composition of fluoropolymers on the market, as well as co-occurring substances, to enable a more accurate understanding of their behaviour and fate during end-of-life treatment processes.

Table 7. Examples of observed generation of PFASs and other fluorinated substances during the thermolysis (with the presence of oxygen) or pyrolysis (without the presence of oxygen) of various fluoropolymers in the literature

References	Fluoropolymers	Testing types	Temperatures	Detected fluorinated degradation products [weight%]
Jiang et al., 1986	various fluoropolymers	Pyrolysis	590 °C	- PTFE: C₂F₄ - PVDF: CF₂=CH₂, CF₂=CH-CF=CH₂, 1,3,5-trifluorobenzene - PCTFE: CF₂=CFCl, C₃F₅Cl - FEP: C₂F₄, C₃F₆ - VDF-HFP copolymer: CF₂=CH₂, C₃F₆, CF₃-CF=CH₂, C₂F₄H₂ - VDF-CTFE copolymer: CF₂=CH₂, CF₂=CFCl, C₃F₅Cl - ECTFE: C₂H₄, CF₂=CH₂, C₂F₃H, C₂FH₃, CF₂=CFCl, CH₂=CFCl - VDF-TFE-HFP copolymer: C₂F₄, CF₂=CH₂, C₃F₆, CF₃-CF=CH₂ - MFA: C₂F₄, C₂F₆, C₃F₆, C₃F₈, C₄F₈, C₄F₁₀, CF₃OC₂F₃, CF₃OC₃F₅ - VDF-TFE-PMVE copolymer: C₂F₄, CF₂=CH₂, C₃F₆, CF₃OC₂F₃, C₂F₄H₂, CF₃-CF=CH₂
Baker Jr. and Kasprzak, 1993	various fluoropolymers	Thermal decomposition with air and nitrogen	150 °C to 525 °C	- FEP, 400 °C, 50% RH air, quartz: PFIB (0.003–0.015 %), C₂F₄ (ND–0.06 %), C₃F₆ (ND–0.38 %), CF₃COF (ND–0.19 %), CHF₃ (0.04–0.19 %) - FEP, 400 °C, dry air, quartz: PFIB (NM–0.006 %), C₂F₄ (ND), C₃F₆ (ND–0.13 %), CHF₃ (ND–0.03 %), others ND - FEP, 400 °C, dry nitrogen, quartz: PFIB (0.005–0.006 %), C₂F₄ (ND), C₃F₆ (0.3–0.31 %), others ND - TFE-ethylene-perfluorobutylethylene copolymer, 350 °C, 50% RH air, quartz: TFE (0.06 %), others ND - PFA (TFE-PPVE copolymer), 400 °C, 50% RH air, Quartz: all ND - PFA (TFE-PPVE copolymer, with –CF₃ end groups), 400 °C, 50% RH air, quartz: all ND
Samms et al., 1996	Nafion™ membranes (pure and loaded with ca. 20 weight% platinum)	Thermal decomposition under nitrogen and air	400 °C to 600 °C (decomposition started to complete)	SOF ₂ , COF ₂ , C ₂ F ₄ , C ₃ F ₆ , C ₃ F ₆ O, C ₂ F ₄ O ₂ , C ₂ H ₂ F ₄ , C ₃ H ₆ F ₂ , and HF (only above 450 °C), noting that the presence of oxygen or platinum affected the composition of the decomposition products, but they did not substantially affect the overall stability of Nafion™ membrane (i.e., changing decomposition temperatures)
Simon and Kaminsky, 1998	PTFE	Pyrolysis with steam	500 °C to 600 °C	PTFE with 25 % carbon black, 505 °C: oligomeric PTFE (11 %), CHF₃ (0.01 %), difluoroethylene (0.01 %), CF₂=CHF (0.01 %), C₂F₄ (71 %), C₃F₆ (6.3 %), heptafluoropropane (below 0.01 %), c-C₄F₈ (3.9%), not identified (0.42 %)

				- PTFE with 25 % carbon black, 545 °C: oligomeric PTFE (1.9 %), CHF₃ (0.18 %), difluoroethylene (0.07 %), CF₂=CHF (0.09 %), C₂F₄ (68 %), C₃F₆ (7.8 %), heptafluoropropane (below 0.01 %), c-C₄F₈ (12 %), not identified (1.0 %) - PTFE with 25 % carbon black, 555 °C: oligomeric PTFE (7.0 %), CHF₃ (0.01 %), difluoroethylene (0.01 %), CF₂=CHF (0.01 %), C₂F₄ (76 %), C₂F₅H (0.05 %), C₃F₆ (7.1 %), heptafluoropropane (below 0.01 %), c-C₄F₈ (5.2 %), hexafluorobutane (0.03 %), not identified (0.1 %) - PTFE with 25 % carbon black, 600 °C: oligomeric PTFE (1.9 %), CHF₃ (0.05 %), difluoroethylene (0.07 %), CF₂=CHF (0.05 %), C₂F₄ (71 %), C₂F₅H (0.05 %), C₃F₆ (7.5 %), heptafluoropropane (below 0.01 %), c-C₄F₈ (11 %), octafluorobutanes (0.03 %), hexafluorobutane (0.16 %), not identified (0.26 %) - PTFE with 25 % glass fibres, 600 °C: oligomeric PTFE (0.64 %), CHF₃ (0.04 %), difluoroethylene (0.03 %), CF₂=CHF (0.03 %), C₂F₄ (75 %), C₂F₅H (0.03 %), C₃F₆ (6.6 %), heptafluoropropane (below 0.01 %), c-C₄F₈ (9.9 %), octafluorobutanes (0.01 %), hexafluorobutane (0.05 %), not identified (0.12 %) - PTFE with 60 % bronze, 600 °C: oligomeric PTFE (below 0.01 %), CHF₃ (0.24 %), difluoroethylene (0.47 %), CF₂=CHF (0.14 %), C₂F₄ (51 %), C₃F₆ (7.3 %), heptafluoropropane (below 0.01 %), c-C₄F₈ (21 %), not identified (0.72 %)
			600 °C to 700 °C	605 °C: C₂F₄ (78.5 %), C₃F₆ (4.6 %), c-C₄F₈ (3.7 %) 650 °C: C₂F₄ (75.0 to 75.9 %), C₃F₆ (4.7 to 5.2 %), c-C₄F₈ (8.7 to 5.9 %) 700 °C: C₂F₄ (60.2 %), C₃F₆ (6.0 %), c-C₄F₈ (16.1 %) - Other fluorocarbons were found only in traces.
Ellis et al., 2001	various fluoropolymers	Thermolysis under air	360 °C and 500 °C	- PTFE: C₂F₄, C₃F₆ (10.8 %), CF₃COOH (7.8 %), c-C₄F₈, CF₃(CF₂)_nCOOH (>0.01 %), CF₃O(CF₂)_mCOOH, CHF₂COOH (>0.01 %), CH₂FCOOH (>0.01 %) - PCTFE: CF₂=CFCl, C₃F₅Cl (13.1 %), CF₂ClCOOH (9.5%), CF₃COOH (>0.01 %), 1,2-dichlorohexafluorocyclobutane, CFCl₂CF₂Cl, CF₂ClCF=CFCl, CF₃CCl=CCl₂, CF_xCl_y(CF_zCl_{y-1})_yCOOH - ECTFE: CF₃COOH (6.3 %), CF₂ClCOOH (7.2%), C₃F₆, C₃F₅Cl - PFA (TFE-PPVE copolymer): C₂F₄ (2.5 %), C₃F₆
Ellis et al., 2003	various fluoropolymers	Thermolysis under air	300 °C and 500 °C	- PTFE: C₂F₄, C₃F₆, fluoroformaldehyde, CF₃COOH and longer chain PFCAs—CF₃(CF₂)_nCOOH, CF₃O(CF₂)_mCOOH, perfluoroalkene acids (1 double bond in the perfluorocarbon chain), CHF₂COOH, CH₂FCOOH, CF₂ClCOOH - PCTFE: CF₂ClCOOH, CHF₂COOH, CH₂FCOOH, CF₃COOH, CF₂ClCF=CF₂, CF₂=CFCl, CF₃CFCICF₂CFClCF₂CFClCOOH and its homologues,

				ECTFE and PFA (TFE-PPVE copolymer): no major differences in the acids and acid precursors (e.g., CF_3COOH, CF_2ClCOOH, C_3F_6 and $\text{C}_3\text{F}_5\text{Cl}$) were observed.
García et al., 2007*	PTFE	Thermal decomposition under nitrogen and air	750 °C to 1050 °C	850 °C, under air, with Φ_{O_2} [the ratio between the oxygen found as ($\text{CO} + \text{CO}_2$) and the oxygen required for the total oxidation of the carbon fed in the sample] between 22.9% and 57.3%: CF_4 (2.4–8.4 %), C_2F_6 (25.7–68.0 %), C_3F_6 (ND–25.4 %) 850 °C, under nitrogen, with $\Phi_{\text{O}_2} = 0$: C_3F_6 (81.9 %), C_2F_4 (12.2 %) 750 °C, under air, with $\Phi_{\text{O}_2} = 30.2$ %: CF_4 (17.8 %), C_2F_6 (67.9 %) 850 °C, under air, with $\Phi_{\text{O}_2} = 36.3$ %: CF_4 (5.5 %), C_2F_6 (60.9 %) 950 °C, under air, with $\Phi_{\text{O}_2} = 34.2$ %: CF_4 (16.9 %), C_2F_6 (41.6 %), C_3F_6 (5.8 %) 1050 °C, under air, with $\Phi_{\text{O}_2} = 49.9$ %: CF_4 (9.3 %), C_2F_6 (12.5 %)
Myers et al., 2014	PCTFE	Thermolysis under air	400 °C and 800 °C	400 °C: including $\text{C}_n\text{X}_{2n+1}\text{COOH}$ such as $\text{C}_2\text{F}_3\text{Cl}_2\text{COOH}$, $\text{C}_5\text{F}_9\text{Cl}_2\text{COOH}$, $\text{C}_3\text{F}_4\text{Cl}_3\text{COOH}$, and $\text{C}_7\text{F}_{12}\text{Cl}_3\text{COOH}$, $\text{C}_n\text{X}_{2n-1}\text{COOH}$ (containing one double bond), $\text{C}_n\text{X}_{2n-3}\text{COOH}$ (containing two double bonds), $\text{HOCC}_n\text{X}_{2n}\text{COOH}$, $\text{HOCC}_n\text{X}_{2n-2}\text{COOH}$, $\text{X} = \text{F}$ or Cl 800 °C: mainly aromatic species, including pentafluorobenzoic acid, Cl/F-substituted polycyclic aromatic hydrocarbons such as octafluoronaphthalene
Schlummer et al., 2015	PFOA-free PTFE-coated cooking pans (the amounts not measured)	Thermolysis under air	250 °C, 300 °C and 370 °C	C_4 – C_{12} PFCAs, ranging from 1 to 4939 ng per pan and hour, with PFBA and PFPeA being the dominant congeners. Highest emissions were recorded for pan C, which reached the highest temperature of 370 °C. Total emission of PFCA from pan A (300 °C) and pan B (250 °C) were calculated as 376 and 529 ng per item and hour, respectively.
Feng et al., 2015	Nafion™ N117 membrane	Thermolysis under air	Up to 600 °C	Including CF_3COOH and longer-chain PFCA homologues, $\text{CF}_3(\text{CF}_2)_5\text{CHF}_2\text{COOH}$, $\text{CF}_3(\text{CF}_2)_8\text{CHF}_2\text{COOH}$, $\text{CF}_3(\text{CF}_2)_4\text{CF}=\text{CFCF}_2\text{COOH}$, $\text{CF}_3(\text{CF}_2)_4\text{CF}=\text{CF}(\text{CF}_2)_3\text{COOH}$, $\text{CF}_3(\text{CF}_2)_3\text{CF}(\text{COOH})\text{COOH}$, $\text{CF}_3(\text{CF}_2)_4\text{CF}(\text{COOH})\text{COOH}$, $\text{CHF}_2\text{SO}_3\text{H}$
Cui et al., 2019	various fluoropolymers	Thermolysis under air	Up to 700 °C (mainly between ca. 400 °C and 650 °C)	- TFA was generated after being heated to 500 °C and above. - PTFE: average TFA yield of 1.2 % - VDF-HFP copolymers: average TFA yield of 0.9 % - VDF-CTFE copolymers: average TFA yield of 0.3 %

Note: Additional details of these studies can be found in Table S5 in the separate supporting material file. ND = not detected; NM = not measured

* The experiments of Garcia et al, 2007 were carried out under substoichiometric conditions unrepresentative of full-scale incineration processes.

Specific cases of fluoropolymer incineration

Beyond the significant temperature differences between high-temperature incineration (≥ 850 °C) and open burning, another key distinction lies in the presence of flue gas treatment in incineration systems. These systems are subject to strict operational requirements such as minimum temperature, sufficient residence time, and adequate oxygen levels, which can significantly enhance the breakdown of organic compounds in the flue gas. For example, according to Article 50 of the Industrial Emissions Directive 2010/75/EU,¹¹⁸ waste incineration plants in the European Union must be designed to ensure that flue gases reach a temperature of at least 850 °C for at least 2 seconds. These two factors significantly influence the formation and releases of thermal degradation products, many of which are PFASs, during the high-temperature treatment of fluoropolymer waste.

RIVM (2021) concluded that complete thermal degradation of PTFE is achieved at around 800 °C, consistent with findings from existing studies (e.g., Baker Jr. and Kasprzak, 1993). Given that PTFE materials are considered the most thermally stable fluoropolymers, it is reasonable to expect that other fluoropolymers should also face complete thermal degradation at or below such temperature.¹¹⁹ Therefore, the key question concerning the incineration of fluoropolymers is the ultimate fate of the diverse degradation products formed during the process—an issue that remains inconclusively answered to date.

In 2005, the US EPA and four major fluoropolymer and fluoroelastomer producers (AGC, Daikin, Dyneon and E.I. du Pont de Nemours) reached an enforceable consent agreement (ECA) for a laboratory-scale incineration testing on fluoropolymers (US EPA, 2005). Results from the study indicate that waste incineration of fluoropolymers does not emit detectable levels of PFOA under conditions representative of typical municipal waste combustor operations in the United States (ca. 1000 °C; Taylor, 2009).

In a recent study, Aleksandrov et al. (2019) conducted another incineration study of PTFE, specifically targeting various PFCAs, perfluoroalkanesulfonic acids (PFSAs), and their precursors based on perfluorooctanesulfonyl fluoride (POSF) and fluorotelomer chemistries. However, this study has been inconclusive for the following three reasons: (1) The study was conducted with an waste incinerator (870 °C and 4 seconds residence time), as opposed to the less strict 850 °C and 2 seconds required in the EU for municipal solid waste incinerators as stated above. (2) PFOA was regularly detected in the exhaust, but the study was marred by elevated blanks. (3) The authors were only able to account for 56–78% of the fluorine mass balance during incineration, meaning that a wide variety of other fluorinated substances including PFASs were potentially formed and released (see Table 7), but this needs to be confirmed by further studies. The authors noted that low recovery rates were expected since fluorides are very reactive, especially with silicates, which are a main component of the refractory in the incinerator.

In a follow-up study, Gehrmann et al. (2024) investigated the incineration of a fluoropolymer mixture consisting of 63% PTFE tubes, 7% PTFE tape, 18% PVDF, 6% PFA, and 6% FKM. The mixture was co-incinerated with woodchips at a fluoropolymer mass fraction of 0.3 weight% under two conditions of flue gas treatment: 860°C and 1095°C, both with a 2-second residence time. The study specifically targeted various PFCAs, PFSAs, their precursors based on POSF, perfluorobutanesulfonyl fluoride (PBSF) and fluorotelomer chemistries, several perfluoroalkylether carboxylic acids, and several F-gases (CF₄, C₂F₆, CHF₃, HFP, CF₃CHF₂ and c-C₄F₈). The authors found that no long-chain PFCAs were detected in the flue gas, except for PFOA, which was present at a very low concentration of 0.2 ng/m³ (when incinerated at

¹¹⁸ <http://data.europa.eu/eli/dir/2010/75/oj>. Further details on best available techniques (BAT) for waste incineration can be found in EU Commission (2019).

¹¹⁹ As noted in the previous subsection, PVDF may exhibit thermal stabilisation at around 460 °C, which has been attributed to the formation of substantial double bonds and cross-linking within the polymer chain. However, Zulfiqar et al. (1994) observed complete weight loss in nitrogen at approximately 800 °C.

1095 °C). Additionally, trifluoroacetic acid (TFA) and the F-gases analysed were not detected downstream of the boiler for heat recovery.

However, the study has several limitations that may affect the conclusiveness of its results: (1) The reported fluorine recovery rates were approximately 80% at 860°C and 70% at 1095°C, leaving a significant portion unaccounted for—likely due in part to the same analytical challenges as those encountered in the earlier study by Aleksandrov et al. (2019) as noted above. (2) The use of a fluoropolymer mixture introduces additional complexity, as different polymers may generate distinct radicals during incineration. These radicals can interact in ways that alter the composition of degradation products, making the results less directly comparable to the incineration of individual fluoropolymers—though they may better reflect real-world incineration scenarios. (3) The study focused primarily on atmospheric emissions, while degradation products may also be present in bottom ash and fly ash (RIVM, 2021; Johansson et al., 2024). For example, as reviewed by RIVM (2021), existing literature indicates that TFE and PFIB, typical degradation products of PTFE, can undergo further thermal breakdown above 700 °C to non-volatile products, along with other gases (C_2F_6 and CF_4 for TFE, CF_4 for PFIB). However, the analysis of these solid residues was limited to long-chain PFASs.

Furthermore, several studies have investigated the presence of PFASs in flue gases and residues from operational waste incinerators. For example, a recent study found PFOA in the flue gases from the incinerator of Harlingen, the Netherlands (Arkenbout, 2016). Johansson et al. (2024) reported the presence of eight perfluoroalkyl acids (PFAAs) in flue gas (3.4–19 ng/m³), liquid residues (46–220 ng/L), and solid residues (0.16–1.5 ng/g) during two monitoring campaigns at a waste-to-energy plant in Sweden. The authors further collected samples of fly ash, bottom ash, and flue gas condensate from 27 of Sweden's 38 waste incineration plants. The sum concentrations of 13 PFAAs ($\Sigma 13PFAA$) ranged from 0.28–180 ng/L in condensate, 0.22–1.6 µg/kg in bottom ash, and 0.18–38 µg/kg in fly ash, with detection frequencies of 79%, 21%, and 30%, respectively. Extractable organic fluorine (EOF) exceeded $\Sigma 13PFAA$ by up to three orders of magnitude—0.70–16 µg F/g in fly ash (n = 3) and <0.80–9.0 µg F/L in condensate (n = 2)—indicating that most fluorine in municipal waste incineration residues remains unidentified. These results suggest that, even at temperatures above 1000 °C, PFAAs and other fluorinated compounds can form or persist and may be released into the environment through such residues, in line with the findings of Solo-Gabriele et al. (2020). Additionally, monitoring studies in the vicinity of incinerators from Czech Republic, Lithuania, Slovakia, Spain, and the Netherlands showed PFASs being emitted into the environment, under actual operating conditions of the incineration plants (Kaunas et al., 2022; Pilsen et al., 2021; Turna and Bodvou, 2024; Turna and Bodvou, 2023; Spanish Basque Country, 2024; Spanish Basque Country, 2019-2023; Harlingen, 2025; Harlingen, 2023-2024). Due to the complexity of waste streams, the specific sources of these detections cannot be traced; however, given the widespread use of fluoropolymers, it is likely that they contribute to the presence of fluorinated compounds in these residues.

Therefore, PFAS emissions from large-scale incineration of fluoropolymers remains partially unclear. There is evidence suggesting that atmospheric emissions may be low from municipal incinerators operating at temperatures of 850 °C or greater, particularly those exceeding 1000 °C.

It remains unclear to what extent other unmonitored substances including PFASs may form in municipal waste incinerators and subsequently be released into the environment—particularly if flue gas, bottom ash, and fly ash are not properly treated. Further investigation that comprehensively analyses degradation products in flue gas, bottom ash, and fly ash, taking into account variations in operating conditions¹²⁰ and waste composition, may be warranted to develop a more complete understanding of the destruction efficiency of organofluorine compounds, including fluoropolymers, during incineration. This information may also inform future modifications and improvements to incineration processes.

¹²⁰ More details on the different incineration technologies can be found in RIVM (2021).

Further work is necessary to determine whether municipal incinerators in other regions consistently operate at temperatures of 850 °C or higher. This may be particularly critical for developing countries and countries with economies in transition, where wastes are often not incinerated to high temperatures and without proper treatment of flue gases due to a lack of adequate facilities, if not openly burned.

Specific cases of recycling post-processing PTFE scraps into micropowders

Furthermore, as noted in Chapter 3, one common approach of re-processing PTFE scraps is to produce micropowder PTFE via irradiation degradation or thermal degradation at approximately 500°C, reducing the molecular chain length to about 1% of its original state. However, the breakdown of polymer chain length may also generate additional degradation products. For example, irradiation degradation using electron beams, widely used commercially in continuous processes (Hintzer and Schwertfeger, 2014), can lead to the formation of substances such as hydrogen fluoride vapor (Lakshmanan and Chakraborty, 2015) and long-chain PFCAs (ECHA, 2020). Additionally, as shown in the Section “*General overview of the thermal degradation of fluoropolymers*” the thermal degradation of PTFE at approximately 500°C may produce a range of degradation products (for examples, see Table 7). These products may be partially released and partially retained within PTFE micropowders. In the EU, processes have been developed to reduce the concentration of PFOA in PTFE micropowders to below the 25 ppb threshold set by the EU POP Regulation, with successful implementation by most PTFE micropowder manufacturers (ECHA, 2020). Similar processes for reducing C₉–C₁₄ PFCA impurities in PTFE micropowders were either under development or had already been implemented (ECHA, 2020). However, the formation and fate of other degradation products remain unclear, including their potential release during processing and the use of micropowders containing them.

6 Environmental releases of fluoropolymers and other associated PFASs along their life cycle

Chapter summary:

Various fluorinated substances, including many PFASs, can be intentionally or unintentionally introduced at each life-cycle stage of fluoropolymers, from monomer synthesis and polymerisation to processing, use, and end-of-life treatment.

- Mass flow analyses show that fluoropolymer production releases various fluorinated substances—including monomers, intermediates, polymerisation aids, byproducts, and polymer particles—some at substantial levels. While emissions in Europe have declined, global releases of potent greenhouse gases such as HFC-23 and c-C₄F₈ remain high due to limited controls. Historical data show significant emissions of PFOA and PFNA before improved abatement after 2002 in developed regions, with slower progress elsewhere. Novel PFASs and byproducts continue to emerge near production sites, underscoring the need for comprehensive, site-specific mass flow analyses covering a broad chemical scope and full system perspective, including solvents, chain transfer agents, coolants, and emissions from waste treatment.
- Environmental measurements show that fluoropolymer production plants are significant sources of PFAS contamination in nearby water, soil, and air, with both legacy (e.g., PFOA) and novel PFASs (e.g., HFPO-DA, ADONA, Cl-PFESAs, EEA) detected. While legacy PFASs are well-studied, data on newer compounds remain limited due to analytical challenges. Contamination patterns vary by region and production methods, and both wastewater and atmospheric deposition contribute to environmental release, underscoring the need for improved monitoring and advanced screening techniques.
- Mass flow analyses of fluoropolymer processing sites show that fluoropolymer solid products emit little PFASs, but dispersion products contain more non-polymeric PFASs that can be released during processing and heating. While thermal steps reduce some PFASs, emissions still occur. Past products had high PFOA residues, now reduced, but limited data show elevated PFAS near processing sites. More mass flow analysis and monitoring are needed to understand environmental releases from fluoropolymer processing.
- Moreover, fluoropolymers can also be present as microplastics, particularly PTFE, in environmental media such as wastewater, sediments, and biota. PTFE microplastics have been found in various global regions, including aquatic environments, where they accumulate in bottom-dwelling species. While PTFE is the most frequently reported fluoropolymer microplastic, there is limited research on other fluoropolymer microplastics and their environmental transport. Future studies are necessary to address these gaps and assess the full scope of fluoropolymer-related environmental contamination.
- Immediate attention is needed to mitigate these releases and further investigate the role of fluoropolymer microplastics in environmental contamination.

Various fluorinated substances, including many PFASs, can be intentionally or unintentionally introduced at each life-cycle stage of fluoropolymers, from monomer synthesis and polymerisation to processing, use, and end-of-life treatment (see Chapters 3 and 5). Many of these substances are highly persistent or degrade into persistent forms. In other words, once introduced, these substances do not simply disappear but may partly remain in products or waste (see Chapter 4) and be partly released into the environment, unless effectively removed through extra purification and emission control measures. Fluoropolymers, like other plastic materials, can also exist as, or degrade into, micro- and nanoplastics, thereby contributing to environmental releases and increased exposure throughout their life cycle. While this report focuses on providing an overview of releases during the life cycle of fluoropolymers, including production and processing, it does not specifically delve into emission control configurations. Readers seeking detailed information on this aspect may refer to other literature such as SPI (2005), Plastics Europe (2021), Chemours (2023b), and Shields et al. (2025).

This section provides a comprehensive overview of existing evidence on environmental releases of fluoropolymers, PFASs, and other fluorinated substances throughout the fluoropolymer life cycle. Two main study approaches have been observed: “bottom-up” mass flow studies, which analyse individual processes to estimate/quantify emissions from specific sources, and “top-down” environmental monitoring, which measures the presence of specific substances in the environment. Each approach has its own strengths and limitations—mass flow studies offer quantitative insights but require detailed process understanding and data, while environmental measurements can detect substances without prior assumptions and provide evidence on environmental accumulation but are harder to interpret or link back to specific sources, particularly in a quantitative manner. These two approaches are complementary and together may provide a more complete picture of environmental releases. The following sections examine each relevant life-cycle stage individually, with evidence from each approach summarized separately.

Quantification of mass flows and environmental releases from fluoropolymer production

Monomer synthesis and polymerisation are combined here under fluoropolymer production, as they are often conducted at the same site and some data sources do not distinguish between releases from each step. As described in Chapter 3, various PFASs and other fluorinated substances may be released during these processes, unless proper emission controls are in place. These may include unreacted raw materials and intermediates from monomer synthesis, unreacted monomers, polymerisation intermediates such as oligomers, and polymerisation aids and other ingredients from the polymerisation process, and reaction byproducts (including degradation products) from both steps. Among them, mass flow information is available for some, but not for others. Dalmijn et al. (2024) reviewed the release of various fluorinated substances from fluoropolymer production sites in Europe, based on site-specific reports to the European Pollutant Release and Transfer Register (E-PRTR) and emission permits (which may include reported emissions or estimated maximum allowable emissions). Several key observations emerged from this review.

A wide range of fluorinated substances have been, and are being, released from these sites (for details, see Tables A H.1 and A H.3 in Annex H). Many releases are expected, such as unreacted raw materials and intermediates (e.g., HCFC-22, HFC-143a), byproducts from monomer synthesis (e.g., HFC-23, PFIB, c-C4F8), unreacted monomers (e.g., TFE, TrFE,¹²¹ HFP, VDF, PMVE, PEVE, PPVE), polymerisation aids (e.g., EEA, HFPO-DA, C6O4, ADV, and 6:2 FTSA), and particles of fluoropolymer themselves.

¹²¹ It is used, e.g., as a co-monomer for VDF-TrFE copolymer (CASRN 28960-88-5, Piezotech™ FC) (Plastics Europe, n.d.).

However, others may be less immediately apparent. Among them, some may be explained by their use as chain transfer agents (e.g., HFC-152a, HFC-32, DIOFE, DIOFB and DIOFH)¹²² and as solvents (e.g., HFC-4310mee, 1H-PFHx) in the polymerisation (see Table 3). Interestingly, the release of HFC-125 is linked to its use as a coolant (Dalmijn et al., 2024), highlighting the need to consider the broader fluoropolymer production system at large, not just the substances directly added to reactors. Additionally, some substances, such as E1, Ether A, and Ether B,¹²³ are either degradation products of HFPO-DA (i.e., E1) or reaction products formed from PFIB and methanol used to mitigate PFIB release (i.e., Ether A and Ether B) (Dalmijn et al., 2024). This underscores the need to consider a broader chemical scope that includes transformation products. Meanwhile, the sources of some other substances such as C₃F₈, C₆F₁₄, HFC-134a, HFC-227ea, and HFC-365mfc remain unclear. Further investigation is needed to determine whether these are linked to fluoropolymer production, other fluorinated gas activities occurring at the same sites, or both.

At the same time, the analysed emission permits do not necessarily account for all expected releases, particularly reaction byproducts from the polymerisation process, such as polyfluorinated carboxylic acids with –CF₂CH₂– repeating units that have been identified near a PVDF production site (Newton et al., 2017) and many others (see further detail below). Notably, only the emission permit for the Syensqo site in Italy includes fluoropolymer particles (Dalmijn et al., 2024), although other sites may also have similar release patterns that are not explicitly reported. This highlights the need to analyse, understand, and report a broader range of substances released from fluoropolymer production sites, potentially by leveraging advances in suspect and non-targeted screening techniques, as noted in several other contexts above.

Quantitatively, one may conclude that the release of various fluorinated substances, particularly those fluorinated gases, from fluoropolymer production sites has occurred at substantial levels. For example, E-PRTR data groups emissions into categories such as HCFCs, HFCs, and PFCs. When summed across these groups, total emissions from these facilities have been significant, though declining from around 500 tonnes in 2007 to about 150 tonnes in 2021, though noting that some of these emissions may originate from on-site production or processing of fluorinated gases.

This observation is in line with other studies estimating global releases of fluorinated gases. For example, based on atmospheric measurements, global emissions of HFC-23 were estimated at 15 900 ± 900 tonnes per year in 2018 (Stanley et al., 2020) and 17 300 tonnes per year in 2019 (SAP, 2024), primarily originating from the production of HCFC-22 (>80 % used as a feedstock for manufacturing TFE and HFP), an amount equivalent to over 200 million tonnes of CO₂ emissions. The same study noted that this large emission figure likely reflects the non-implementation of reported emission control measures in many countries. Additionally, Mühle et al. (2019, 2022) reported that global atmospheric emissions of c-C₄F₈ began in the late 1960s, plateaued at around 1 200 tonnes per year from the late 1970s to the late 1980s, declined to about 800 tonnes per year in the early 1990s to early 2000s, rose sharply to approximately 2 200 tonnes per year in 2017 and about 2 320 tonnes per year in 2020. Mühle et al. (2022) further found a strong correlation between global HCFC-22 feedstock production and inferred global c-C₄F₈ emissions between 2002 and 2019 ($R^2 = 0.97$, $p < 0.01$), supporting that current global emissions of c-C₄F₈ are dominated by HCFC-22 feedstock use. They further estimated an emission factor of 0.3 weight% of c-C₄F₈ emitted per kg of HCFC-22 produced for feedstock use. Rust et al. (2024) further estimated an emission factor of 0.19% for HFC-23 releases from HCFC-22 production at the Dordrecht site in the Netherlands. This value is broadly consistent with the “practicable” emission factor of 0.1% required by abatement projects recently

¹²² DIOFE = 1,2-diiodoperfluoroethane (CASRN 354-65-4), DIOFB = 1,4-diiodoperfluorobutane (CASRN 375-50-8), DIOFH = 1,6-diiodoperfluorohexane (CASRN 375-80-4).

¹²³ E1 = heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether (CASRN, 3330-15-2), Ether A = 2-[difluoro(methoxy)methyl]-1,1,1,3,3,3-hexafluoropropane (CASRN 382-26-3), Ether B = 1-methoxy(perfluoro-2-methyl-1-propene) (CASRN, 360-53-2). Based on their chemical structures, Ether A and Ether B may be expected to act as precursors to PFBA in the environment. (Wang et al., 2014b).

funded by the Multilateral Fund under the Montreal Protocol. If this emission factor were applied to the total global HCFC-22 production, it would result in approximately 1 900 tonnes of HFC-23 emissions annually, about 11% of the latest top-down global average estimate of 16 900 tonnes per year for 2019–2020. Similarly, Rust et al. (2024) derived an emission factor of 0.013 weight% of $c\text{-C}_4\text{F}_8$ per kilogram of HCFC-22 produced for feedstock use. If similar emission control technologies were implemented globally, up to 95% of current global $c\text{-C}_4\text{F}_8$ emissions could be avoided. These comparisons highlight the significant potential for emission reductions through effective control measures.

In contrast, other fluorinated substances, including many PFAS polymerisation aids, have been released at much lower levels. For example, at the AGC site in the UK, EEA was reported to be released at 0.8 tonnes per year to water and less than 0.1 tonnes per year to air, with the company noting the implementation of emission control measures using ion exchange resin to remove EEA from various product and waste streams after polymerisation (Environment Agency, 2023d). At the Chemours site in the Netherlands, permitted and reported emissions of PFOA and HFPO-DA to air and water ranged in the order of several tonnes per year between 1998 and 2018. Since then, permitted levels of HFPO-DA have been progressively reduced to current limits of 0.005 tonnes per year to water, and 0.004 tonnes/year to air, following the implementation of more stringent emission control measures. Similar changes are also observed for the Syensqo site in Italy. At the 3M/Dyneon site in Germany, maximum permitted releases to the Alz River were set at 2.48 tonnes per year for ADONA, 4.65 tonnes for TFA, and 1.55 tonnes for $\text{C}_3\text{--C}_7$ PFCAs. Additionally, the Syensqo site in Italy is permitted to release approximately 13 tonnes of fluoropolymer particles to air annually. Furthermore, it appears that fluoroelastomers may be more prone to atmospheric releases. For example, at the Chemours site in the Netherlands, the permitted emissions from fluoroelastomer (FKM) production (20.6 tonnes per year, primarily HFP, PMVE, and VDF) were nearly four times higher than those from PTFE and FEP production, despite the latter having almost double the production capacity (12 000 vs. 6 800 tonnes per year) (Dalmijn et al., 2024). A similar trend was also observed in the emission permits for the Syensqo site in Italy (Dalmijn et al., 2024). However, the reasoning for this trend is unclear.

While this review of site-specific E-PRTR reports and emission permits provides valuable insights, broader quantitative extrapolation to other regions remains challenging due to the lack of intermediate data such as emission factors reported alongside final results. In contrast, several other mass-flow studies have been conducted by fluoropolymer manufacturers, with the aim of understanding the fate of PFOA during fluoropolymer production, and they are reported in a more comprehensive manner (see Table 8).¹²⁴ The findings of these studies are useful for estimating both past releases of PFOA and potential current releases from those manufacturers that are still using PFOA as polymerisation aids for fluoropolymer production in a similar way without additional emission control techniques (i.e., worst case scenarios). They may also serve as a benchmark for cases where PFAS polymerisation aids replace PFOA, noting that many manufacturers have implemented more stringent emission controls to significantly reduce related emissions, as outlined above.

For example, it was estimated that 86% of consumed PFOA was released from E.I. du Pont de Nemours 's Washington Works at Parkersburg, WV, United States in 1951–1962 (Paustenbach et al., 2007; Wang et al., 2014a). In 1963–1990, fluoropolymer manufacturers did not install facilities to capture PFOA from exhaust gases and wastewater and thus had high emissions (ca. 80% of PFOA consumed). After 1990, E.I. du Pont de Nemours started to recycle PFOA from exhaust gases and wastewater (Paustenbach et al., 2007). For instance, the quantity of PFOA recovered grew from about 1 t/yr in 1992 to about 10 t/yr in

¹²⁴ In 2000, the US EPA opened a non-regulatory public docket file—Administrative Record AR-226—to collect information on PFOS, PFOA, fluorotelomers, and related fluorinated chemicals. At the same time, the Agency began expressing concerns to the global fluorochemical industry. In response, the industry started submitting information to the EPA, all of which was placed into AR-226. Information from AR-226 has not necessarily been vetted. Several data sources referenced here and below are drawn from this Administrative Record.

1997 (Chapman, 1998). In contrast, other manufacturers had not improved their technologies to recycle PFOA (only 2% in 1999) (Pinchot, 2004). In the same period, releases of PFNA at PVDF production sites were estimated to be at the same level, supported by a mass balance study reported by Solvay in 2009 (Solvay, 2009).

Table 8. Reported mass-flow of PFOA in the fluoropolymer manufacturing processes, in weight percent of total annual PFOA consumption

Company	Year	Site	Use [t]	Emission to			Repro-cessed	Destroyed	In prod.	Ref.
				Air	Water	Land				
EIDP**	1951-1962	WV	27	58%	10%	18%	0%	0%	14%	A
	1963-1980		160	42%	18%	22%	0%	0%	18%	A
	1981-1989		237	38%	28%	14%	0%	6%	14%	A
	1990-1999		452	24%	34% ^s	2%	29% *		11%	A
	2000-2003		241	15%	15%	1%	62% *		7%	A
EIDP	1991	WV	32	5%	45%	3%	27% *		16%	B
	2003		57	5%	3%	2%	N.A.	33%	N.A.	C
EIDP	1991	Global	55	10%	68%	3%	6%	2%	13%	D
EIDP	1999		104	14%	36%	3%	23%	12%	13%	E, F
Others	1999		96	15%	49%	13%	2%	1%	21%	E, F
FMG	1999		200	14%	42%	8%	13%	7%	17%	E, F

Notes:

* Includes both reprocessed and destroyed APFO.

** The use amounts here refer to the total amounts consumed in the specific time period, not an average per year.

WV = E.I. du Pont de Nemours (EIDP) Washington Works in West Virginia; FMG = the Fluoropolymers Manufacturers Group, including Asahi Glass (now AGC), Arkema (former Atofina), Solvay (former Ausimont, now Syensqo), Daikin, E.I. du Pont de Nemours & DuPont/Dow Elastomers (DDE, now Chemours), and 3M/Dyneon; Others = FMG excluding EIDP; prod. = products; N.A. = not applicable.

Source: A = Paustenbach et al. (2007); B = Zipfel (2005); C = DuPont (2004); D = DuPont (2005a); E = Pinchot (2004); F = DuPont (2005b)

After 2002, major fluoropolymer manufacturers in the US, Western Europe and Japan greatly improved their technologies to recycle PFOA and PFNA from waste streams (see Tables A G.1. and A G.2. in Annex G). For example, the APFN Work Group in the Plastics Industry Trade Association (SPI) reported a reduction of emissions at PVDF production sites by 49% by 2004 and by 67% by 2006 in comparison to the baseline year 1999–2000 (APFN Work Group, 2003).

Using these mass flow data, Wang et al. (2014a) estimated that global emissions of C₄–C₁₄ PFCAs associated with the use of PFOA and PFNA as polymerisation aids in fluoropolymer production totalled about 1700–9500 tonnes between 1951 and 2002, and 800–4900 tonnes between 2003–2015. These estimates align well with ocean inventories of C₄–C₁₄ PFCAs derived from monitoring studies (Wang et al., 2014a). Similarly, based on recent field data, Wang et al. (2016) estimated the total Chinese annual riverine mass discharges of PFOA to be 16.8–168 t/yr, which corresponds closely with theoretical PFOA emission estimates from PFOA and fluoropolymer production. This suggests that, at the time, there had likely been little to no improvement in emission control at the manufacturing sites in this region.

Fluoropolymer producers worldwide have transitioned, or are in the process of transitioning, to alternative polymerisation aids including non-fluorinated ones, while also implementing more stringent emission control technologies. At the same time, novel PFASs have been identified downstream of fluoropolymer production sites using high-resolution mass spectrometry and non-targeted screening and are hypothesized to be byproducts from different production lines (for examples, see above). These

developments underscore the continued need to conduct and report similarly detailed mass flow analyses at fluoropolymer production sites globally, using a broad chemical scope that includes various fluorinated gases, novel polymerisation aids, curing agents (e.g., bisphenol AF), and their associated byproducts. Notably, non-fluorinated polymerisation aids may lead to the formation of more reaction byproducts (see Chapter 3). Such detailed mass flow analyses should also adopt a broader system perspective, accounting for often-overlooked aspects such as fluorinated chain transfer agents, solvents, coolants, and the treatment of waste streams, including those arising from emission controls¹²⁵ (Dalmijn et al., 2024).

Quantification of PFASs near fluoropolymer production plants

Many studies have reported PFAS contamination in water, sediment, and biota collected near fluoropolymer production plants. Both legacy and novel PFASs have been detected. Legacy PFASs refer to PFCAs and PFSAs, and they have been routinely monitored and well-studied. In contrast, findings on newer alternatives to long-chain PFCAs, e.g., HFPO-DA, ADONA, or Cl-PFESAs (components of the ADV series¹²⁶; see Figure 3) are emerging, but still limited, particularly regarding their occurrence and transport across environmental media. Overall, these findings not only complement mass flow analyses by providing evidence of PFAS contamination but may also reflect the potential accumulation of PFASs in the surrounding environment over time, depending on the environmental media analysed.

This section first presents evidence that fluoropolymer production plants act as sources of PFAS contamination in their vicinity, followed by a brief review of PFAS release from the fluoropolymer production sites, with a focus on novel PFASs. Supporting data on the measurements of legacy and novel PFASs in the vicinity of fluoropolymer production plants are listed in Table A I.1. in Annex I and Table S6 in the separate supporting material file.

Impact of fluoropolymer production sites on nearby environment

Many studies have investigated the impact of fluoropolymer production facilities on their nearby environment. In general, the highest PFAS concentrations have been found around the fluoropolymer production facilities. For example, in France, high concentrations (maximum 176 ng/g dw) of odd-numbered long-chain PFASs (PFUnDA and PFTrDA) were found in sediment samples. This is likely because the river water was receiving discharges from two production plants (Bach et al., 2017). Gebbink et al. (2017) reported that the concentration of HFPO-DA in river water samples upstream of a fluorochemical production plant ranged from <MDL to 22 ng/L. An increase in HFPO-DA concentration in water samples from downstream of the plant was found (6.3 to 810 ng/L), suggesting the fluoropolymer production plant as the main source. Recent studies show that with enhanced emission control technologies, the levels have been significantly reduced (Jonker, 2021). Likewise, elevated PFAS concentration were reported in river water that were collected near a fluoropolymer production plant in UK (Dalmijn et al., 2024), France (Dauchy et al., 2012), Germany and China (Joerss et al., 2020).

In addition to PFAS emission through wastewater discharge into water bodies, atmospheric deposition is another route of transport. Dauchy et al. (2023) examined soils and dust samples within 200 m of a PVDF and fluoroelastomer production facility in France. The authors found that PFUnDA was the predominant PFAS in surface soil (12 to 250 ng/g dw), whereas PFTrDA predominated in outdoor dust (<0.5 to 59 ng/g dw). These were the highest PFCA concentrations reported in ambient soils. It was suggested that wet

¹²⁵ For example, Environment Agency (2023a) estimated that approximately 30 tonnes per year of 1H-PFHx were released across multiple release points in the wastewater treatment process associated with the AGC site in the UK.

¹²⁶ Noting ADV series have been replaced by C6O4 and others non-fluorinated technologies.

and dry atmospheric deposition accounted for the highly contaminated soils.¹²⁷ Similar source-receptor concentration gradient is observed in soils (Galloway et al., 2020) and air (Zhou et al., 2022) near a fluorochemical production facility in the US.

PFAS release from fluoropolymer production plants

HFPO-DA and ADONA are PFOA alternatives used in the fluoropolymer production industry, as stated in Chapter 3. HFPO-DA has been detected in water bodies near production plants in Germany, China and the Netherlands (Heydebreck et al., 2015; Gebbink et al., 2017; Song et al., 2018; Joerss et al., 2020). For instance, Heydebreck et al. (2015) reported that HFPO-DA was the predominant PFAS in the river water near a facility in Germany, with concentration of 73 ng/L. HFPO-DA is also found in water along the coastline of the North Sea (with concentration ~1.0 ng/L), indicating that the compound may be transported from the Rhine-Meuse delta into the German Bight via the water current. Joerss et al. (2020) reported that in Alz River, where water samples were collected near a fluoropolymer production plant, HFPO-DA (mean 29 ng/L) and ADONA (mean 1060 ng/L) were the predominant PFASs.

Figure 4 compares the concentrations of PFOA and HFPO-DA in river water. In European rivers, the levels of HFPO-DA were either higher than PFOA (e.g. river in Netherlands, Alz River in Germany), or the concentrations of two compounds were similar (e.g. Rhine River in Germany). However, in China, PFOA was the predominant PFAS in river water nearby fluorochemical production plants. In the Xiaqing River water samples, the mean concentration of PFOA was 59 000 ng/L, while HFPO-DA was found at a much lower level with a mean concentration of 340 ng/L (Heydebreck et al., 2015). Similar findings in the water samples from the Xi and Yangtze rivers have been reported (Song et al., 2018; Joerss et al., 2020). The different profile of PFASs between Europe and China is due to the different substances employed in the fluoropolymer production process, as described in Chapter 3 above.

Other novel PFASs reported included EEA, which was found in air and surface water nearby the AGC plants in the UK (Dalmijn et al., 2025). Surface water concentration of EEA was up to 1,700 ng/L, which is about 10 times lower than PFOA concentration (maximum concentration 20 600 ng/L). EEA was also found in air collected about 20 km downwind of the AGC plants, with concentrations ranging from 0.28 to 2.0 pg/m³. PFOA in air was similar to EEA, with concentration ranged from 0.69 to 2.5 pg/m³.

A non-target chemical study identified chloro-perfluoro-polyether carboxylates (Cl-PFPECAs, which are components of the ADV series, see Figure 3) in the surface and groundwater near an active fluoropolymer plant in New Jersey (McCord and Strynar, 2020; Washington et al., 2020). The authors estimated that the levels of Cl-PFPECAs exceeded the state drinking water standards for PFOA and PFNA, despite limited data available.

The emissions of PFOA polymerisation aid substitutes (ADV series, cC6O4) have been monitored and determined in the air and groundwater at Spinetta Marengo (Italy), outside the former Solvay, now Syensqo, fluoropolymer plant, by the competent local Environmental Protection Agency (ARPA Piemonte), during the period 2022-2024. Analysis of depositions from the most impacted urban area of Via Genova revealed the presence of cC6O4 at an average of 1.270 µg/m²/day (0.230 to 3.580) and of the ADV series N2 congener at 0.196 µg/m²/day. In 2024, the PM10 fraction showed an average cC6O4 contamination of 1.601 ng/m³ (0.476 to 3.822), and the ADV series (Σ6 congeners) was reported in the range 0.075 - 0.842 ng/m³. The monitoring of the Montecastello groundwater well, which has not been used as a drinking water source since June 2020, showed in 2024 average concentrations of PFOA at 1,467 ng/L (1,190 -1,380), cC6O4 at 292 ng/L (220 - 360), and the ADV series (Σ6 congeners) at 1,000 ng/L (790-1,400). Analyses

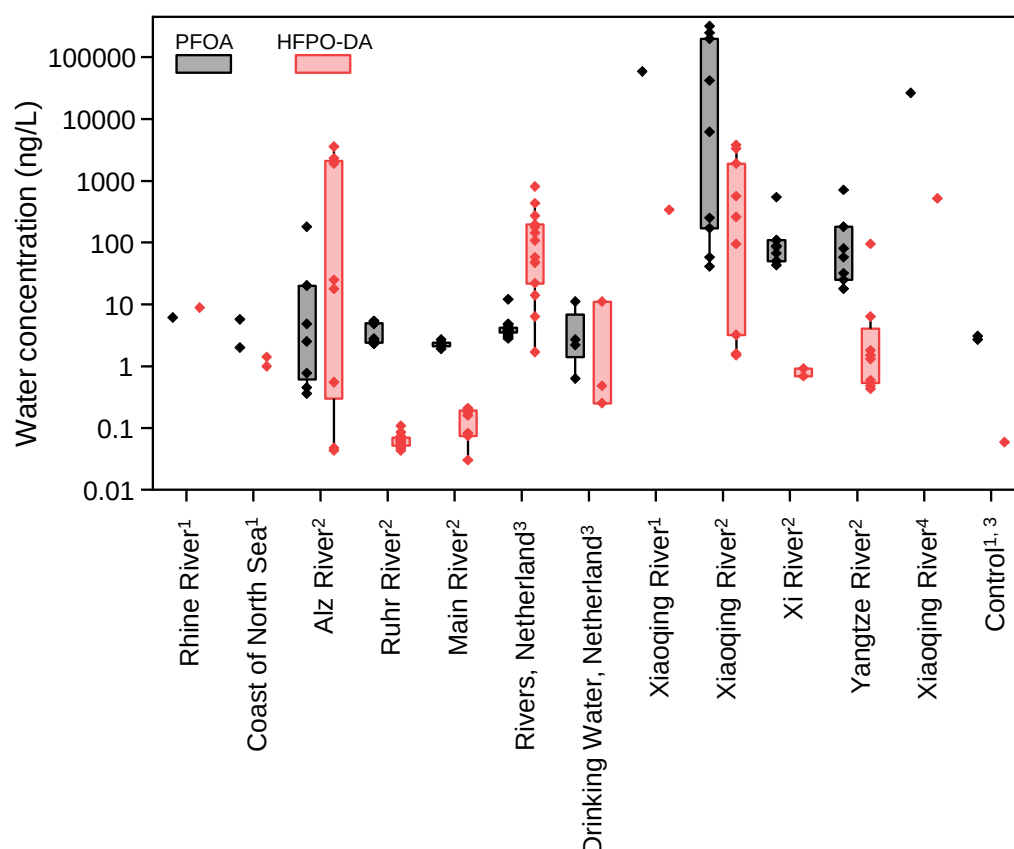
¹²⁷ During the preparation of this report, a stakeholder suggested that the contamination might have been caused by a large industrial fire, which led to the use of large quantities of PFAS-containing fire-fighting foams. This claim remains to be verified.

were carried out upon the availability of analytical standards as reference materials provided by the company (Arpa Piemonte, 2024b).

6:2 fluorotelomer sulfonic acid (6:2 FTSA) may be used in the polymerisation of PVDF. Bach et al. (2017) reported that the maximum concentration of 6:2 FTSA in river water was 52 ng/L in discharges from a manufacturing facility, but it was never detected in the nearby wells. Instead, total PFAS concentration was the highest in the nearby wells with concentrations up to 235 ng/L. Bach et al. (2017) suggested that the reason is that 6:2 FTSA is not mobile in the aquifer and is likely transformed into other PFASs such as PFHxA and PFPeA.

In summary, there is considerable evidence supporting that fluoropolymer production plants are source of PFAS contamination to various environmental matrices. Table A I.1 in Annex I shows that data on the novel PFAS are very limited and scattered. It may partly be due to analytical difficulties as technical standards for performing target quantification for these novel PFAS are not available. Therefore, future studies on the releases of non-polymeric PFASs from the fluoropolymer production sites may continue to be needed, particularly using novel tools such as suspect and non-targeted screening using HRMS to identify and potentially quantify those unknown PFASs. In addition, a clear distinction should be made between historical and current activities.

Figure 4. Concentrations of PFOA and HFPO-DA in rivers in Europe and China



Note: PFOA is shown as black dots/box, and HFPO-DA is shown as red dots/box. Box plot is only shown for the datasets with more than 3 data points. The box represents 25–75th percentile of the data.

Source: References are shown as superscript: ¹Heydebreck et al. (2015); ²Joerss et al. (2020); ³Gebbink et al. (2017); ⁴Song et al. (2018).

Quantification of mass flows and environmental releases from fluoropolymer processing

Mass flow analyses are also available for fluoropolymer processing, though to a more limited extent. Since the levels of non-polymeric PFASs, including low-molecular-weight oligomers and polymerisation aids, in granular and fine powder products are fairly low (as discussed in Chapter 4), emissions from the processing of these fluoropolymer products are expected to be negligible.¹²⁸

In contrast to solid form products, dispersion products contain a rather larger amount of non-polymeric PFASs such as PFOA and other PFAS polymerisation aids. They are processed for a variety of applications, most of which involve a final “sintering” step, where some of the non-polymeric PFASs are thermally decomposed (Lines and Sutcliffe, 1984; Krusic and Roe, 2004), while other PFASs may be introduced (see Chapter 3 and Chapter 5). However, all steps before the final “sintering” step can release non-polymeric PFASs through waste streams. In addition, there are several applications where customers heat the dispersion products to temperatures that allow non-polymeric PFASs to sublime, which results in air emissions. There are also a small number of applications where products are not heated at all, resulting in the non-polymeric PFASs potentially staying in the products such as compressor packing materials and industrial filter fabrics (some finishing might extract those residues that are then treated) (Pinchot, 2004; DuPont, 2005c).

For example, industrial fabric coating facilities apply fluoropolymer dispersions to fabrics, followed by thermal processing to dry and fix the polymer. The targeted coated surface temperatures range from about 100 °C in the bottom drying furnace, to 165–190 °C in the middle baking furnace, and up to 360–400 °C in the upper sintering furnace (noting that these high temperatures may also cause fluoropolymer degradation, see Chapter 5). In a recent study, Wickersham et al. (2023) used a bench-scale three-furnace tower to simulate this industrial coating and thermal processing, analysing releases from PTFE and FEP dispersions. They observed the formation and release of low but measurable levels of C₂F₄, C₃F₆, c-C₄F₈, and E1 for the PTFE dispersion, and CHF₃, C₂F₄, C₃F₆, c-C₄F₈, and E1 for the FEP dispersion under industry-relevant conditions, resulting from the decomposition of the fluoropolymers, other PFASs in the dispersions (e.g., E1 from the decomposition of HFPO-DA), or both. The authors have also derived emission factors but noting that these values require validation through additional studies involving bench-scale systems and process gas emission sampling at commercial facilities.

Table 9 shows more comprehensive global mass-flow analyses of the fate of PFOA residuals in aqueous dispersion products in 2003, which are similar for the estimated fate of PFNA residuals in aqueous dispersion products (Prevedouros et al. 2006). These findings may be useful for estimating both past releases of PFOA and potential current emissions from products still manufactured using PFOA as a polymerisation aid without additional purification (i.e., worst-case scenarios). They may also serve as a benchmark for cases where PFAS polymerisation aids replace PFOA, noting that many manufacturers have implemented more stringent purification steps to significantly reduce related residual content in products.

It should be noted that not all PFOA in waste streams is ultimately released to the environment, since some might be removed/decomposed during various waste treatment processes; but little to no information is available on the amounts potentially removed during waste treatment. Also, based on the survey data in 2003, approximately 15% of the PFOA consumed to make fluoropolymers in the US, Western Europe and

¹²⁸ For example, AGC Chemicals Europe Ltd. estimated that less than 0.1 tonnes per year of 1H-PFHx were released to air from ETFE during thermal processing at downstream user sites (Environment Agency, 2023a). Similarly, assuming a removal efficiency between 41.1% and 99.97%, AGC Chemicals Europe Ltd. estimated that less than 0.1 tonnes per year of EEA were released to air during thermal processing of PTFE (however, the company noted that the EEA releases from the PTFE products supplied to customers is confidential; Environment Agency, 2023d)

Japan in 1951–2002 remained as residues in dispersion products (DuPont, 2005c). After 2002, major manufacturers in the US, Western Europe and Japan developed technologies to reduce residual levels of PFOA, PFOA precursors, and related higher homologues in their aqueous dispersion products (see Tables A F.1 and AF.2 in Annex F). In the same period, a Chinese manufacturer also reported a reduction of residual levels to 40 ppm in its aqueous dispersions (Feng and Su, 2007); but no information from other manufacturers is available.

Table 9. Reported global fate of PFOA residuals in aqueous dispersion products in 2003

Destinations	of total residuals in dispersions
Decomposed in processing	62%
Exhausts streams	16%
Wastewater streams	5%
Solid waste streams	5%
Undetermined *	12%

Note: * The remaining 12% PFOA was mostly used in low temperature processes and its fate was described as “undetermined” in the report ²⁵
Source: Baar et al., 2005

Currently, limited measurements clearly demonstrate PFAS emissions from fluoropolymer processing sites. A review by Gebbink and van Leeuwen (2020) noted PFOA concentrations in local enclosed ponds near Helmond, Netherlands, ranging from 170 to 4,900 ng/L, compared to much lower levels of <20 to 80 ng/L in nearby rivers in 2018. Similarly, HFPO-DA concentrations reached up to 6,800 ng/L in ponds, versus <20 to 50 ng/L in rivers.¹²⁹ Such elevated contamination in ponds have been linked to atmospheric emissions from a local company that processed and dried fluoropolymer dispersions from the production site in Dordrecht, Netherlands, between 1996 and 2017 (Gebbink and van Leeuwen, 2020; RIVM, 2021; Dalmijn et al., 2024). Future studies are needed to monitor and assess additional fluoropolymer processing sites, covering a broad range of PFASs and other fluorinated substances beyond just polymerisation aids. This will help to better understand their contributions to environmental sources and reconcile these findings with mass flow analyses, ultimately enabling a more comprehensive global overview of environmental releases from fluoropolymer processing.

Environmental occurrences of fluoropolymer microplastics

Fluoropolymer may also be present in the form of microplastics (such as fibres, microbeads, films and fragments), with sizes ranging from 5 mm to 1 nm. PTFE materials are the most commonly investigated fluoropolymers in studies characterising microplastics in the environment. This section outlines the detection of fluoropolymer microplastics in various environmental matrices, and supporting data are listed in Table A J.1. in Annex J. Consideration of the potential hazards of these microplastics is not within the scope of this report.

Wastewater treatment plants (WWTPs) are considered as a contributor to the release of microplastics to the environment as effluents containing microplastics are discharged directly to the water bodies. Lee et

¹²⁹ Using the new EFSA health-based limits for PFASs established in 2020, and considering the amounts of PFOA and HFPO-DA ingested through vegetable garden crops based on 2018 measurements, RIVM has advised against consuming crops from the municipality. This recommendation also takes into account additional exposure to these substances from other sources (RIVM, 2021).

al., (2024) analysed the influent and effluent from WWTPs in Republic of Korea revealed that PTFE materials are the predominant component of microplastics, accounting for 46% in the influent. Similar findings were reported in China, in which PTFE materials were one of the most abundant microplastics in water collected near a wastewater outlet (Fan et al., 2022). In ambient water, PTFE has been ubiquitously detected in Han River in the Republic of Korea (Park et al., 2020), and seawater from East Asian Seas (Huang et al., 2022). It is noted that PTFE materials were found at a low percentage of the total MPs identified in most of the above studies (less than 20%).

In drinking water, traces of PTFE microplastics were reported in Spain (Dalmau-Soler et al., 2022). The concentration ranged from 0.02 to 0.08 particles per litre. The presence of PTFE microplastics was potentially related to the use of PTFE tape in the junctions and plugs in the sampling cabinets to prevent water leaking. The sampling cabinets are installed in different sectors of the water supply network that facilitate the routine monitoring of water along the distribution network.

Edo et al., (2020) found PTFE microplastics in sediments from a lagoon which received effluent from a WWTP in Spain. They made up ~23% of the total microplastics. Others have similarly reported PTFE microplastics in ambient sediments from New Zealand (Ribó et al., 2023), Malaysia (Mishira et al., 2023) and India (Nithin et al., 2023), and PVDF in sediments in Gulf of Mexico (Osten et al., 2023).

Most studies on microplastics in biota have focused on aquatic organisms. As PTFE has high density (2.16 g/cm³), it is heavier than saline water and thus settles to the bottom of the water column, accumulates in the sediments, and is likely to be consumed by bottom-feeding species. PTFE microplastics are found in the freshwater fish in the Republic of Korea (Park et al., 2020 and 2022; Kim et al., 2024) and South Africa (Saad et al., 2022), and crab in wetland in Malaysia (Rahim et al., 2023). PVDF microplastics were found in fish from Mexico (Borges-Ramirez et al., 2020) and Saudi Arabia (Khattab et al., 2022).

Kim et al. (2024) discovered that the microplastic types in fish vary by season. For instance, microplastics found in *Z. platypus* were PP > PE > PTFE in the normal season, while PP and PTFE portions in the total microplastics found in fish increased dramatically in the rainy season. The reason for the increased PTFE microplastics in fish collected in the rainy season is related to PTFE density, which easily rises into the stream from the sediment in the rainy season (Park et al., 2022). Hence, the increase of PTFE microplastics concentration in the fish collected in October is strongly associated with the weather.

Moreover, PTFE microplastics have been found in remote regions. González et al., (2020) found PTFE microplastic in stream water in Antarctic, with atmospheric transmission being the most likely source, supplemented by a secondary hypothesis of marine-origin transport. Few studies reported the presence of PTFE or other fluoropolymer microplastics in the atmosphere. Klein and Fisher (2019) revealed that PTFE accounted for a small portion of microplastics in air from Germany. Both PTFE (5%) and PVDF (10%) were found in road dust in China which suggested that they are from the abrasion from tires (Fan et al., 2024), which may be associated with rainwater outfalls to the road.

In conclusion, the most frequently reported fluoropolymer microplastics in the environment are PTFE and only few studies measured others such as PVDF. PTFE microplastics are widely found in water, sediment and aquatic biota, despite not being routinely analysed in microplastic studies. There is a lack of research in the presence of PTFE microplastic in groundwater, landfill leachate, and air. Little is known about the occurrences and transport of other fluoropolymer microplastics. Action is needed to address such information gaps in order to assess their impacts to human and environmental health (Lohman and Letcher, 2023).

7 Overarching summary and options for way forward

This report provides a synthesis of the global fluoropolymer market, exploring the identities and life cycles of fluoropolymers, the presence of other PFASs in commercial products, their degradation throughout various stages of processing, use, and end-of-life treatment, as well as their environmental release and occurrences. Throughout the report, specific gaps in knowledge and data have been identified and discussed in detail. Rather than reiterating these points here, this summary aims to highlight several overarching insights.

A major finding from this study is the highly fragmented and dispersed nature of available information. Data regarding fluoropolymers is scattered across a variety of sources that cover long time periods, including regulatory documents across jurisdictions at the international, national and local levels, a vast array of scientific literature spanning multiple disciplines, technical handbooks, and company-specific documents. While much valuable information has been available for some time, it remains difficult to capture and consolidate it into a comprehensive resource. In light of this, the establishment of a centralized knowledge and data repository for fluoropolymers may be warranted, engaging regulators, industry, scientists from various disciplines and civil society. Such a repository would ensure that relevant information is systematically captured, organized, and made accessible, enabling the synthesis of a clearer, more cohesive understanding of the global fluoropolymer landscape over time.

Additionally, it is important to emphasize the interconnected nature of the various aspects explored in this report—namely, the presence of other PFASs in commercial products, their degradation during processing, use, and end-of-life treatment, and their environmental occurrence. While these issues have been examined separately throughout the report, their interlinkages cannot be overstated. A holistic approach that accounts for the full life cycle of fluoropolymers, from production to disposal, is essential for accurate environmental and health risk assessments. This underscores the need for a mass balance approach that carefully considers the full flows of substances at each stage—by improving access to existing data and knowledge, and by employing comprehensive, robust analytical methods, including suspect and non-targeted screening—ensuring a more complete and accurate evaluation of their impacts.

In conclusion, this report contributes valuable insights into the complexities surrounding fluoropolymers and related chemicals. By recognizing the fragmented nature of existing data, advocating for centralized knowledge-sharing, and promoting a holistic life cycle approach, it is possible to enhance understanding and facilitate more informed decision-making in the future. Further research and collaboration across regulatory, industry and academics will be critical in addressing the remaining gaps and in developing more sustainable practices for the management of fluoropolymers and PFASs in general.

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Annex A. Supplementary information on the identities of fluoropolymers on the market

Table A A.1. Major manufacturers of commercial fluoropolymers* and their known trade names

Fluoropolymers	Manufacturers	Trade names	Forms	Notes
PTFE	Daikin	Polyflon™	Powder, granular, dispersions, micropowders, fibres	
	Chemours	Teflon™ PTFE, Tefzel™		
	3M/Dyneon	Dyneon™ PTFE, Dyneon™ FTM™ PTFE		formerly Hostaflon™ PTFE and Hostaflon™ TFM™ PTFE
	Syensqo	Agloflon™, Polymist™		
	AGC	Fluon™		
PVDF	Arkema	Kynar™, Kynar 500™	Powder, pellets, dispersions, latex	
	3M/Dyneon	Dyneon™ PVDF		
	Syensqo	Hylar™, Solef™		
PVDF (VDF-HFP copolymers)	Arkema	KynarFlex™	Pellets, powder	
	Syensqo	Solef™		
PVDF (VDF-CTFE copolymers)	3M/Dyneon	Dyneon™ PVDF		
FEP	Daikin	Neoflon™	Powder, pellets, dispersions, film, fibres, monofilaments	
	Chemours	Teflon™ FEP		
	3M/Dyneon	Dyneon™ FEP		formerly Hostaflon™ FEP
	AGC	Fluon™		
EFEP	Daikin	Neoflon™		
PFA	Daikin	Neoflon™	Powder, granular, dispersions, fibres	
	Chemours	Teflon™ PFA		
	3M/Dyneon	Dyneon™ PFA		formerly Hostaflon™ PFA
	Syensqo	Hyflon™ PFA		Discontinued in 2024
	AGC	Fluon™		
MFA	Syensqo	Hyflon™ MFA	Powder, pellets, film	Discontinued in 2024
PCTFE	3M	Kel-F™		Discontinued in 1995
	Honeywell	Aclon™, HydroBlock™	Powder, granular,	

	(formerly Allied-Signal)		dispersions	
	Arkema	Voltalef™		
	Daikin	Neoflon™, Daiflon™		Daiflon™ discontinued
ETFE	Chemours	Tefzel™	Powder, pellets, film	
	3M/Dyneon	Dyneon™ ET		formerly Hostaflon™ ET
	AGC	Fluon™		formerly Aflon™ COP (before 2005)
	Daikin	Neoflon™		
ECTFE	Syensqo	Halar™	Powder, pellets	
THV	3M/Dyneon	Dyneon™ THV	Powder, pellets, dispersions	
FEVE	AGC	Lumiflon™		
Amorphous	Chemours	Teflon™ AF	Powder, pellets, film	
Fluoroelastomers based on VDF (FKM)	Chemours	Viton™		
	Daikin	Dai-EI™		
	3M/Dyneon	Dyneon™		
	Syensqo	Tecnoflon™		
	Gujarat	Fluonox™		
	HaloPolymer	Elafter™		
Fluoroelastomers based on TFE and propylene (TFEP/FEPM)	AGC	Aflas™		marketed in the mid-1970s
Fluoroelastomers based on TFE and PAVE (FFKM)	DuPont Specialty Products USA, LLC	Kalrez™		
	Daikin	Perfluor™		
	Syensqo	Tecnoflon™ PFR		
Others	3M/Dyneon	Dynamar™		Polymer polymerisation aids, including various fluoropolymers

Note: * There are other downstream processors/distributors not included in this table, such as Whitford Corp. of West Chester, Pennsylvania under the trade names Dykor™, Eclipse™, Excalibur™, QuanTanium™, Quantum2™, Ultralon™, Xylac™, Xylan™, Xylar™, KC America under the trade name FluoroPlast™, and HeroFlon under the trade name HeroFlon™ (acquired by Daikin in 2017).

Source: Feiring, 1994; Logothetis, 1994; Yamabe and Miyake, 1994; SPI, 2005; Kálin et al., 2012

Annex B. Supplementary information on the production history of major fluoropolymers

A2.1 PTFE

PTFE was discovered in 1938 and first commercialized by E.I. du Pont de Nemours in 1946 under the trade name Teflon™. In the US, the first commercial plant went on stream at Parkersburg, WV in 1950 (Plunkett, 1986), where E.I. du Pont de Nemours produces its Teflon™ granular, fine powder and aqueous dispersion PTFE (Paustenbach et al., 2007). In 1963, Allied Chemical came on stream with a 1400 t/yr plant at Elizabeth, NJ, producing granular PTFE under the trade name Halon™ and also fine powder and aqueous dispersion PTFE later on in 1964 (C&EN, 1964). In 1964, former Thiokol Chemical Co. started a plant at Moss Point, MS, with a production capacity of about 900 t/yr (C&EN, 1964). In 1970, ICI started using the so-called “steam cracker” technology to produce granular PTFE under the trade name Fluon™ at its site at Bayonne, NJ (Powell, 2000). In 1990, Ausimont (formerly a subsidiary of Montedison, acquired by Solvay by the first half of 2002) started operating a new PTFE finishing facility in Orange, TX, which is designed to supply finished grades of material using imported PTFE resin (Ring et al., 2002). In early 1994, Daikin started a plant at the Decatur, AL site (Will et al., 2005). In 1999, Asahi Glass bought ICI’s fluoropolymer assets, including the plant at Bayonne, NJ (Ring et al., 2002), which was closed at the end of 2007 (Kälin et al., 2012). In 2018, Daikin expanded its granular PTFE production capacity by 50 percent at its Decatur, Alabama facilities in the United States (US ITC, 2021).

In Western Europe, ICI Co. started its PTFE production in Widnes, UK under E.I. du Pont de Nemours license at the end of 1947 (Pugachev, 2009). ICI Co. produced 4.6 tonnes of PTFE between April 1947 and August 1948 under the trade name Fluon™ (Powell, 2000). However, due to an explosion at a TFE facility on the Widnes site, its PTFE production suffered a set-back in 1950. In 1953, ICI re-initiated a 20 t/yr pilot plant at the Hillhouse facility and started a 200 t/yr commercial plant on the same site in 1956, which was acquired by Asahi Glass in 1999 (Powell, 2000). In the same period (at the beginning of the 1950s), Montecatini (later Montedison, Ausimont, Solvay and Syensqo since 2023) started its PTFE production at Spinetta Marengo with the trade name Algoflon™ (Gambaretto, 2004). In 1964, ICI doubled its production capacity at the Hillhouse site from 700 t/yr to 1400 t/yr (C&EN, 1964). In the same year, Hoechst started its production of Hostaflon™ PTFE at Gendorf, Germany under E.I. du Pont de Nemours license (Alois, 2006). In 1967, E.I. du Pont de Nemours (now Chemours) initiated its production in Western Europe at the Dordrecht site in Netherland (Consonni et al., 2013). In 1996, 3M and Hoechst formed a joint venture (Dyneon) at Gendorf in Germany, producing Dyneon™ PTFE. This site was purchased by 3M in 1999 (Will et al., 2005). 3M has announced that they will stop production at the Gendorf facility by the end of 2025.

In Japan, Daikin developed and launched its PTFE products under the trade name Daiflon™ in 1955 (Daikin, 2012). In 1965, the joint venture of E.I. du Pont de Nemours and Nitto Chemical started up a plant with a PTFE production capacity of about 900 t/yr at Shimizu (C&EN, 1966). One year later, Mitsui Petroleum Chemicals took over the 50% holding, formerly held by Nitto Chemical (C&EN, 1966). In 1982, the joint ICI-Asahi Glass plant at Chiba came on stream with a production capacity of 1.5 kt/yr (Ring et al., 2002) and commissioned the “steam cracker” technology in 1983 (Powell, 2000). This site was acquired

by Asahi Glass in 1999 (Powell, 2000). In 1983, Daikin established the Kashima plant, where PTFE has been produced on a large-scale since then (Daikin, 2012).

In Russia, research on designing a pilot plant for PTFE production started in 1948 (Baskin et al., 2009). In 1956, the large-scale industrial production of granular PTFE (under the trade name fluoroplastic-4) started at the Kirovo-Chepetsk Chemical Industrial Complex (Baskin et al., 2009). In 1966, Ural Chemical Plant in Perm started to produce fluoroplastic-4 and fluoroplastic-4D (fine powder PTFE) (Baskin et al., 2009). Today, both sites belong to the company HaloPolymer, and it is reported that the two sites produced over 7 kt of fluoropolymers including PTFE in 2010 (HaloPolymer, 2024).

In China, research on PTFE production started at the beginning of the 1960s (Fang et al., 2004). From the 1960s to the 1990s, there was a gradual development of China's fluoropolymer industry. In the late 1990s, the PTFE production started to boom in China through rapid expansion of the following international and domestic producers (Will et al., 2005; Kälin et al., 2012): [i] Shandong Dongyue (built up a 3 kt/yr unit in 2002, expansion to 10 kt/yr in 2004, to 22 kt/yr in mid-2007, and to 30 kt/yr in 2009); [ii] Zhonghao Chenguang (expanded its capacity from 1 kt/yr to 2kt/yr in 2001, to 5kt/yr in 2004, to 10 kt/yr in 2006 and further to 12 kt/yr by 2012); [iii] Jiangsu Meilan (cooperation with Dyneon since 2004, expansion from 1 kt/yr to 2 kt in 2000, to 3kt/yr in 2003, to 6 kt/yr in 2006, and to 10 kt/yr in 2009); [iv] Shanghai 3F (acquired the fluorochemicals business of Shanghai Tianyuan in 2001, expansion from 2.75 kt/yr in 2001 to 5.5 kt/yr in 2004, to 6 kt/yr in 2006, and further to 7.5 kt/yr); [v] Daikin (came on stream in 2004, expansion from 3.5 kt/yr to 7 kt/yr in 2010); [vi] E.I. du Pont de Nemours (came on stream in 2004, with a capacity of 4.5 kt/yr, mainly fine powder and dispersion); [vii] Zhejiang Jusheng (started in 1999, using Russian technology, expansion from 3 kt/yr to 3.95 kt/yr in 2004); [viii] Solvay (started up its PTFE micronized powder plant with a capacity of 2 kt/yr); [ix] Fuxin Hengtong (expansion from 1.1 kt/yr to 1.6 kt/yr in 2001, and to 2 kt/yr in 2002).

There is also some small-scale production in other parts of the world. In Poland, PTFE (under the trade name Tarflon™) was produced at Tarnow in a plant with a capacity of 500 t/yr; however, information about recent activity at this plant is not available (Will et al., 2005). In India, Gujarat Fluorochemicals set up a plant (of Inflon™ PTFE products) with a capacity of 6 kt/yr at Dahej in 2007, while Hindustan Fluorocarbons has an annual capacity of 500 t/yr PTFE (under the trade name Hiflon™) (Kälin et al., 2012).

A2.2 FEP

FEP was first discovered by E.I. du Pont de Nemours in the late 1950s and commercialized in 1960 with the trade name Teflon™ FEP (Teng, 2012). Thereafter, a few producers joined this sub-branch of fluoropolymer production industry (Ring et al., 2002; Will et al., 2005; Kälin et al., 2012). The historical production of FEP is orders of magnitude lower than that of PTFE (Kälin et al., 2012); its production history is also much less reported than that of PTFE in the public domain. In the US, E.I. du Pont de Nemours started its large-scale production of FEP at Parkersburg in 1960–1963, where a production capacity of 10 kt/yr was reached after 1996–1997 (Ring et al., 2002). In the late 1995, Daikin began its production of FEP at Decatur with an initial production capacity of about 1.4 kt/yr, which was expanded to about 4.5 kt/yr in 2000, and further to 6.75 kt/yr by October 2012 (Will et al., 2005; Kälin et al., 2012).

In Western Europe, FEP has been produced by Chemours (formerly E.I. du Pont de Nemours) at Dordrecht, Netherlands (with a production capacity of 3 kt/yr in 2002) and by 3M/Dyneon at Gendorf, Germany (formerly Hoechst; with a production capacity of 2 kt/yr in 2005 and expanded to 5 kt/yr by 2012) (Ring et al., 2002; Will et al., 2005; Kälin et al., 2012).

In Japan, Daikin first industrialized its FEP production at Kashima under the trade name (Neoflon™) in 1962 (with a production volume of 20 tonnes in 1967 and 30 tonnes in 1968) (Su, 1993). The production capacity at this site has reached 4.5 kt/yr by 2002, 5 kt/yr by 2005, and 5.5 kt/yr by 2012 (Ring et al., 2002; Kälin et al., 2012). In 1983, E.I. du Pont de Nemours-Mitsui started its production of Teflon™ FEP at

Shimizu (Su, 1993). The production capacity at this site was 1.4 kt/yr in 2002 and has been expanded to 2.6 kt/yr by 2005 (Ring et al., 2002; Kälén et al., 2012).

In Russia, KCKK (later HaloPolymer) developed FEP synthesis in 1964 (HaloPolymer, 2009). It is unknown when the large-scale production started and what level it reached; however, the company launched a new production line in 2012, which was envisioned to increase the production ten times in the future (Wang et al., 2014a). In China, four producers started large-scale FEP production after 2000 (Kälén et al., 2012): [i] Shandong Dongyue (came on stream in 2005; with a production capacity of 0.5 kt/yr); [ii] Shanghai 3F (expanded its production capacity from 0.8 kt/yr to 1.2 kt/yr in 2007–2008); [iii] Zhejiang Juhua (came on stream in 2004; with an initial production capacity of 0.6 kt/yr and expanded to 1.2 kt/yr by 2007); and [iv] Zhejiang Xingteng (came on stream in 2006; with a production capacity of 0.6 kt/yr).

A2.3 PFA/MFA

PFA was first commercialized by E.I. du Pont de Nemours at Parkersburg in 1972 (Teng, 2012). Later on, [i] Hoechst (later Dyneon, with a swing capacity of up to 0.4 kt/yr) in Western Europe as well as [ii] Daikin (came on stream at Settsu in 1982; with a production capacity of 1 kt/yr in 2002 and expanded to 2.5 kt/yr by 2012), [iii] Asahi Glass (came on stream at Ichihara in 1987; with a production capacity of 1 kt/yr) and [iv] E.I. du Pont de Nemours-Mitsui (came on stream at Shimizu in 1976; with a production capacity of 1.3 kt/yr in 2002 and expanded to 2.6 kt/yr by 2012) in Japan started its PFA production (Su, 1993; Ring et al., 2002; Will et al., 2005; Kälén et al., 2012). In 1988, KCKK (later HaloPolymer) developed PFA synthesis in Russia, but its actual production is not reported (HaloPolymer, 2009). In 1995, Ausimont (later Solvay and Syensqo) commercialized methyl-perfluoroalkoxy polymer (MFA) at Spinetta-Marengo under the trade name Hyflon™, with a capacity of <1 kt/yr by 1998 (Ring et al., 2002; Will et al., 2005; Kälén et al., 2012). Syensqo discontinued the production of PFA and MFA in 2024. Besides the ones listed above, no other producers in other regions are known to produce PFA/MFA.

A2.4 PVDF

PVDF production and consumption took place mainly in the US, Western Europe and Japan, with smaller amount produced in Russia, China, and possibly some other countries, in 1975–2002 (Wang et al., 2014a). Major manufacturers include Arkema (formerly Atochem; under the brand name Kynar™ and Forafon™), Daikin (under the brand name Neoflon™) and Kureha Corporation (formerly Kureha Chemical Industry; under the brand name KF™) (Feiring, 1994). In this period, it was reported that the ammonium salt of perfluorononanoic acid (APFN) was mainly used as a polymerisation aid in the emulsion polymerisation of PVDF (Prevedouros et al., 2006). In 2003–2015, PVDF production in the US, Western Europe and Japan continued to increase steadily in this period, and so did the APFN production and consumption (Wang et al., 2014a). In the same period, producers started a transition, working to eliminate APFN in PVDF production. Arkema (formerly Atofina) commercialized APFN-free KYNAR 500™ product for coating and painting in 2009 (Arkema, 2011). After 2008, PVDF production in China started to boom, in particular after 2010, where the annual production volume reached 10 kt/yr (Kälén et al., 2012). Among all producers in China, the domestic producers do not use APFN, but rather APFO as a polymerisation aid in the production of PVDF (Zhao et al., 2011). In addition, Arkema's new plant in China (with a production capacity of 4 500 t/yr) came on stream in 2011, producing PVDF products such as KYNAR 500™. Arkema production worldwide is now conducted without fluorosurfactants.

A2.5 Fluorinated ionomers

Fluorinated ionomers¹³⁰ were first developed and commercialized by E.I. du Pont de Nemours in the early 1970s, under the trade name Nafion™. They were made of the perfluorinated sulfonic acid ionomer called XR resin, were first employed as a separator in fuel cells that were used in space exploration, and then as ion-exchange membranes that opened the way to the innovative electrolytic process for chlor-alkali production. Flemion™, a type of perfluorinated carboxylic acid membrane, was developed in 1975, and has been commercially produced since 1978 by Asahi Glass. Later on, Asahi Kasei developed Aciplex™, which is characterized as a two-layer membrane having a carboxylic acid layer on the cathode side of the sulfonate membrane and a woven PTFE web embedded in the membrane.

A2.6 Fluoroelastomers based on VDF and CTFE¹³¹

They were first described in 1955, prepared by M.W. Kellogg and Co. under contract to the United States Army Quartermaster Corps, which exhibited solvent and heat resistance superior to any of the then existing elastomers. An even better fluoroelastomer, made from VDF and HFP was described by E.I. du Pont de Nemours and M.W. Kellogg workers shortly afterward, which was then commercialized under the trade name Viton® A. In the same period, 3M acquired M.W. Kellogg and introduced a similar fluoroelastomer under the trade name Fluorel®. A fluoroelastomer based on VDF, HFP and TFE, under the trade name Viton® B, was introduced in the late 1960s with even better solvent and thermal resistance than the previous ones. Also in the 1960s, fluoroelastomers based on VDF and 1H-pentafluoropropylene (PFP) and based on VDF, PFP and TFE were introduced by Mont-Edison Co. (later Solvay and then Syensqo). However, these polymers, under the trade name Tecnoflon®, lacked the stability of similar HFP-containing compositions and were replaced soon after with HFP analogues as the early patents were expired. Daikin Kogyo Co. began production of VDF-based fluoroelastomers (Daiel®) in 1970. In the same time, a fluoroelastomer known as SKF-32 was introduced in the Soviet Union, but had not yet been traded on the world market by the early 1990s. Asahi Glass briefly entered the world market, while in the late 1980s, Nippon Mektron Co. started to make such fluoroelastomers, but for internal use. In the mid-1970s, E.I. du Pont de Nemours Co. introduced VDF-based compositions that contain small amounts of a bromine-substituted olefin as a cure-site monomer. These polymers are curable either with peroxides or dinucleophiles and have the advantage that polymers with higher fluorine content (70 wt%) and better low-temperature performance can be made.

A2.7 Others

FEVE were developed in 1982 as the first solvent-soluble fluoropolymers in the world (Korzeniowski et al., 2023). 3M commercially introduced THV in 1995 (Kälin et al., 2012). Amorphous fluoropolymers were introduced in 1989 by E.I. du Pont de Nemours and Asahi Glass (Kälin et al., 2012).

¹³⁰ For information from Yamabe and Miyake (1994) and references therein, the specific reference is not additionally cited, whereas for information from other sources, the reference is always cited for the specific information.

¹³¹ For information from Logothetis (1994) and references therein, the specific reference is not additionally cited, whereas for information from other sources, the reference is always cited for the specific information.

Annex C. Supplementary information on fluoropolymer production sites

Table A C.1. Non-exhaustive overview of fluoropolymer manufacturing sites

Location	Company	Fluoropolymers
Italy		
Collebeato BS	Daikin (formerly Heroflon S.p.A.)	PTFE compounds and micropowders
Spinetta-Marengo ¹³²	Syensqo (formerly Solvay Solexis SPA)	FKM, FFKM, PFSA, PTFE (discontinued) and MFA (discontinued)
France		
Pierre-Bénite Cedex ¹³³	Arkema	PVDF (emul.)
Pierre-Bénite Cedex ¹³⁵	Daikin Chemical France S.A.S.	High-performance fluoroelastomers
Tavaux ¹³⁴	Syensqo (formerly Solvay Solexis)	PVDF
Villers St. Paul	Chemours	No specific data
Germany		
Burgkirchen ¹³⁵	Dyneon	PTFE, PFA, FEP, ETFE
Burgkirchen	Gore	PTFE, PFA and FEP (Gore, 2023)
Belgium		
Zwijndrecht	Dyneon LLC	Compounding of fluoro-elastomers
Mechelen	Chemours	Teflon coatings
The Netherlands		

¹³² This site uses APFO (unknown–2012), ADV (1996–2021), cC6O4 (2013–present), and VEFS (co-monomer, unknown–present) as polymerisation aids, although it is unclear for which fluoropolymers these polymerisation aids were or are used (Dalmijn et al., 2024). This site also uses thermal oxidation for air emission abatement, with emission permits from 2010 and 2021 for air and water, respectively.

¹³³ This site produces 8 kt/year PVDF and 3.65 kt/year FKM, using APFO (for PTFE, 1965–1986; for FKM, 2004–2008), Surflon S-111 (for PVDF, 2003–2016), 6:2 FTSA (for PVDF, 1973–present), and PFHxA (for FKM, 2008–present) as polymerisation aids, and using unknown system for water emission abatement (Dalmijn et al., 2024). In addition to PVDF, Arkema produces a mixture of different H(C)FCs at the site (Dalmijn et al., 2024).

¹³⁴ This site produces 34 kt/year PVDF, but it is unknown if and which fluorosurfactants have been used. This site uses thermal oxidation for air emission abatement, and with an emission permit from 2011 for air and water (Dalmijn et al., 2024). In addition, Syensqo produces the blowing agent HFC-365mfc at the site (Dalmijn et al., 2024).

¹³⁵ This site produces 17 kt/year PTFE, PFA, PFPEs, ETFE, THV and FKM together, using APFO (all emulsions, 1968–2008), MV31/DONA and ADONA (all emulsions, 2008–present) as polymerisation aids (Dalmijn et al., 2024).

Dordrecht ¹³⁶	Chemours	PTFE, FEP, FKM
Oss	Daikin chemical Netherlands B.V.	Pre-compounded base-polymers (i.e. processing of fluoroelastomers)
Poland		
Tarnow	Zakłady Azotowe, Poland	PTFE (Tarflen)
UK		
Thornton-Cleveley, Lancashire ¹³⁷	AGC	PTFE (emul. + sus.), ETFE, PFA, PTFE micropowders
United States		
Bayonne, NJ (closed in 2007)	AGC	PTFE
Calvert city, KY	Arkema	PVDF (emul.)
Orange, TX	Syensqo	PTFE (not anymore), ETFE
Thorofaro, NJ	Syensqo	PVDF (emul.)
Decatur, AL	3M/Dyneon (formerly Solvay)	PVDF (sus.)
Decatur, AL	Daikin	PTFE, FEP
Parkersburg, WV	Chemours	PTFE, FEP, PFA
Japan		
Ichihara, Chiba Prefecture	AGC	PTFE (including micropowders), PFA
Kashima, Ibaraki Prefecture	Daikin	PTFE, FEP
Settsu, Osaka Prefecture	Daikin	PTFE, PFA, PVDF
Shimizu, Shizuoka Prefecture	Chemours	PTFE, FEP, PFA
Ube, Yamaguchi Prefecture	Central Glass	PVDF
Iwaki, Fukushima Prefecture	Kureha Corporation	PVDF
China		
Changshu, Jiangsu	Arkema	PVDF
Changshu, Jiangsu	Daikin	PTFE
Changshu, Jiangsu	Chemours	PTFE
Changshu, Jiangsu	Syensqo	PTFE micropowders
Changshu, Jiangsu	Kureha Corporation	PVDF
Changshu, Jiangsu	Changshu Xinhua Chemical Co., Ltd.	PVDF
Zigong, Sichuan	Chenguang Research Institute of	PTFE, PVDF

¹³⁶ This site produces 8.5 kt/year PTFE, 3.5 kt/year FEP and 6.8 kt/year FKM, using APFO (for PTFE and FEP, 1967–2012), 6:2 FTSA (for FKM, unknown–present), and HFPO-DA (2012–present), using activated carbon scrubbing for air and water emission abatement, and with emission permits from 2022 for air and water (Dalmijn et al., 2024). In addition, Chemours loads and blends various fluorinated gases in canisters and tanks at the site (Dalmijn et al., 2024).

¹³⁷ This site produces 4 kt/year PTFE and 2 kt/year ETFE, using APFO (for PTFE, 1952–2012) and EEA (for PTFE, 2012–present) as polymerisation aids, using thermal oxidation for air emission abatement, and with an emission permit from 2017 for air and water (Dalmijn et al., 2024).

	Chemical Industry	
Fuxin, Liaoning	Fuxin Fluorous Chemical Co, Ltd.	PTFE (emul.)
Taizhou, Jiangsu	Jiangsu Meilan Chemical Group Corporation	PTFE
Jinan, Shandong	Jinan 3F Fluorochemical Co., Ltd.	PTFE/FEP (sus.)
Shanghai	Shanghai 3F New Materials Co., Ltd	PTFE, PVDF, FEP
Quzhou, Zhejiang	Zhejiang Juhua Stock Co., Ltd.	PTFE, FEP
Zibo, Shandong	Shandong Dongyue Chemical Co., Ltd.	PTFE, FEP, PVDF
Fengzhen, Inner Mongolia	Inner Mongolia Wanhao Fluoro Chemical Co., Ltd.	PVDF
Jinhua, Zhejiang	Zhejiang xingteng Chemical Co., Ltd.	FEP
Russia		
Perm	HaloPolymer	PTFE
Kirovo-Chepetsky	HaloPolymer	PTFE
India		
Dahej, Gujarat (since 2007) + another site	Gujarat	(Astute Analytica, 2021)
Rudraram	Hindustan Fluoro	PTFE
Morocco		
	Gujarat	(Astute Analytica, 2021)

Note: Emul. = emulsion polymerisation; sus. = suspension polymerisation

Source: Kälin et al., 2012; AGC, 2020a; Daikin, 2020; Baua et al., 2023

Annex D. Supplementary information on the replacement of fluorinated polymerisation aids in fluoropolymer production

Table A D.1. Some reported characteristics of the replacement fluorinated polymerisation aids

	Use	Processing of respective fluoropolymers in the context of food contact materials	Physiochemical characteristics	Residual levels in the final products	Source
HFPO-DA (CASRN 13252-13-6)	Used as a polymer production/surfactant aid during emulsion polymerisation of fluoropolymers	These materials are processed at high temperatures (265°C–420°C) to produce items such as tubing, gaskets, seals, pipes, conveyor belts and similar items as well as coatings used on repeated use articles such as frying pans or baking articles. For coatings, the maximum use temperature is about 260°C during frying applications. During baking the temperature at the food/coating interface (not the oven temperature) will most likely not exceed 175°C.	The substance completely decarboxylates under the high temperatures of the production process to a heat stable and volatile product.	Due to the high volatility of the decarboxylation product, the applied thermal treatments of the polymers reduce the amount of the product to very low levels. The residual content of this decarboxylation product was determined, and the worst-case migration was calculated using the total mass transfer assumption. For a number of typical polymer applications, these calculations indicated migration to be 5 µg/kg in food or less.	EFSA CEF Panel (2009)
Krytox™ 157FSH (CASRN 5179-33-5)	Used as a polymer production aid during emulsion polymerisation of fluoropolymers	These materials are processed at high temperatures (265°C - 420°C) to produce items such as tubing, gaskets, seals, pipes, conveyor belts and similar items	It is manufactured from HFPO and has a MW distribution between 600 and 12000 Da. The	The residual content of this product was determined, and the worst-case migration was calculated using the total mass transfer assumption. For a number of typical polymer applications, these calculations indicated migration from 2 to 26 µg/kg in food for the	EFSA CEF Panel (2009)

		as well as coatings used on repeated use articles such as frying pans or baking articles. For coatings, the maximum use temperature is about 260°C during frying applications. During baking the temperature at the food/coating interface (not the oven temperature) will most likely not exceed 175°C.	highest fraction of oligomers with MW <1000 Da is 13.5%. It completely decarboxylates during the production process to form a defined heat stable product, starting at >150°C.	fraction below 1000 Da. Considering that perfluorinated substances have a smaller size to mass ratio than their non-fluorinated counterparts, these calculations were also made for the fraction below 1500 Da, for comparison. The calculated migration was very slightly higher at levels from 2 to 29 µg/kg.	
ADV Series (CASRN 329238-24-6)	Up to 0.5 weight% as an emulsifier and as a dispersing agent for processing fluorinated polymers.	These polymers are processed at high temperatures (340–400°C) and extruded or moulded to make parts for food processing equipment (fittings, valves) and food contact articles such as tubes, sheets, and tape. The polymers can also be applied as antistick coatings onto cooking utensils for which they are baked on and/or sintered at high temperatures up to 420°C for up to 10 minutes.	It is expected to be stable to heat and not to react with food constituents, but it is volatile and is completely evaporated at 190°C.	A polymer sheet of 400 µm thickness was taken as an example of materials and articles made using the substance. The sample was processed at the lower end of the temperature range used for such fluoropolymers (340–400°C) and therefore it is considered to be a worse case for the residual level of the substance and for any impurities. The polymer sheet was extracted using solvents and neither the substance nor any substance derived impurities were detected at the detection limit of 11 µg/kg of solvent.	EFSA CEF Panel (2010)
ADONA (CASRN 958445-44-8)	Used as an emulsifier in the production of various fluoropolymers	Coatings are sintered to surfaces using temperatures between 300–380°C for approximately 10 minutes. The producer recommends at least 280°C for 10 minutes to achieve the desired effect. Likewise, other articles made from these polymers are also produced by sintering. In rare cases, single-use articles and unsintered applications are	It is volatile and starts to thermally degrade at 125°C with completion at 175°C. Decomposition leads to formation of more volatile substances.	The decomposition products as well as the substance itself are expected to be removed from the polymer during thermal processing (high temperature extrusion, baking or sintering) into a final article. For examples, no residual was detectable in samples spiked with the substance at a detection limit of 0.02 mg/kg in the final material after sintering. For an unsintered fluoropolymer micropowder, a residual concentration of 3.3 mg/kg of the substance was determined. It would be only used for polyoxymethylene (POM) blends at a maximum level	EFSA CEF Panel (2011b)

		foreseen.		of 30%, and worst-case migration was calculated to be 31 µg/kg food. However, in view of the volatility and when considering compounding and extrusion conditions of approximately 200°C, effective removal of the substance and negligible migration potential is expected.	
EEA (CASRN 908020-52-0)	Used as an emulsifier during polymerisation of PTFE in amounts up to 0.83 weight% polymer	These polymers are processed at high temperatures (sintering), typically 380°C for one hour or more and in the case of coatings or thin articles up to 430°C for 10 minutes	The substance is volatile and is completely evaporated and in a very small part decomposed into volatiles at temperatures up to 250°C.	It can be expected that any post-polymerisation residual content of the substance is efficiently removed during thermal processing (high temperature extrusion, baking or sintering) into a final article.	EFSA CEF Panel (2011c)
TFEE5 (CASRN 37486-69-4)	Used as a polymer production aid (PPA) in the manufacture of various fluoropolymers	Most articles made from fluoropolymers are sintered typically at 360°C for ca. 10 minutes. Non-sintered articles are processed at temperatures higher than the melting point of the respective material at around 300°C for polyfluorinated and typically around 360°C for perfluorinated polymers for ca. 10 minutes.	Decomposition of the substance starting from 370 °C.	The substance could, as a result of the manufacturing process, contain impurities up to 10% in total by mass; the main impurities are structurally related to the substance. Due to the perfluorinated character of the substance, degradation products which may be formed at this temperature are expected to be volatile and removed from the polymer during this sintering/processing step. The residual content, expressed as the sum of TFEE5 and TFEE6. After processing at 300°C for ca. 10 minutes, residual content was 0.4 mg/kg polymer.	EFSA CEF Panel (2012)
C6O4 (CASRN 1190931-27-1)	Used as an emulsifier / dispersing agent during polymerisation process of fluoropolymers such as PTFE and others.	Manufacturer of these articles includes high temperature treatments during extrusion, baking or sintering at 380°C and higher for several minutes.	The substance is thermally unstable and starts to decompose at 138–140°C with complete decomposition at	Due to the high temperatures (ranging from 380–420°C) applied for manufacture of food contact articles, it can be expected that both the substance itself as well as the decomposition products are efficiently removed during thermal processing (high temperature extrusion, baking or sintering) and not	EFSA CEF Panel (2014)

			230°C. The two volatile degradation products have been identified.	present anymore in the final articles. Concerning the impurities of the substance, the major impurities (ca 2 %) are structurally related to the substance itself and are expected to decompose thermally in an analogous way. The minor impurity (ca 0.7 %) is a byproduct of the substance synthesis and is expected to be volatilised and lost during the high temperature processing conditions of the fabricated articles.	
C6 fluorotelomer compounds	Used as process media in the production of several fluoropolymers (including fluoroelastomers) and PFPEs	-	-	The threshold of 25 ppb and 1000 ppb for PFHxA and PFHxA-related substances cannot be achieved by fluoropolymers produced with a C6 process medium. Within the framework of the REACH restriction process, the manufacturer requested a higher impurity threshold than 150 ppm for both PFHxA and related compounds in products.	AGC, (2020a, 2020b)
PFHxA	Used in the production of several fluoropolymers (including fluoroelastomers)—mainly for polymerisation, but also as stabilizers (for fluoroelastomers)	-	-	Within the framework of the REACH restriction process, the manufacturer requested a higher impurity threshold than 150 ppm for both PFHxA and related compounds in products (an actual value is proposed based on its measurements by CEN/TS15968, but is not made publicly accessible).	Daikin (2020)
HFPO-TA	Used as a polymerisation aid in fluorinated polymer production ¹³⁸	-	-	-	Pan et al. (2017)

Note: MW = molecular weight.

¹³⁸ In 2017, high concentrations of HFPO-TA (68.5 µg/L) were first reported in water samples from the Xiaoqing River in China, at levels 30 times higher than that of HFPO-DA (2 100 ng/L) and ranking only second to PFOA among all PFASs measured, with an estimated annual discharge of 4.6 tonnes. HFPO-TA has also been detected in animals and residents living near fluoropolymer plants (Pan et al., 2017).

Annex E. Supplementary information on the production and use volumes of fluoropolymers

Table A E.1. Global exports of PTFE resin in 2017 to 2020

[tonnes]	2017	2018	2019	2020
United States	10817	10456	14172	8893
India	9876	11101	11317	10382
Russia	7032	8800	6510	9004
China	24982	22908	21535	34218
Saudi Arabia	39	99	15056	N.A.
Germany	10251	11607	10031	9041
Italy	10528	11293	9999	8371
Netherlands	7706	8721	7512	612
Japan	4938	4584	4904	4258
Belgium	5925	5264	4798	3772
United Kingdom	2854	3107	2785	2430
Malaysia	N.A.	24	684	908
Republic of Korea	480	843	871	904
All other exporters	2830	6070	3595	2893
All reporting exporters	98263	104858	113090	101206

Source: US ITC, 2021, 2022

Table A E.2. Estimated tonnages of sum fluoropolymers used in European Economic Area (EEA) in 2020 (Baua et al., 2023) in comparison to the values reported in Wood (2022) in brackets.

Industrial sectors/applications	Estimated tonnages of sum fluoropolymers used in EEA in 2020		
	Lower estimates [t/yr]	Mid points from the lower and higher estimates [t/yr]	Higher estimates [t/yr]
Automotive and road transport			
In new road vehicles	6410	10531 (15500)**	14653
In stock	87216	154712	222208
Building & Construction			

Total	4254	7287	10320
Electronics + Photolithography & semiconductor			
Total	1551	2807 (3500)	4063
Energy + nuclear industry			
Total	2590	2754	2917
Food processing			
Industrial food production	3000	4500	6000
Beverage can coating	4880	4880	4880
Household and cleaning products			
Consumer cook and bakeware	3500	4550 (2000)	5600
Lubricants			
Micropowder PTFE additive	800	1000	1200
Medical products			
Coatings in medical devices	3233	7633 (500)	12032
Oil and gas			
Total	3500	5500	7500
Textiles (upholstery, carpets), leather, and apparel*			
Home textiles	4658	13354	22049
Consumer apparel	5801	19077	32353
Professional apparel	5119	12031	18943
Technical textiles	4845	13252	21659
Medical textiles	331	714	1096
Others	11551	11657	11762
Total	32305	70083	107861
Miscellaneous			
Manufacture of metal products	960	960	960

Note: * Home textiles include carpets and rugs, curtains and blinds, and textile-based coverings (e.g., fabrics for soft-furnishings, tablecloths, bedding). Consumer apparel includes indoor and outdoor wear, sportswear, footwear, and accessories (e.g., umbrellas, bags, wallets). Professional apparel includes professional sportswear and footwear, personal protective equipment (PPE) for industrial and professional use (other than sportswear). Technical textiles include outdoor technical textiles (e.g., canvas, awnings, tarps, tents, sails, rope) and high-performance membranes (e.g., automotive and medical). Medical textiles include surgical drapes, gowns and curtains. Others include home fabric treatments (sprays) for leather/textiles. Noting that for textile surface treatment, side-chain fluorinated polymers have been used, but not fluoropolymers.

** Values in brackets are from Wood (2022). However, sector definitions in Wood (2022) may not fully align with those in Baua et al. (2023), so comparisons should be interpreted with caution.

Table A E.3. Estimated tonnages of individual fluoropolymers used in EEA in 2020

Industrial sectors / fluoropolymer types	Estimated tonnages used in EEA in 2020	
	Lower estimates [t/yr]	Higher estimates [t/yr]
Textiles (upholstery, carpets), leather, and apparel		
PTFE	15202	68465
PVDF	1058	5082
FEP	55	189
PFA	7	21
Others	15984	34104

Source: Baua et al., 2023

Annex F. Supplementary information on the reduction of PFOA levels in dispersion products

Table A F.1. Reported (2006–2012) and estimated (2013–2015, in *italic*) reductions of PFOA residual levels in dispersion products made in the United States, in % of the level of baseline year (in parentheses)

Company	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Asahi Glass (2000)	12%	63%	100%	100%	100%	100%	100%	<i>100%</i>	<i>100%</i>	<i>100%</i>
Daikin (2000)	34%	99%	99%	95%	95%	>97.5%	>97.5%	<i>100%</i>	<i>100%</i>	<i>100%</i>
EIDP (2003)	44%	96%	99%	99%	99%	99%	99%	99%	99%	99%
Dyneon (1999)	100%	100%	100%	100%	100%	100%	100%	<i>100%</i>	<i>100%</i>	<i>100%</i>
Solvay (2000)	59%	59%	98%	99%	99%	99%	99%	<i>100%</i>	<i>100%</i>	<i>100%</i>

Note: N.A. = not applicable. Noting that some reduction may have been caused by replacement of polymerisation aids from PFOA to its alternatives.

Source: US EPA, 2024b

Table A F.2. Reported (2006–2012) and estimated (2013–2015, in *italic*) reductions of PFOA residual levels in dispersion products made in non-US countries, in % of the level of baseline year (in parentheses)

Company	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Asahi Glass (1999)	23%	43%	54%	78%	98%	100%	100%	<i>100%</i>	<i>100%</i>	<i>100%</i>
Daikin (2000)	76%	95%	95%	95%	95%	95%	95%	<i>100%</i>	<i>100%</i>	<i>100%</i>
EIDP (2003)	25%	88%	95%	94%	99%	99%	99%	99%	99%	99%
Dyneon (2000)	91%	99%	99%	100%	100%	100%	100%	<i>100%</i>	<i>100%</i>	<i>100%</i>
Solvay	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.

Note: N.A. = not applicable. Noting that some reduction may have been caused by replacement of polymerisation aids from PFOA to its alternatives.

Source: US EPA, 2024b

Annex G. Supplementary information on the emission reductions of PFOA, PFOA precursors and related higher homologues at fluoropolymer production sites

Table A G.1. Reported (2006–2012) and estimated (2013–2015, in *italic*) emission reductions of PFOA, PFOA precursors and related higher homologues at fluoropolymer production sites in the United States, in % of the level of baseline year (in parentheses)

Company	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Asahi Glass (2000)	6%	4%	100%	100%	100%	100%	100%	<i>100%</i>	<i>100%</i>	<i>100%</i>
Daikin (2000)	94%	99%	99%	95%	95%	>97.5%	>97.5%	<i>100%</i>	<i>100%</i>	<i>100%</i>
EIDP (2000)	98%	98%	99%	99%	99%	99%	99%	<i>99%</i>	<i>99%</i>	<i>99%</i>
Dyneon (1999)	100%	100%	100%	100%	100%	100%	100%	<i>100%</i>	<i>100%</i>	<i>100%</i>
Solvay (2000)	N.A.	14%	36%	39%	97%	100%	100%	<i>100%</i>	<i>100%</i>	<i>100%</i>

Note: N.A. = not applicable. Noting that some reduction may have been caused by replacement of polymerisation aids from PFOA to its alternatives.

Source: US EPA, 2024b

Table A G.2. Reported (2006–2012) and estimated (2013–2015, in *italic*) emission reductions of PFOA, PFOA precursors and related higher homologues at fluoropolymer production sites in non-US countries, in % of the level of baseline year (in parentheses)

Company	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Asahi Glass (1999)	39%	60%	61%	86%	96%	98%	<i>100%</i>	<i>100%</i>	<i>100%</i>	<i>100%</i>
Daikin (2000)	90%	40%	85%	85%	95%	>97.5%	>97.5%	<i>100%</i>	<i>100%</i>	<i>100%</i>
EIDP (2000)	86%	93%	96%	97%	96%	97%	97%	<i>97%</i>	<i>97%</i>	<i>97%</i>
Dyneon (2000)	74%	91%	93%	100%	100%	100%	100%	<i>100%</i>	<i>100%</i>	<i>100%</i>
Solvay	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<i>N.A.</i>	<i>N.A.</i>	<i>N.A.</i>

Note: N.A. = not applicable. Noting that some reduction may have been caused by replacement of polymerisation aids from PFOA to its alternatives.

Source: US EPA, 2024b

Annex H. Supplementary information on the PFAS releases from fluoropolymer production sites

Table A H.1. Emissions of fluorinated gases (kg / year) in the municipalities of Tavaux/A-la-Ronce, France (Syensqo's production site) and Pierre-Bénite, France (Arkema's and Daikin's production sites) from INERIS database

[kg / year]	Tavaux, France*			Pierre-Bénite, France**		
	2004	2007	2012	2004	2007	2012
C ₃ F ₈ (CASRN 76-19-7)	0.1	0	0	0.1	0	0
C ₆ F ₁₄ (CASRN 355-42-0)	18	0	0	4	0	0
HFC-125 (CF ₃ CF ₂ H, CASRN 354-33-6)	30	144	110	9835	5811	3015
HFC-134a (CF ₃ CFH ₂ , CASRN 811-97-2)	582	762	479	13760	6190	6427
HFC-143a (CF ₃ CH ₃ , CASRN 420-46-2)	1302	1359	83	19170	10960	8094
HFC-152a (CF ₂ HCH ₃ , CASRN 75-37-6)	14	39	23	29	61	46
HFC-227ea (CF ₃ CFHCF ₃ , CASRN 431-89-0)	257	289	334	131	18	175
HFC-23 (CF ₃ H, CASRN 75-46-7)	11	12	14	26070	17700	5608
HFC-32 (CF ₂ H ₂ , CASRN 75-10-5)	4	13	30	5439	883	817
HFC-365mfc (CF ₃ CH ₂ CF ₂ CH ₃ , CASRN 406-58-6)	2475	1373	24	10	1380	1221
HFC-4310mee [CF ₃ (CFH) ₂ C ₂ F ₅ , CASRN 138495-42-8)	16	20	4	31	41	8
Sum	4709	4011	1102	74479	43173	25410

Notes: All numbers have been rounded up to the nearest integer, except for those below 1

* Syensqo have also produced HFC-365mfc at this site, which may have contributed to some of the H(C)FC emissions listed here.

** At this site, Arkema and Daikin share infrastructure, and thus, were considered together. Arkema have also produced a mixture of different H(C)FCs at this site (Dalmijn et al., 2024), which may have contributed to some of the H(C)FC emissions listed here.

Source: Dalmijn et al. (2024).

Table A H.2. Substances mentioned on the emission permits of European producers with substance specific information

	PFASs	Other fluorinated substances
AGC site at Thornton-Cleveleys, UK	HFP, HFC-125, EEA-NH ₄	TFE, TrFE, HCFC-22, HFC-23
Chemours site at Dordrecht, Netherlands*	HFP, PFC-318, PFIB, PMVE, PPVE, PEVE, HFC4310-mee, E1, Ether A/B, PFAC, HFPO-DA, 6:2 FTSA, C ₄ -C ₁₄ PFCAs, PFBS	TFE, VDF, HCFC-22, HFC-23, H(C)FCs
Syensqo site at Spinetta Marengo, Italy	HFP, PFIB, PFC-318, PFOA**, PMVE, PPVE, DIOFB, DIOFH, inert particulate fluoropolymers, cC6O4***, ADV***, FSVE***	TFE, VDF, HCFC-22, DIOFE

Note: TrFE = trifluoroethylene (CASRN 359-11-5), E1 = heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether (CASRN, 3330-15-2), Ether A = 2-[difluoro(methoxy)methyl]-1,1,1,3,3,3-hexafluoropropane (CASRN 382-26-3), Ether B = 1-methoxy(perfluoro-2-methyl-1-propene) (CASRN, 360-53-2), PFAC = perfluoroallylchloride (CASRN 2804-50-4), DIOFE = 1,2-diiodoperfluoroethane (CASRN 354-65-4), DIOFB = 1,4-diiodoperfluorobutane (CASRN 375-50-8), DIOFH = 1,6-diiodoperfluorohexane (CASRN 375-80-4), and FSVE = perfluoro-2-(vinylxy)ethane-1-sulfonic acid (CASRN 29514-94-1).

* While Chemours loads and blends various fluorinated gases in canisters and tanks at this site, the values here are reported in the emission permit per substance and emission point, and thus, are linked to fluoropolymer production.

** currently phased out

*** mentioned in an addition to the original permit

Source: Dalmijn et al. (2024)

Table A H.3. Overview of the permitted and reported air emissions of PFASs and other fluorinated substances (t / year) on the emission permits of various fluoropolymer production sites

Substance Use	Substance	AGC (Thornton- Cleveleys, UK)	Chemours (Dordrecht, Netherlands)	Syensqo (Tavaux, France)**	Arkema-Daikin (Pierre-Bénite, France)***
Monomer production	HCFC-22	2.35	1.98	unknown	unknown
	HFC-23	1.75	40.32	-	15.4
	HFC-32	0.35	-****	-	-
Monomers	TFE	12	8.9	7.5	unknown
	HFP	5	19.1	unknown	12.18 (by Daikin)
	VDF	-	1.02	unknown	unknown
	TrFE	7	-	-	-
	PMVE	-	3.8	unknown	-
	PEVE/PPVE	-	0.139	unknown	-
Monomer production byproducts	PFIB	unknown	0.056	unknown	unknown
	PFC-318 (c-C ₄ F ₈)	unknown	2.53	unknown	unknown
Chain transfer agents	DIOFE	-	-	unknown	-
	DIOFB	-	-	unknown	-
	DIOFH	-	-	unknown	-
Coolant	HFC-125	0.35	-****	-	-
Various uses	(H)(C)FCs and halons	-*****	54.231	unknown	34.9 (HCFCs), 29 (HFCs), 0.152 (CFCs), 0.889 (BTFM)
Byproducts	Ether A/B	-	21	-	-

	PFAC	unknown	1.4	unknown	unknown
Solvents	HFC-4310mee	-	0.9	-	-
	1H-PFHx	30.9	-	-	-
Fluorosurfactants	EEA	<0.1	-	-	-
	HFPO-DA	-	0.004	-	-
	6:2 FTSA	-	0.002	-	0.01
	cC6O4	-	-	unknown	-
	ADV	-	-	unknown	-
Fluorosurfactants and impurities	C ₄ -C ₁₄ PFCAs and PFBS	unknown	~0.002	unknown	0.01

Note: "-" = not applicable, "unknown" = amount unknown. BTM = bromotrifluoromethane.

* While Chemours loads and blends various fluorinated gases in canisters and tanks at this site, the values here are reported per substance and emission point, and thus, are linked to fluoropolymer production.

** Syensqo have also produced HFC-365mfc at this site, which may have contributed to some of the H(C)FC emissions listed here.

*** At this site, Arkema and Daikin share infrastructure, and thus, were considered together. Arkema have also produced a mixture of different H(C)FCs at this site, which may have contributed to some of the H(C)FC emissions listed here.

**** Part of the H(C)FC category

***** mentioned individually

Source: Source: Dalmijn et al. (2024)

Table A H.4. Reported emissions of CFCs, HCFCs, HFCs, PFCs at various fluoropolymer production sites to the European E-PRTR system [t / year]

		2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021
AGC (Thornton- Cleveleys, UK)	HCFCs	13.1	2.27	2.29	2.52	2.61	2.52	3.14	2.66	2.32	1.97	2.04	1.86	2.16	0	2.64
	HFCs	1.5	0.905	0.68	1.36	2.24	12.478	14.3	9.25	9.11	16.3	17.3	13.5	7.78	0	9.73
	PFCs	0	0	0	0	0	12.478	14.3	9.25	9.11	16.3	17.3	13.5	7.78	0	9.73
Arkema- Daikin* (Pierre-Bénite, France)	CFCs	5.59	4.22	2.17	0.434	0.013	0.019	0.117	0.045	0.011	0.062	0.016	0.152	0.066	0.06	0.069
	HCFCs	61.6	42.8	30.7	51.4	40.9	36.8	45.4	35.8	43.2	43.8	31.4	34.9	23.7	36	21
	HFCs	39.5	61.7	46.7	33.9	22.9	21.3	16.7	24.3	41.7	54.3	40.3	29.1	26.2	18.5	11.5
Chemours** (Dordrecht, Netherlands)	CFCs	8.62	6.28	20.2	8.83	9.19	3.13	3.61	1.2	2.6	20.6	5.06	20.7	10.5	2.46	4.63
	HCFCs	104	126	120	121	106	126	96.1	76.5	85.9	83.5	45.9	17.3	26.5	21.7	22.1
	HFCs	31	24.4	70.1	67.7	23.3	25.3	23	8.53	15.3	12.4	9.12	17.8	35	14.1	27.4
	PFCs	0.943	0	0.206	0.576	0.212	0.402	0	0	0	0.272	0	0.654	0	0	0
3M/Dyneon (Gendorf, Germany)	CFCs	0.12	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	HCFCs	0	0.029	0.023	0.026	0.026	0.036	0.015	0.015	0.016	0.015	0.016	0.023	0.018	0.016	0.225
	HFCs	0	0	0	0	0	0	0	0	0	0.231	0.234	0.231	0.198	0.14	0.138
Syensqo*** (Tavaux, France)	HCFCs	17.3	17.2	11.7	23.5	13.9	11.4	1.57	3.32	0	0	3.64	2.35	3.16	2.26	1.37
	HFCs	2.88	1.67	3.27	1.9	1.74	2.68	1.22	3.19	1.99	2.39	4.782	4.583	6.78	3.202	2.848
Syensqo**** (Spinetta Marengo, Italy)	HCFCs	11.4	4.77	4.46	8.57	7.12	5.62	13.6	13.7	16.5	16.8	16.1	4.209	4.516	4.931	4.912
	HFCs	1.62	0.6	2.11	4.5	1.21	0.9	1.07	3.29	3.27	4.21	27.4	10.887	17.548	2.547	11.67
	PFCs	210	200	130	176	195	182	213	190	210	202	161	204.5	117.7	56.5	39.4
	CFCs	0	0	0	0	0.172	0.095	0.1	0.09	0.07	0.09	0.084	0.08	0.08	0.084	0.041

Notes: * At this site, Arkema and Daikin share infrastructure, and thus, were considered together. Arkema have also produced a mixture of different H(C)FCs at this site (Dalmijn et al., 2024), which may have contributed to some of the H(C)FC emissions listed here.

** At this site, Chemours loads and blends various fluorinated gases in canisters and tanks, which may have contributed to some of the F-gas emissions listed here. At the same time, the yearly reported emissions from the emission permit are higher than the values reported in the E-PRTR, suggesting underreporting in the E-PRTR, overreporting in the emission permit, or a combination of both for individual substances.

*** Syensqo have also produced HFC-365mfc at this site, which may have contributed to some of the H(C)FC emissions listed here.

**** It is noted that a large part of the air emissions reported in the E-PRTR is unaccounted for in the emission permit. The reasoning is unclear. Source: Dalmijn et al. (2024).

Annex I. Supporting data on the environmental occurrence of PFASs close to fluoropolymer manufacturing sites

Table A I.1. Summary of the reported PFAS measurements in the vicinity of fluoropolymer manufacturing sites

Sampling		Legacy PFASs (Mean and Range)				Emerging PFASs (Mean and Range)		Reference
Location	Year	PFHxS	PFOS	PFBA	PFOA	HFPO-DA	Others	
<i>Water (ng/L)</i>								
Rhine River, Germany	2013–2014	2.1 (1–4.4)	1.5 (<MDL–3.4)	2.1 (0.3–3.3)	6.1 (4.4–8.9)	8.8 (<MDL–107)	–	Heydebreck et al., 2015
Elbe River, Germany	2013–2014	1 (0.4–1.7)	2.4 (<MDL–13)	1.3 (<MDL –2.3)	2.5 (1–4.5)	–	–	
LP, Coast of North Sea	2013–2014	0.6 (0.1–1.2)	1.7 (<MDL–3.3)	1.2 (0.3–2.2)	2.0 (0.4–6.4)	1.0 (<MDL–3.7)	–	
LP08/14 Coast of North Sea	2013–2014	0.5 (0–1.9)	0.1 (<MDL–0.9)	0.8 (<MDL –4.6)	5.7 (1.8–13)	1.4 (<MDL–2)	–	
Xiaoqing River, China	2013–2014	–	–	–	–	339 (<MDL–3830)	–	
Alz River, Germany	2018	0.32	0.41 (0.28–0.47)	58 (0.65–190)	29 (0.36–180)	29 (0.043–3600)	ADONA: 1060 (1.2–2500)	Joerss et al., 2020
Ruhr River, Germany	2018	0.93 (0.56–2)	2.9 (2.3–4.7)	6.1 (4.6–6.9)	4.5 (2.5–5.4)	0.067 (0.06–0.085)	ADONA: <MDL –0.079	

Rhine River, Germany	2018	1.9 (1.8–2.0)	2.4 (2.1–2.9)	4.0 (3.8–4.4)	2.4 (2.3–2.7)	0.059 (0.043–0.108)	ADONA: <MDL	
Lahn River, Germany (Control site)	2018	0.83	4.5	4.5	2.7	0.059	ADONA: <MDL	
Main River, Germany	2018	1.2 (0.87–1.4)	1.3 (1.0–2.0)	3.9 (3.1–5.2)	2.3 (1.9–2.7)	0.13 (0.03–0.21)	ADONA: <MDL	
Xiaoqing River, China	2018	1.6 (0.41–2.8)	4.1 (2.7–5.3)	1,320 (12–4,100)	90970 (41–320,000)	1100 (1.6–3800)	ADONA: <MDL	
Xi River, China	2018	2.6 (0.51–11)	1.5 (0.26–2.8)	1120 (130–4,100)	130 (41–540)	0.69, 0.91	ADONA: <MDL – 0.197	
Yangtze River, China	2018	1.1 (0.57–2.8)	1.2 (0.69–2.5)	22 (4.9–120)	160 (18–710)	13 (0.43–95)	ADONA: <MDL	
Xiaoqing River, China	2016	<MDL (<MDL–1.7)	0.9 (<MDL–6.8)	250 (<MDL–5,400)	26,400 (6.4–321,000)	519 (<MDL–9,350)	HFPO-TrA: 3,790 HFPO-TeA: <MDL ADONA: <MDL C8 Cl-PEFSA: 0.49 (<MDL–3.0)	Song et al., 2018
Rivers in the Netherlands	2016	2.0 (1.5–2.2)	3.7 (2.7–7.1)	7.5 (4.1–13)	4.3 (2.8–12)	170 (1.7–433)	–	Gebbink et al., 2017
Drinking water in the Netherlands	2016	0.24 (0.02–0.43)	0.25 (0.054–0.41)	13	4.1 (0.63–11)	3.9 (<MDL–11)	–	
Control site (for river water)	2016	1.9	3.7	11	3.0	–	–	
River Wyre, UK (Near AGC Chemicals)	2021	5.9 (1.9–9.5)	–	43 (1.6–100)	8500 (5.3–20,600)	–	Ether PFBA: 12 (<MDL–18) Ether PFOA: 230 (<MDL–430) EEA: 370 (17–1,740)	Dalmijn et al., 2024
Tennessee River, Alabama, US	2015	39	85 (15–220)	24 (10–60)	43 (11–120)	–	–	Newton et al., 2017
Groundwater from soil borings, Ohio River,	Unknown	–	–	–	–	–	APFO: 12,000 (<MDL–78,000)	Davis et al., 2007

US								
Groundwater (ng/L)								
Montecastello (Alessandria), Italy ^{*1}	2022 - 2023	–	–	–	2,630 (1,800– 2,630)	–	cC6O4: 630 (470–760). ADV N2 Congener: 1,807 (1,720– 1,870)	Arpa Piemonte, 2023
Montecastello (Alessandria), Italy ^{*1}	2024	–	–	–	1,467 (1,190 –1,380)	–	cC6O4: 292 (220–360) ADV series (Σ 6 congeners): 1,000 (790– 1,400)	Arpa Piemonte, 2025
Trissino (Vicenza), Italy ^{*2}	2021-2024	11 (9–15)	116 (67– 303)	187 (144– 377)	958 (786– 1,171)	87 (<MDL – 532)	cC6O4: 299 (<MDL –2,502)	Arpa Piemonte, 2024a (Data referred to the MW28 groundwater site external to the plant.)
Sediments (ng/g)								
Xiaoqing River, China	2016	–	–	–	–	<MDL (<MDL–22)	HFPO-TrA: 350 (<MDL–8,370) HFPO-TeA: 15 (<MDL–360) ADONA: <MDL C8 Cl-PFESA: 0.37 (<MDL–1.6)	Song et al., 2018
Tennessee River, Alabama, US	2015	0.51 (0.21–0.99)	15 (0.22–32)	0.74 (0.3–1.4)	7.4 (1.3–12)	–	–	Newton et al., 2017
Soils (ng/g)								

Ohio, US	2018	–	–	–	7.5 (2.9–11)	–	–	Galloway et al., 2020
Lyon, France	2022	–	1.2 (0.6–1.8)	–	0.65 (0.60–0.70)	–	PFUnDA: 90 (12– 250) C8 Cl-PFESA: 26 (3.6–75) 6:2 FTSA: 1.9 (0.5–3.3)	Dauchy et al., 2023
Ohio, US	Unknown	–	–	–	33 (<MDL–170)	–	–	Davis et al., 2007
<i>Air (pg/m³)</i>								
North Carolina, Chemours Fayetteville Works (2 sites)	2019	–	0.88, 1.3	0.41, 0.40	<MDL	<0.048, 0.1	PMPA: 1.2, 0.37 PFO2HxA: <MDL, 0.059 NVHOS: 0.65, 0.73 PFO5DoA: 0.38, 0.43 Nafion BP1: 0.1, 0.29 Nafion BP2: 0.039, 0.029 Nafion BP4: 0.07, 0.014 Hydro Eve: 0.034, <MDL	Zhou et al., 2022
North Carolina, US. Background site	2019	–	–	<MDL	<MDL	<MDL	PMPA: < MDL PFO2HxA: < MDL NVHOS: < MDL PFO5DoA: < MDL Nafion BP1: < MDL Nafion BP2: < MDL Nafion BP4: < MDL Hydro Eve: < MDL	Zhou et al., 2022
Hazelrigg, Lancaster,	2021	<MDL	0.18	<MDL	1.5	–	EEA: 0.28, 0.67,	Dalmijn et al.,

UK*3			(0.09–0.49)		(0.69–2.5)		2.0	2024
Air depositon (µg/m2/day)								
Via Genova, Spinetta Marengo (Alessandria), Italy	2022-2025	–	–	–	–	–	cC6O4: 1.270 (0.230 –3.580) ADV N2 Congener: 0.196 (<MDL – 0.800)	Arpa Piemonte, 2024b Arpa Piemonte, 2025
Air PM10 fraction (ng/m3)								
Via Genova, Spinetta Marengo (Alessandria), Italy	2024 (January/July)	–	–	–	0.006–0008	–	cC6O4: 1.601 (0.476– 3.822) ADV series (Σ6 congeners): 0.075 – 0.842	Arpa Piemonte, 2024b Arpa Piemonte, 2025
Dust (ng/g)								
Lyon, France	2022	–	0.80 (<MDL–1.4)	–	<MDL	–	6:2 FTSA: 9.6 (1.4–28)	Dauchy et al., 2023

Notes:

Note that the mean is estimated from the reported values, where values less than the respective method detection limit (<MDL) are not included in the calculation of the mean. The mean and range are only determined for those datasets with 2 or more data points. Otherwise, the individual data are listed.

Abbreviations: PMPA = perfluoro-2-methoxypropanoic acid; PFO2HxA = perfluoro (3,5-dioxahexanoic) acid; NVHOS = 1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoro-ethoxy) ethane sulfonates; PFO5DoA = perfluoro-3,5,7,9,11-pentaoxadecanoic acid; Nafion BP1 = 2-[1-[difluoro[(1,2,2-trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoroethanesulfonic acid; Nafion BP2 = 1,1,2,2-tetrafluoro-2-[1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl]oxyethanesulfonic acid; Nafion BP4 = 2,2,3,3,4,5,5,5-4-(1,1,2,2-tetrafluoro-2-sulfoethoxy)pentanoate; Hydro Eve = 2,2,3,3-tetrafluoro-3-((1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy) propan-2-yl)oxy) propanoic acid; EEA = 2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(1,1,2,2,2-pentafluoroethoxy)ethoxy]acetic acid; HPFO-DA = hexafluoropropylene oxide dimer acid; ADONA = 2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]propionate; 6:2 FTSA = 6:2 fluorotelomer sulfonic acids; C8 Cl-PEFSA = 1-chloro polyfluoroalkyl ether sulfonic acid.

*1 Well providing drinking water to the Montecastello town till June 13, 2020.

2 From 2012 to 2018, the Miteni fluoro plant recovered HFPO-DA from sludges (CER 070201) imported from Chemours (Netherlands). In the Miteni plant, C6O4 production started from C6O4 resins delivered by the former Solvay plant in Spinetta Marengo, Italy. The Miteni plant was closed at the end of 2018.

*3 This site is at about 20 kilometres northeast (downwind) of the AGC Chemicals site.

Annex J. Supporting data on the environmental occurrence of fluoropolymers as microplastics

Table A J.1. Summary of measured occurrence of fluoropolymers as microplastics in the environment

Location/ Media	Sample type	Sampling Year	Fluoropolymers identified, its % of total MPs (if available)	Concentration of Total MPs, Mean (range)	Reference
<i>Water</i>					
Han River, South Korea	Surface water	2018	PTFE: Han River (0, 2 m): 3% Anyang Stream: 39.9%	Han River (0 m): 7.0 ± 12.9 (0–42.9 particles/m ³) Han River (2 m depth): 102.0 ± 50.3 (20.0–180 particles/m ³) Anyang Stream: 91.1 ± 72.3 particles/m ³ (39.0 – 235 particles/m ³)	Park et al. (2020)
Patos Lagoon,	Filtered water	-	PTFE	0.0846 g microplastics/400 L	e Silva and de Sousa

Brazil					(2021)
East Asian Seas to Arctic central Basin	Seawater	2017	PTFE: < 28% ¹	2.91 ± 1.93 items/m ³	Huang et al. (2022)
Wuxi, China	River water	2018–2019	PTFE	2.3 ± 1.2 to 104.6 ± 5.6 particles/L	Fan et al. (2022)
Antarctic	Freshwater	2018	PTFE	0.95 (0.45–1.43 items/1000m ³)	Gonzalez-Pleiter et al. (2020)
Spain	Tap water	2019	PTFE: 0.02 to 0.08 /L	LOD to 0.05 particles/L	Dalmau-Soler et al. (2021)
South Korea	WWTP Influent and effluent	2021-2022	PTFE: Influent: 46.5% Effluent: 56.5%	Influent: 1042 ± 1025 (160–5,180 particles/L) Effluent: 1.9 ± 2.3 (0.2–11.4 particles/L)	Lee et al. (2024)
Sediments and Soils					
NW Borneo	Coastal sediment	2013, 2014, 2022	PTFE: Pre-COVID: 36% Post-COVID: LOD	Monsoon: 5–21 particles/30g Post-monsoon: 9–33 particles/30g Post-COVID: 16–43 particles/30g	Mishra et al. (2023)
New Zealand	Marine sediments	2020	PTFE: 38% (Both sites)	Site 1: 0.02–0.09 particles/cm ³ Site 2: 5 cm depth: 0.25 particles/cm ³ 10–15 cm depth: 0.005 particles/cm ³ 30 cm depth: 0.1 particles/cm ³	Ribó et al. (2023)
Gulf of Mexico	Sediments from	2017	PVDF: 91.1–98.9 %	16.46 ± 17.76 particles/kg	Osten et al (2023)

	Gulf of Mexico				
Lake Michigan, US	Sediment	2010	PTFE Site M009: 45.7 count/g dw Site M032: 145 count/g dw (Results based on Method 1)	1110 count/g dw	Cheng et al. (2022)
Spain	Lagoon water receiving WWTP effluent	2019	PTFE: < 23% ¹	2.9±1.2–36.3±7.7 particles/g	Edo et al. (2020)
Xinjiang, China	Soils	2019	PTFE: 12.93 ± 6.09 %	1.57 x 10 ⁵ - 3.2 x 10 ⁵ particles/kg soil	Jia et al. (2022)
Biota					
Han River, South Korea	Fish	2018	PTFE: 74%	22.0 ± 14.6 particles/fish (4–48 particles/fish)	Park et al. (2020)
Han River, South Korea	Fish		PTFE	34–284 particles/individual	Kim et al. (2024)
South Korea	Fish	2019	PTFE: 16%	17.4 ± 11.9 particles/fish	Park et al. (2022)
Campeche Bay, Mexico	Fish	2019	PTFE: 18/101 individuals	1.31 ± 2.59 microplastics/fish	Borges-Ramírez et al. (2020)
Saudi Arabia	Fish purchase from market	Unknown	PVDF 10/22 fish were detected with PVF and/or PVDF	1–10 particles/fibre	Khattab et al. (2022)
Vaal River, South Africa	Fish (Carp)	2019	PTFE	41 ± 53 particles/kg	Saad et al. (2022)

Setiu Wetlands, Malaysia	Crab	2021-2022	PTFE	-	Rahim et al. (2023)
Air					
Hamburg, Germany	Urban	2017-2018	PTFE: < 72% ¹	275.0 microplastics/m ² /day	Klein and Fisher (2019)
China	Road dust	2020-2021	PTFE: 4.7% PVDF: 10.8%	143.3±40.8 particles/m ²	Fan et al. (2024)

Note: ¹ Percentage not provided. This is an estimated value

Synthesis Report on Understanding Fluoropolymers and Their Life Cycle

OECD Series on Risk Management of Chemicals

Fluoropolymers, a type of polymeric PFAS, are widely used across industries as standalone materials, coatings, or additives, often in small amounts within complex products. With global consumption increasing, this report takes a life-cycle perspective to examine fluoropolymer chemical identity, production, use, degradation and environmental emissions. It also includes the role of polymerisation and processing aids used during fluoropolymer production. Recommendations for future research and policy actions highlight that improved data access, integrated methodologies and coordinated global efforts are essential for informed decision making and the development of sustainable fluoropolymer management practices.