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#### **Fluorinated Elastomers: Current Status and Future Applications**

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### Abstract

Fluorinated elastomers (FEs) are unique materials bearing exceptional properties and involved in High Tech applications (electronics, car, aerospace and petrochemical industries and microelectronics) where they resist to stringent conditions, showing peculiar softness and resilience over a wide range of temperatures. This review mainly report on (per)fluorocarbon elastomers, fluorophosphazenes, fluorosilicones and perfluoropolyethers as well as controlled thermoplastic elastomers for which several properties and applications are provided.

Keywords: fluorinated elastomers, glass transition temperature; hexafluoropropylene; radical copolymerization; tetrafluoroethylene; vinylidene fluoride.

### Introduction

Thanks to the presence of fluorine atoms that make the C-F bond short and strong, fluoroelastomers are endowed with exceptional properties as high thermal, chemical, aging, UV and weather resistance, high repellency towards oils, solvents, water and soil, low refractive index/flammability/dielectric constants as well as a high protection from oxidative and hydrolytic degradation (1-4). These unique properties offer innovative applications in several emerging High Tech applications (electronics, car, aerospace and petrochemical industries and microelectronics) where the requirements are demanding regarding the chemical inertness and preserving their outstanding properties, including softness and resilience on a wide range of temperatures.

Compared to fluorinated homopolymers which are crystalline and difficult to cure, fluorinated elastomers can be crosslinked due to their low crystallinity arising from disorganized or amorphous structure (1-4).

An elastomer is a polymer material having both viscous and elastic properties (5). These materials display rather weak intermolecular forces, low Young's modulus and high failure strain (Figure 1) (6-9). That is why it is essential to crosslink them to reach enhanced mechanical properties.



Figure 1: Different conformations of molecular chains ranging from thermoplastic to elastomer and thermoset.

One of the first comprehensive review was suggested by Worm and Grootaert (1) followed by a quasi-exhaustive books (3- 4). This present review completes and updates these text books, mainly focusing on fluorinated elastomers (FEs), ranging from (per)fluorocarbon elastomers to fluorophosphazenes, fluorosilicones and perfluoropolyethers. Compared to conventional elastomers (Figure 2 and Table 1), FEs are produced in low volumes but their price is obviously higher also linked those of the monomers. Then, several properties are supplied while relevant applications further discussed.



Figure 2: conventional elastomers compared to fluorine-containing elastomers; comparable produced amounts *versus* price (arbitrary scale). Reproduced with permission from Elsevier (2).

#### **Fluorocarbon Elastomers.**

These types of specialty polymers are usually prepared *via* radical copolymerization of different fluoroalkenes such as VDF, HFP, TFE, PMVE, CTFE and pentafluoropropylene (PFP), and functional comonomers containing a crosslinking group, called cure site monomers, CSMs with

the following structure  $F_2C=CFOR_FX$  where X stands for Br, I, CN OCN, CN crosslinked either thermally or with SnPh or from trialkoxysilane (1-4, 10). Various examples of commercially available FEs (1-4, 10-13) can be cross-linkable thanks to a few CSM amount enabling to get enhanced properties (chemical, thermal and mechanical stabilities). The crosslinking process creates a three-dimensional network that turns the elastomer resistant for long-term mechanical service under a sustained stress or constant deformation (or strain).

Туре	Continuous service Temperature (°C)	T <sub>g</sub> (°C)	%F	Trademark (supplier)
$CH_2 = CF_2/C_3F_6$	- 18 to 210	- 18	66	See Table 2
$C_2F_4/C_3H_6$	0 to 200	0	54	Aflas <sup>®</sup> (AGC)
$\begin{array}{c} C_2F_4/CF_2 = CFOCF_3\\ C_2F_4/CF_2 = CFOR_FCN \end{array}$	0 to 280	- 2	73	See Table 2
$CH_2 = CF_2/C_3F_6/C_2H_4$	- 12 to 230	- 16	67	Daiel <sup>®</sup> (Daikin)
Fluorosilicone	- 65 to 175	- 68	37	Silastic <sup>®</sup> (Dow Corning)
Fluorophosphazene	- 65 to 175	- 65	55	NPF <sup>®</sup> (Firestone)

Tableau 1: Nature and thermal characteristics of commercially available fluorinated elastomers (trade names and producers)

Poly(VDF-*co*-HFP) copolymers, also called FKM® industrially produced from decades by various companies, are chemically inert and show lower degree of crystallinity than that of PVDF due to the presence of the bulky  $CF_3$  side groups (6,15-17,20-21), even to reach amorphous states from ca. 20 mol.% HFP (Figure 3) (16).

However, the tendency is different for poly(VDF-co-CTFE) copolymers (Figure 4).

The CSM and curing mechanism was originally developed for an improved low-temperature poly(VDF-*co*-PMVE) fluoroelastomer. The quite acidic VDF and the ionic cure mechanisms

(diamine and bisphenol AF) induces cleavage of the trifluoroalkoxy group in PMVE units resulting in backbone cleavage, and a perfluoromethanol by product. Shimizu and Inagaki (14) studied the use of various fluorinated dienes as cross-linking agents for perfluoroelastomers (mainly FFKM as a terpolymer based on TFE, PAVE and a cure site monomer) in order to bring two keys features: resistance to high-temperature vapor and cross-linking efficiency. These dienes were:  $F_2C=CF-R_1-CF=CF_2$  (where  $R_1$  stands for  $C_6H_4$  ( $CF_2$ )<sub>6</sub> $C_6H_4$  or biphenyl) or  $H_2C=CH-(CF_2)_6-CH=CH_2$  (15).

Tableau 2: Main commercially	available fluoroelastomers.
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	HFP	PMVE	CTFE	Р
VDF	Daiel <sup>®</sup> G 801 (Daikin)		Dyneon <sup>®</sup> Elastomer	
	Dyneon <sup>®</sup> Elastomer		(3M/Dyneon)	
	(3M/Dyneon) Tecnoflon <sup>®</sup>		SKF <sup>®</sup> -32 (Russia)	
	N/FOR (Solvay Specialty	,	Voltalef <sup>®</sup> (Arkema,	
	Polymers) SKF <sup>®</sup> -26 (Russia)		USA)	
	Viton <sup>®</sup> A (Chemours)			
TFE		Daiel <sup>®</sup> Perfluoro (Daikin)		Aflas®
		Dyneon <sup>®</sup> Elastomer		(AGC)
		(3M/Dyneon)		Viton
		Kalrez <sup>®</sup> (DPE) Tecnoflon <sup>®</sup>		Extreme®
		PFR (Solvay Specialty		TBR
		Polymers)		(DPE)
VDF	Daiel <sup>®</sup> G 901 (Daikin)	Daiel LT (Daikin)		Aflas®
+ TFE	Dyneon <sup>®</sup> Elastomer	Dyneon <sup>®</sup> Elastomer (3M/		(AGC)
	(3M/Dyneon) Tecnoflon <sup>®</sup>	Dyneon) Tecnoflon <sup>®</sup> PL		
	P/T/ TN/FOR (Solvay	(Solvay Specialty		
	Specialty Polymers)	Polymers) Viton <sup>®</sup>		
	Tecnoflon <sup>®</sup> BR (Solvay	Tecnoflon <sup>®</sup> VPL (Solvay		
	Specialty Polymers)	Specialty Polymers)		

<sup>a</sup> DPE: DuPont Performance Elastomers (now Chemours); CTFE: chlorotrifluoroethylene ( $F_2C=CFCI$ ); HFP: hexafluoropropylene ( $F_2C=CFCF_3$ ); HPFP: 1-hydro-pentafluoropropene (FHC=CFCF\_3); P: propene ( $H_2C = CHCH_3$ ); PMVE: perfluoromethyl vinyl ether ( $F_2C = CFOCF_3$ ); TFE: tetrafluoroethylene ( $F_2C=CF_2$ ); VDF: vinylidene fluoride ( $F_2C = CH_2$ ); X: «cure site monomer» (XCY = CZ – R– G; G: function).



Figure 3: Semicrystalline or amorphous poly(VDF-*co*-HFP) copolymers according to the HFP content in the copolymer (16). Copyright 2007. Reproduced with permission from the American Chemical Society.



Figure 4: Relationship between the CTFE content and the thermoplastic or elastomeric behavior of poly(CTFE-*co*-VDF) copolymers. (17) Copyright 2014. Reprinted with permission from the Amer Chem Soc.

Besides such above examples, the literature is also abundant on the terpolymerizations involving VDF, as reviewed by Hull et al. (18) on industrially produced THV® terpolymers (usually based on TFE, VDF and HFP) or, more recently by Thrasher's group (13), in which the poly(TFE-*ter*-VDF-*ter*-HFP) terpolymers have various states (Figure 5). Similarly, poly(TFE-*alt*-P) copolymer is a well-known Aflas® elastomer (although having a high Tg value of ca. -5 °C) marketed by AGC. Hence, inserting VDF led to poly(TFE-*ter*-P-*ter*-VDF) terpolymers as a new generation of elastomers with lower Tg values and base resistance (19-21). Advantageously, the presence of VDF units, as a possible weak points brought from hydrogen atoms, favors some crosslinking, comprehensively reviewed by Moore (3), Schmiegel (22) or Taguet et al. (12).



Figure 5: Ternary diagram showing elastomer and elastoplastic zones of poly(VDF-*ter*-HFP-*ter*-TFE) terpolymers, the remaining part being thermoplastic. Reproduced with permission from Elsevier (2)

#### Fluorophosphazenes

Fluorophosphazenes (FPZ, Scheme 1) are synthesized by polymerization of a cyclic phosphazene produced from phosphorous pentachloride and ammonium chloride (23). This was followed by a nucleophilic substitution reaction of fluorinated alcohols with dichlorophosphazenes, as well reviewed by Allcock (23). Possibly, a small unsaturated alcohol amount acts as a cure site monomer.



Scheme 1: Synthesis of fluorophosphazenes where R<sub>F</sub> stands for fluoroalkyl group (23)

Firestone Polymers was the first company to commercialize fluorophosphazenes under PNF<sup>®</sup> tradename endowed with low  $T_g$ s (ca. -70 °C). The synthesis, properties and applications of alkoxy and aryloxy substituted fluorophosphazenes were reviewed by Gleria *et al.* (24) In

addition, Allcock's team (25) also reported block copolymers based on such phosphoronitrogenous polymers by sequential polycondensation reactions.

## Fluorosilicones.

Dow Corning Corporation was the first company to commercialize poly[methyl(3,3,3-trifluoropropyl)siloxane] (FVMQ) as Silastic<sup>®</sup> fluorosilicones (26) (Figure 6) by alkaline catalyzed ring opening polymerization of a cyclic trimer of trifluoropropylmethylsiloxane produced by reaction between a methydichlorosilane and 3,3,3-trifluoropropene (TFP). Advantageously, these polymers exhibited low  $T_g$  (-65 °C) but their thermal stability was not quite high since a backbiting occurs from 230 °C (Scheme 2).

$$\begin{array}{c} C H_{3} \\ -(S i - O)_{p} \\ \\ C_{2}H_{4} - C F \end{array}$$

Figure 6: Chemical structure of poly[methyl(3,3,3-trifluoropropyl)siloxane].



Scheme 2: mechanism of backbiting of poly(dialkylsiloxane)s starting from T >220-230 °C.

Kobayashi's (27) and Boutevin's (28) teams reported the synthesis of "hybrid" fluorosilicones containing polysiloxane and fluorocarbon moieties (Figure 7) to increase such a thermal stability. These unique hybrids also exhibited improved oleophobic, hydrophobic, thermal and surface properties compared to conventional silicones or to Silastic®.



Figure 7: Chemical structures of hybrid fluorinated silicones (y = 2, 3 and n = 3, 4, 6) (26-28).

Subsequently, the Dow Corning and Shin-Etsu Companies (29) produced fluorosilicones as original hybrid silicones (Figures 7 and 8 and Scheme 3) with very low  $T_g$ s.



Figure 8: Chemical structure of fluorosilicones commercialized by the Dow Corning Company.

Furthermore, Sifel<sup>®</sup> material, developed by Shin-Etsu in multiple steps (Scheme 3), contains one dimethyl siloxane unit only per ca. 50-100 hexafluoropropylene oxide (HFPO) units to allow PFPE-*b*-PDMS multiblock copolymers. These fluorinated silicones are classified in terms of their ability to form liquid rubber compositions. For molding, the rubbers feature easy handling and simple mold configurations, which are more suitable than the liquid injected molding silanes (LIMS) compositions that request complex mold conformations.



Scheme 3: strategy to synthesize SIFEL® fluorosilicone (29).

## Fluorinated Thermoplastic Elastomers (F-TPEs)

The future prospects of FEs depend on the possibility of successfully synthesizing new fluorinated TPEs possessing low  $T_gs$ , high melting temperatures ( $T_m$ ) and low coefficient of rubbing.

#### **Synthesis of F-TPEs**

One of the main strategies to design high performance FEs is based on the copolymerization of monomers of desired functionalities dedicated to achieve innovative architectures (e.g, block or graft copolymers (30-31). This approach advantageously supplies opportunities to combine the properties of the monomers of the diverse families and synthesize unique materials with enhanced thermal and mechanical properties. One of the key examples is fluorinated thermoplastic elastomers (F-TPEs) synthesized by one or multiple reaction steps (Scheme 4) to create each block independently.

Since mid 1990's, a major development on controlled radical polymerization (or reversible deactivation radical polymerization RDRP) (32) has been developed, without often mentioning the achievement of F-TPEs produced by sequential iodine transfer copolymerization (ITP) discovered in the late 1970's. This strategy, pioneered by Tatemoto (33), is based on ITP as the first RDRP method. Actually, the control of the reaction is induced by the terminal dynamic bond ("*pseudo-living*") of the propagating polymer chain which is generated from the weak C-I bond in  $-CF_2I$  of the iodofluorinated chain transfer agent (CTA). Indeed, various combinations of synthetic block microstructures have been designed and well-documented in various reviews (30, 34-35) based on the choice of comonomers involved in the different blocks to achieve both thermoplastic and elastomeric segments and, hence, to reach suitable  $T_g$  (though not low enough since > -30 °C) and  $T_m$  values. Various strategies first applied at Daikin, followed by Dupont Performance Elastomers (now Chemours) and then by Solvay Specialty Polymers have led to commercially available F-TPEs, regarded as the first fluorinated block copolymers produced in an industrial scale (Scheme 4) (30).

$$I - R_F - I + n M_1 + m M_2 \xrightarrow{rad.} I[(M_1)_x(M_2)_y]_z - R_F - [(M_1)_x(M_2)_y]_z - I$$

$$I - Soft - I$$

$$I - Soft - I$$

$$I - Soft - I + p M_3 + q M_4 \longrightarrow poly(M_3 - co - M_4) - b - poly(M_1 - co - M_2) - b - poly(M_3 - co - M_4)$$

Scheme 4: iodine transfer copolymerization of various monomers for the synthesis of Hard-Soft-Hard triblock thermoplastic elastomers (where  $M_1$ ,  $M_2$ ,  $M_3$  and  $M_4$  are fluoroalkenes (30-31).

Actually, such Hard-Soft-Hard triblock copolymers are phase segregated with amorphous and crystalline zones combining various advantages including low Tg values (from the soft part) and thermoplastic behavior as well as broad temperatures of service. These fluorinated triblock copolymers are synthesised from a two step-procedure: first, a telechelic diiodofluorinated copolymer [usually an elastomeric I-Soft-I block made from various compositions of VDF/M (30-31, 34-36)] is produced that can be further used as a novel CTA in a second ITP insert both Hard semi-crystalline sequences (e.g. PTFE, PVDF, ETFE, etc.) (Scheme 4).

Various *quasi*-exhaustive summaries of synthesis and properties of these F-TPEs have been reported (31) (Scheme 7) involving well-chosen monomers among TFE, VDF, HFP, PMVE, CTFE, ethylene (E) and propylene (P) to design low Tg while high melting temperatures of the second sequence,  $T_m$ , reached sometimes more than 250 °C or 300 °C. Typical combinations of comonomers by pair, trio or quartet enabled the authors to design both soft and hard sequences (Scheme 4) (30). Usually, the central elastomeric segments have molar masses of 30,000 or more while those of the plastomeric (or hard) blocks are higher than 10,000, although Yagi *et al.* already claimed molar masses of F-TPE up to 1,000,000.

Tatemoto (30,34) compared the thermal decomposition of three TPEs and supplied the following order: poly(E-*alt*-TFE)-*b*-poly(VDF-*co*-HFP)-*b*-poly(E-*alt*-TFE);  $T_{dec} = 345$  °C < poly(E-*alt*-CTFE)-*b*-poly(VDF-*co*-HFP)-*b*-poly(E-*alt*-CTFE);  $T_{dec} = 379$  °C < PVDF-*b*-poly(VDF-*co*-HFP)-*b*-poly(VDF-*co*-HFP);  $T_{dec} = 410$  °C, such TPEs being easily processed as gums.

The crosslinking occurs from the crystalline domains.

Further, diiodide CTA was involved in the homopolymerization of either VDF or TFE, leading to the hard segment composed of either PVDF or PTFE, respectively, or a combination of VDF (in high amount) with HFP or CTFE, or copolymers of TFE with E, PMVE, VDF or with HFP, or terpolymers TFE/E with P, HFP, PMVE, 3,3,3-trifluoropropene, 1H-pentafluoropropene, or hexafluoroisobutylene.

Most of these TPEs are currently used from -30 °C to 250 °C (30-31,33-34) and in continuous service at 200 °C in contrast to conventional elastomers that decompose at this temperature. Another peculiar F-TPE is Cefral Soft® (37), marketed by the Central Glass Company, as a graft copolymer composed of poly(VDF-*co*-CTFE) elastomeric backbone bearing PVDF grafts As a matter of fact, as for FEs, F-TPEs can be crosslinked from several process: in presence of peroxide / triallyl (iso)cyanurate system (1-4, 10-12) or by gamma (<sup>60</sup>Co) rays which induces an improved thermal stability, a high resistance to vapor, UV, chemical agents, ozone, and hydrocarbons, and better mechanical properties (tensile modulus, compression set).

Table 3. Thermal and mechanical characteristics of two commercially available block (Daiel®) and graft (Cefral® soft) F-TPEs.

Copolymers	Daiel®		Cefral Soft®
	E/TFE	VDF	
$T_m$ (°C)	220	160	162-165
$T_g$ (°C)	-9	-10	-25
$T_{dec}$ (°C)	380	400	380
E' (Mpa)	5	4	80-100
$\varepsilon_{e}$ (%)	650	1000	500
$\sigma_{\rm R}~({\rm kN/m}^2)$	29	31	110-120

Table 3 compares the thermal and mechanical properties of block (Daiel®) and graft (Cefral Soft®) F-TPEs. Commercially available Daiel® (38) exhibits relevant properties such as a high melting point (160-220 °C), a high thermostability (up to 380-400 °C), a high specific volume (1.90), a low refractive index (1.357), and rather good surface properties ( $g_c \sim 19.6-20.5 \text{ mN.m}^{-1}$ ). These characteristics offer excellent resistance against aggressive chemicals and fuels, oils, strong acids and ozone. In addition, their tensile moduli are close to that of cured fluoroelastomers. Regarding their optical properties, poly(E-*co*-M)-*b*-poly(VDF-*co*-CTFE)-*b*-poly(E-*co*-M) triblock copolymers (where M stands for TFE or CTFE) displayed lower transmittance than PMMA does in the UV 200-300 nm range, while they showed same transmittance as that of PMMA in the visible range (39). Hence, such A-B-A block copolymers cut the UV light which is dangerous for eyes and were applied in optics and contact lenses (39).

Other applications deal with compatibilizers for polymer blends composed of a hydrocarbon polymer and a fluoropolymers, dispersants for a fluorinated paints, carriers for electrophotography, and electrostatic charges adjusting or melting to prevent agent for toner particles.

In conclusion, throughout the last 45 years, ITP has emerged as one of the innovative RDRP techniques to prepare F-TPEs which have been industrialized and led to many applications.



Scheme 5: Idealized schematics of network structures as  $C_3$  content increases and  $B_2$  content decreases. Magnified sections show detail of chemical structure for linear sections ( $A_2 + B_2$ ) and cross-linking knots ( $A_2 + C_3$ ) (42).

In addition, other strategies to synthesize fluorinated multiblock copolymers were reported from hydroxytelechelic perfluoropolyethers (PFPEs produced by photochemical radical polymerization of TFE, HFP, or PMVE in the presence of oxygen while other PFPEs can be industrially achieved by ring-opening polymerization of oxetane or of HFPO) (37). As an example, the Ausimont Company (41) claimed original fluorinated polyurethanes containing a Fomblin®-based PFPE sequence to lower the Tg values.

Besides many opportunities from such above bis(hydroxyl) telechelic PFPE, reviewed in 2018, a recent study reported their chemical modification into telechelic PFPE-diyne  $A_2$ , PFPE-diazide  $B_2$ , prior alkyne-azide reactions in presence of a cross-linker  $C_3$  (Scheme 5). Such a reaction led to cross-linked PFPE networks. Increasing the amount of crosslinking agent  $C_3$  versus  $B_2$  increases the cross-link density while the alkyne-azide stoichiometry was kept constant (42).

The thermomechanical properties showed a secondary relaxation peak at -105 °C attributed to PFPE moieties located away from cross-links. As known, the Tg transition occurred over a broad temperature range and appeared broader by increasing the  $C_3$  amount in the formulations as this crosslinking agent bears a free hydroxyl group from which a hydrogen bond could occur with a nitrogen from the triazole rings. Another transition took place at higher temperatures due either to a mixed phase or to an interphase region, containing both fluorinated and hydrogenated segments (42).

From an appropriate combination of these telechelic PFPEs, the functionals PFPEs were "clicked" together to form a wide range of materials ranging from elastomers to very viscous polymers (42). In a later patent, Charlas *et al.* (43) used a pentaerythritol triazide as a crosslinking agents with telechelic bis(propargyl) PFPE to form elastomeric materials endowed with low  $T_g$ s and high temperature performance (Scheme 6).



Scheme 6: alkyne-azide "click" chemistry of telechelic PFPAE bispropargyl with pentaerythritol triazide (40).

# Properties of Fluorinated Thermoplastic Elastomers Mechanical and Dynamic Properties

Copolymers can be classified based on the mechanical strength like rigidity which has an elastic modulus > 690 MPa, semi rigid materials of modulus ranging between 69 and 690 MPa, and non-rigid materials of modulus < 69 Mpa (44). Actually, FTPEs display elastomeric properties and are considered non-rigid materials. Table 4 gathers physical and mechanical properties of such FEs. Generally, fully fluorinated polymers exhibit about 1.5 times lower mechanical strength as compared to the fluoropolymers bearing hydrogen atoms in their structure (45). On the other hand, perfluorinated polymers display higher maximum service temperatures and improved elongation (30).

Table 4. Physical and mechanical properties of fluorinated elastomers. Reproduced with permission from William Andrew (45).

Property		Type of Material			
		Fluorinated	TFE/P	Fluorosilicone	Perfluoro-
		hydrocarbon	copolymer		elastomer
Continuous-	Min	-29 to -57	-29	-80 to -68	-38
use	Max	227	204 to 230	232	290 to 315
temperature,					
°C					
Tensile str	ength,	3.4-20.7	13.8-22.1	3.4-9.6	3.4-10.3
MPa* <sup>1</sup>					
Tensile modulus at		1.4-14	6.2-17.2	6.2	6.2-13.1
100% elongation,					
MPa* <sup>1</sup>					
Hardness (duron	neter)	50A-95A	60A-100A	35A-80A	65A-95A
Compression set @		9-16, 70h @24	25, 70h @93	17-25,	20-40,
temperature, °C				22h @149	70h @21
Elongation, %		100-500	50-400	100-480	60-170
* <sup>1</sup> To convert from MPa to PSI, multiply by 145.					

**Thermal Properties** 

FEs generally exhibit outstanding thermal properties, especially when they are crosslinked. There are two types of FEs (1-4) such as i) the fluorinated chain mainly represents the polymer backbone (i.e. most "PTFE" as in KALREZ® from Chemours, oligo(CTFE) or oligo(VDF) moieties etc.) and ii) those in which fluorinated group located in the dangling group [poly(acrylate)s or poly(styrene)s bearing per-fluorinated side chains]. The former copolymer displays good thermostability compared to the latter one. They can be used in gel polymer electrolyte in Lithium ion batteries (e.g., poly(VDF-co-HFP) copolymers, binders for electrode materials, gaskets, shafts, diaphragms). The second one are able to undergo some degradation that will leach out perfluoroalkyl substances (PFASs) (46). Figure 9 represents the overall situation of elastomers regarding the resistance to heat and oils. It shows that FEs are more thermal stable than other materials like silicones, fluorosilicones, and hydrocarbon elastomers as polyepichlorohydrin and nitrile for which the thermal stability is much lower than 250 °C (26,47). Failure in thermal stabilities of silicones relies on the back biting releasing cycles (Scheme 2). Indeed, an increase of the fluorine content and separating silicon atoms by a fluorinated group lead to enhanced thermostability (Figure 8 (28). Furthermore, the best candidates having the lowest swelling rates (in both polar and apolar solvents) are (per)fluorinated elastomers (FFKM, Figure 9).



Figure 9: Compared relative heat and oil resistances of elastomers (ASTM D2000). Reproduced with permission from Elsevier (47).

In addition, PFPEs exhibit excellent low temperature flexibility and heat resistance, together with improved performance in fuels, solvents, acids, and alkalis compared to standard fluoroelastomers (40).

#### **Electrical Properties**

Electrical and computer industrialization has led to a drastic elevation in the need for FEs as ideal candidates for safety and durable insulation for wires and cables. The temperature also influences safety and durable insulation for wiring and cabling processing FEs for their uses in electrical applications since their electrical properties can be tuned by temperature variations (4). Thanks to these relevant properties, FEs are mostly involved in electrical and wire and cable industries (37,48).

#### **Self-healing FEs**

Li et al. (49) synthesized a novel FE starting from low molar mass PFPAEs, with self-healing properties because of the hydrogen bonding. In addition, Simonin et al. (50) suggested a novel concept to obtain self-healing FEs involving a macromolecular synthon which reacts with various segments of the FE, accelerating chain dynamics and leading to self-healing properties to the resulting composite material. Such a chemical change yields to only a limited detrimental effect on the mechanical properties. The authors used this concept to silicone elastomers and successfully produced a self-healing material endowed with a high elastic modulus.

#### Environmental issues and attempts of recycling FEs

FEs are thermally, chemically, and biologically stable, inert and exhibit a high resistance against oxidants, acids, and photolytic and metabolic processes. They are expected not to degrade under environmental conditions or normal use and processing conditions. Indeed, as most fluoropolymers, FEs are not bioaccumulative, not mobile and not toxic and thus not regarded as substances of very high concern (SVHCs) from a regulatory perspective [46, 51-52]. The tiny solubility in n-octanol and in water (they are expected not to be found in sources of drinking water (52)) combined to their very high molar masses demonstrate the inability of FEs to actively or passively penetrate into cell membranes and fulfill the OECD criteria to be PLC (53).

Physical, chemical, thermal, and biological stability are important criteria for a polymer

to

Actually, at the end of life or consumer use, FEs may be disposed *via* the following possibilities: landfill, reuse, recycling [by pyrolysis above 600 °C generating the monomers back which can further be purified by distillation, and then further reused to produce new FEs (54) and incineration (e.g., waste-to-energy facilities). Recycling is limited, due to the presence of fillers, colorants or dies, and other materials added in the final items. Further, it may not be convenient route for all end-of-life components, as they are used predominantly in small components of larger finished items. Therefore, collecting and dismantling for recycling might not be feasible for all products [55]. However, up-cycling treatment is applicable to some articles containing fluoropolymers, such as pipe liners in chemical plants, as well as other plant components as pumps, tank liners, seals, hoses, and many other fluoropolymers components. These are the products for which the high amounts of fluoropolymers are used offering significant recycling potential.

Various data indicate that FEs are too stable and do not degrade in the environment or release toxic substances or are of environmental concern [55]. Additionally, the life-cycle stages of FE creation (i.e. manufacturing) and disposal at the end of industrial or consumer use are important to consider. The primary focus in these life-cycle stages is usually non-polymer PFAS from the manufacturing process or polymer degradation in end-of-life disposal.

Though their tonnage is small, searching strategies to recycle FEs is still a challenge (e.g., VDF units release HF (46,56), as well as to decompose them in a green way. More recently, various VDF-containing FEs have been mineralized into fluoride anions under subcritical water whereas quite a few surveys have reported their recycling (56). But recycling FEs and articles containing such materials is difficult to implement since separation of the FE from the end products (fillers, additives, stabilizers) is not always possible (55) since they are mainly used in small amounts in larger finished articles involving a wide variety of materials.

Recycling treatments can be achieved by the fluoropolymer makers themselves (onsite), or at a larger scale, mainly by specialist recycling companies (56). The up-cycling needs to be co-located to a fluoropolymer fabrication plant that utilizes the recycled monomer.

## Mineralization of VDF-containing copolymers

Super critical water is also able to achieve a *quasi*-complete mineralization of FKM and poly(VDF-*co*-PMVE) elastomers at 250 °C. Actually, Hori's team reported the formation of

 $CaF_2$  from such studies to close the loop on the fluorine chain, as  $CaF_2$  is the natural mineral for fluorinated compounds (57).



Scheme 7: Proposed mechanism for the H<sub>2</sub>O<sub>2</sub>-induced decomposition of poly(VDF-*ter*-HFP-*ter*-TFE) terpolymer. (58). Copyright 2017. Reproduced with permission from Elsevier. This procedure was applied to the successful mineralization of poly(VDF-*ter*-HFP-*ter*-TFE) fluoroelastomer (58) and poly(VDF-*co*-MAF) copolymers (59) (where MAF stands for trifluoromethacrylic acid).

Much information on processing, compounding, formulation, molding, mixing etc.. can be found in Worm and Grootaert's review (1) and we have preferred stressing on the applications, below.

# **Application of Fluorinated Elastomers**

Many applications of FEs have been found in civil, aerospace and engineering materials (Table 5) such as gaskets, O-rings, diaphragms of pumps, pressure sensitive adhesives, medical contact lenses, electronic chemical items, coatings, and other devices involved in high-tech industries (1-4, 30,60).

#### Aerospace and Automotive

Since the dramatic accident of Challenger space shuttle 75 seconds after launching, all gaskets and seals are made of FEs. Actually, modern FEs are endowed with chemical inertness (especially versus the fluids of aeronautics, as phosphoric ester Skydrol®, Figure 8), excellent thermal stability (at low and high temperatures), mechanical, low coefficient of friction and permeation properties which are specific requirements for aerospace and automotive industries (1-4, 61). Indeed, FEs are designed to maintain rubber-like properties and are used as seals, shafts, O-rings and hosing (38, Table 5). According to their molar masses, FEs, mainly PFPEs, are mainly oils or greases, extensively utilized as high-performance lubricants for engines,

machinery, and in specific moving pieces and parts come in contact. PFPE-based lubricants are thermally stable, non-flammable (even in liquid oxygen), chemically inert, and non-volatile over a wide range of temperatures (from -75 to 350 °C). They show a good resistance against ionizing radiations, rending them also suitable candidates in nuclear industries. FEs may swell in polar solvents as DMF and methyl ethyl ketone (40). However, FEs containing a fluorine content higher than 69.5% can overcome such an issue while FEs (e.g. Kalrez®) with 73% fluorine atom display excellent resistance to methanol and methanol-fuel blends (30). Recently, Banerjee and Bhowmick (63) reported the fabrication of a novel thermoplastic elastomeric blends from polypropylene (PP) and FKM via a nano-tailoring approach. Thus, developed nanostructured blends exhibit excellent physical properties, including oil swelling resistance and thermal stability and could have potential use in the automotive industry, as a liner material for car hoses (Figure 10) (3).



Figure 10: FEs utilized in vehicle fuel systems. Reproduced with permission from Elsevier (3).

Table 5 summarizes the use of FEs in aerospace applications.

# **Medical Devices**

Fluorinated elastomers also play a crucial role in medical devices. FEs may be used to make liners in hoses to carry clean fluids. These FEs must be very pure. In place of old-style glass and stainless steel, nowadays pharmaceutical industries make use of fluoroplastics for stirrers, reaction vessels, and other components. The inert, non-stick, and non-destructive nature of FEs have replaced chlorinated or hydrocarbon homologues to give higher yielding and higher virtue measures (64).

The FEs are also involved in cosmetic facial surgery. Furthermore, because of their softness and their optical properties, FEs enter in the composition of contact lenses and corneal inlays (39,64).

Automotive	Aerospace	Industrial
Shaft seals	O-ring in fuel, lubrication,	Hydraulic O-ring seals
	and hydraulic systems	
Valve stem and valve seals	Manifold gaskets	Check valve balls
Fuel injector O-rings	Fuel tank bladders	Military flare binders
Fuel hoses and fuel hose	Firewall seals	Diaphragms
liner		
In-tank and quick connect	Engine lube siphon hose	Electrical connectors
fuel system seals		
Gaskets (valve and	Clips for jet engines	Flue duct expansion joints
manifold)		
Balls for check valves	Electrical connectors	Valve liners
Heat-sealable tubing for	Shaft seals	US FDA approved seals in
wire insulation		food handling processes
Bellows for turbo-charger	Traps for hot engine	Industrial roll covers (100%
lubricating systems	lubricants	FKM or laminates with other

Table 5: Items and parts made of FEs. Reproduced with permission from Elsevier (3-4).

		elastomers)
Lathe cut gaskets	Tire valve stem seals	Safety clothing and gloves
Engine head gaskets	Heat-sealable tubing for	V-ring packers
	wire and cable insulation	

Source: J.G. Drobny, Fluoroelastomer Applications, in: Fluoroelastomers Handb., Elsevier, 2016, pp. 435–438. https://doi.org/10.1016/b978-0-323-39480-2.00011-7 (4).

The applications of PFPEs [telechelic ones being reviewed in 2018 (37)], where telechelic PFPE bis(acylfluoride)s led to polycondensates (polyesters, polyurethanes, polycarbonates, polyethers), triblock copolymers, macromonomers that can further be crosslinked, and (semi) interpenetrated polymer networks are numerous (Scheme 8): self-assembly materials (e.g. anti-bacterial and amphiphilic derivatives, and hydrogels), aerospace materials, microfluidic devices, protective coatings (e.g. deicing, anti-fouling and low surface tension), thermoplastic elastomers, optically transparent films, self-healing materials, specific devices for energy (e.g. Lithium ion and zincair batteries, polymer electrolyte membranes for fuel cells), photoresists for lithographic materials, to theranostics (e.g. intracellular pH measurements and in vivo cell tracking technologies using Magnetic Resonance Imaging).



Scheme 8: Overview of the uses of telechelic dihydroxyl PFPEs, precursors for a wide range of intermediates and well-defined fluoropolymers, including applications therefrom (40).

#### **Summary and Perspectives**

FEs are unique materials with exceptional properties involved in our daily life. They fall into four main varieties and are commercially available [FKM, FFKM copolymers, fluorosilicones and fluorophosphazenes and PFPEs (some being crosslinked)]. Thanks to their amorphous, softness and thermal features, FEs offer unique opportunities for modern applications in high tech industries, engineering, and medical domains. Among them, innovative thermoplastic elastomers, achieved in solution, suspension, emulsion *via* ITP have led to interesting innovations to design original block copolymers comprising of soft (low  $T_g$ ) and hard (high  $T_m$ ) segments with tunable crosslinkability and specific thermal and mechanical properties. Such products have reached the industrial scale regarded as the first ones produced by RDRP. Lowering their  $T_g$  values (below -50 °C) is still a challenge that the first series of Fes cannot reach. Successful FEs for key industrial applications should require clean protocols and processes and use of "green" reactants. Stringent EPA and REACH regulations on the restriction of PFASs (e.g., banning PFOA, PFOS, PFCAs and low molar mass-products) have pushed manufacturers to find out alternatives and abatement conditions. Thus, from new recipes, major manufacturers are currently producing FEs of same performances in presence of non-fluorinated surfactants (or polymerization aids). In addition, new FEs, fulfilling the 13 criteria of PLC, must also be prepared for future recyclability reconsidering life cycle assessment. Hence, original functional groups which do not bring any weak thermal or chemical point should be considered. In addition, further challenges rely on designing sequence-controlled FEs with precisely well-located soft segments able to lower the Tg values. Though expensive, PFPEs should be relevant. Hence, many studies still deserve to be pursued and should attract more and more interest.

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