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# Fluorinated Thermoplastic Elastomers: Current Status and Future Applications

Devendra Kumar<sup>a</sup>, Subrata Dolui<sup>a</sup>, Sanjib Banerjee<sup>a,\*</sup> and Bruno Ameduri<sup>b,\*</sup>

<sup>a</sup>*Department of Chemistry, Indian Institute of Technology Bhilai, Raipur 492015, Chhattisgarh, India*

<sup>b</sup>*ICGM, Univ Montpellier, CNRS, ENSCM, 34095 Montpellier, France.*

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| <b>List of Abbreviations</b>                              |       |
|-----------------------------------------------------------|-------|
| Thermoplastic elastomers                                  | TPEs  |
| Fluorinated thermoplastic elastomer                       | F-TPE |
| Fluorinated elastomers                                    | FES   |
| Ethylene propylene diene monomer                          | EPDM  |
| Polyisobutylene                                           | PIB   |
| Polyurethane                                              | PU    |
| Ground tyre elastic                                       | GTR   |
| Poly(styrene- <i>b</i> -butadiene- <i>b</i> -styrene)     | SBS   |
| Poly(Styrene- <i>b</i> -isoprene- <i>b</i> -styrene)      | SIS   |
| Poly(styrene- <i>b</i> -ethylbutylene- <i>b</i> -styrene) | SEBS  |
| Poly(styrene- <i>b</i> -isobutylene- <i>b</i> -styrene)   | SIBS  |
| Syndiotactic Polystyrene                                  | SPS   |
| Hexafluoropropene                                         | HFP   |
| Vinylidene fluoride                                       | VDF   |
| Perfluoroalkoxy alkanes                                   | PFA   |
| Fluorinated ethylene propylene                            | FEP   |
| Tetrafluoroethylene                                       | TFE   |
| Polytetrafluoroethylene                                   | PTFE  |
| Polystyrene                                               | PS    |
| Polybutadiene                                             | PB    |
| Poly(2- vinylpyridine)                                    | P2VP  |
| Polyisoprene                                              | PI    |
| Iodine transfer polymerization                            | ITP   |
| Chain transfer agent                                      | CTA   |

|                                                                                                        |                                             |
|--------------------------------------------------------------------------------------------------------|---------------------------------------------|
| N,N-dimethylformamide                                                                                  | DMF                                         |
| Poly( <i>tert</i> -butyl acrylate)                                                                     | PtBA                                        |
| Chlorotrifluoroethylene                                                                                | CTFE                                        |
| Polychlorotrifluoroethylene                                                                            | PCTFE                                       |
| Perfluoromethyl vinyl ether                                                                            | PMVE                                        |
| Glass transition temperature                                                                           | $T_g$                                       |
| Melting temperature                                                                                    | $T_m$                                       |
| Dimethyl sulfoxide                                                                                     | DMSO                                        |
| Fluorinated thermoplastic elastomers                                                                   | FluoroTPEs                                  |
| Hydro thermoplastic elastomers                                                                         | HydroTPEs                                   |
| Fluorinated thermoplastic polyurethane                                                                 | FTPU                                        |
| Fluoro modified polytetramethylene-based                                                               | FPTB                                        |
| Fluorinated Polyimide/fluorinated polyhybridsiloxane block copolymers                                  | FPI-FPHSX                                   |
| Poly(vinylidene fluoride)- <i>g</i> -sulfonated polystyrene graft copolymer                            | PVDF- <i>g</i> -SPS                         |
| Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene)                                              | Poly(VDF- <i>co</i> -HFP)                   |
| Poly(vinylidene fluoride- <i>ter</i> -hexafluoropropylene- <i>ter</i> -tetrafluoroethylene) terpolymer | Poly(VDF- <i>ter</i> -HFP- <i>ter</i> -TFE) |
| Poly(vinylidene fluoride- <i>co</i> -chlorotrifluoroethylene)- <i>g</i> -poly(styrene sulfonic acid)   | Poly(VDF- <i>co</i> -CTFE)- <i>g</i> -PSSA  |

## 1. Introduction

Fluoropolymers<sup>1-7</sup> have emerged as a unique class of materials due to a combination of their versatile nature (ranging from thermoplastics to elastomers, and thermoplastic elastomers) and interesting properties such as excellent chemical/thermal/weather resistance, high repellency towards oil, water and soil, low refractive index/flammability/dielectric constants and improved resistance to hydrolytic and oxidative degradation. Thus, these polymers have

increasingly found applications in automotive and petrochemical industries, aeronautics, aerospace, microelectronics, wire and cable industries. Compared to fluorinated homopolymers which are crystalline and difficult to cure/crosslink, fluorinated elastomers can be easily cured due to their low crystallinity arising out from disorganized or amorphous structure. Thermoplastic elastomers have received some attention from the researchers in recent years. Hillmyer and coworkers synthesized a Poly( $\gamma$ -methyl- $\epsilon$ -caprolactone) (P $\gamma$ MCL)-based strong, resilient, and sustainable aliphatic polyester TPEs.<sup>8</sup> Subsequently, the same group developed aliphatic polyester TPEs containing hydrogen-bonding ureidopyrimidinone endgroups<sup>9</sup> and achieved enhanced mechanical properties of aliphatic polyester thermoplastic elastomers through star block architectures.<sup>10</sup> Hillmyer group also reported development of TPEs from the grafting-through polymerization of lactone-containing polyester macromonomers.<sup>11</sup> Bates and coworkers recently developed an asymmetric miktoarm star polymers-based TPE.<sup>12</sup>

Although there has been no report on circularity of F-TPE manufacturing/synthesis. There are some reports on the biodegradability/reuse/recycling of fluoropolymers in general.<sup>13-16</sup> It is to be noted that low molecular weight perfluoroalkoxy (PFA) are different from fluoropolymers. There has been few reports on the decomposition, recycling and reuse of fluoropolymers such as including polytetrafluoroethylene (PTFE)<sup>17</sup> and polyvinylidene fluoride (PVDF).<sup>18</sup>

This chapter mainly focuses on fluorinated thermoplastic elastomers (TPEs), ranging from (per)fluorocarbon elastomers (Figure 1) to fluorophosphazenes, and fluorosilicones. In order to maintain the length of the section succinct, this chapter will give a generally concise study of the recent and exciting developments in the field of fluorinated TPEs, as opposed to giving an extensive account of the field. Fluorinated (co)polymers in general and fluorinated TPEs have picked up some interests from both academic world and industry due to their unique properties (such as excellent hydrophobicity, oleophobicity, anti-sticking and thermal properties) and potential emerging applications.<sup>19, 20</sup>

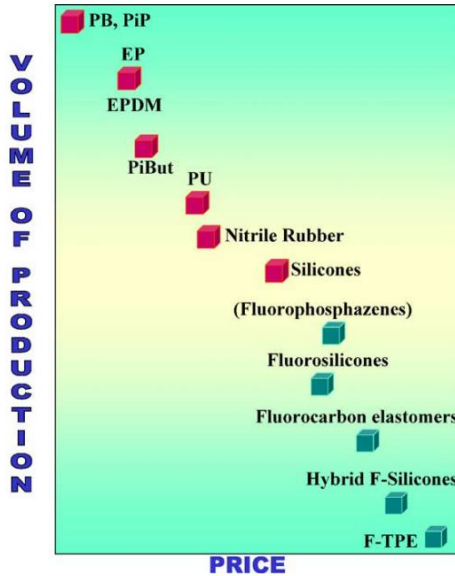


Figure 1. A selection of elastomers; amounts produced vs. price (arbitrary scale). Reproduced with permission from Elsevier.<sup>21</sup>

### 1.1 Elastomers and Elasticity

An elastomer is a polymer material with both viscous and elastic properties.<sup>22</sup> These materials have very weak intermolecular forces and exhibit low Young's modulus and high failure strain (Figure 2).<sup>23-26</sup> That is why it is essential to crosslink them to get better mechanical properties.



Figure 2. Different shapes of molecular chains of thermoplastic, elastomer and thermoset. Reproduced with permission from Wiley.<sup>27</sup>

### 1.2 Thermoplastic Elastomers

TPEs, sometimes called thermoplastic rubbers, are a class of copolymers or a physical blend/mix of polymers (usually a plastic and a rubber) having physical cross-links between two phase materials that govern its structural behavior. Typically, the two parts of TPEs must have two

opposite types of structure: the elastomeric part and the restraining one.<sup>28-32</sup> The elastic segment should have high molar mass and possesses other features of an elastomer. Table 1 provides some well-known examples of TPEs.<sup>33-35</sup>

Table 1.  $T_g$  and  $T_m$  values of some important hydrocarbon TPEs.

| <b>Elastomer Type</b>                                                                       | <b>Soft phase, <math>T_g</math> (°C)</b> | <b>Supplier</b>                                  | <b>Hard phase, <math>T_g</math> or <math>T_m</math> (°C)</b>           |
|---------------------------------------------------------------------------------------------|------------------------------------------|--------------------------------------------------|------------------------------------------------------------------------|
| Poly(styrene-butadiene-styrene) (SBS)                                                       | -90                                      | SINOPEC, and BassTech International              | 95 ( $T_g$ )                                                           |
| Styrenic block copolymer (SBC) consisting of polystyrene blocks and rubber blocks (Kraton®) | -90                                      | Shell                                            | 100                                                                    |
| Polystyrene- <i>b</i> -polybutadiene- <i>b</i> -polystyrene triblock copolymers             | -57                                      | ExxonMobil                                       | 143<br>$T_g$ of the poly(ether) < 0 °C; $T_g$ of the polyester > 70 °C |
| Poly[styrene-(ethylene- <i>co</i> -butylene)-styrene] (SEBS)                                | -60                                      | SINOPEC, Calperene H 6120, and Calperene H 6170  | 95 ( $T_g$ ) and 165 ( $T_m$ )                                         |
| Poly(styrene- <i>b</i> -Isobutylene- <i>b</i> -Styrene) (SIBS)                              | -55                                      | SINOPEC                                          | 95 ( $T_g$ ) and 165 ( $T_m$ )                                         |
| Polyurethane elastomers                                                                     | -40 to -60 <sup>a</sup>                  | American Urethane, Inc. Odenton, MD              | 190 ( $T_m$ )                                                          |
| Polyester elastomers                                                                        | -40                                      | Padmini Innovative Marketing Solutions Pvt. Ltd. | 185 to 220 ( $T_m$ )                                                   |
| Polyamide elastomers                                                                        | -40 to -60 <sup>a</sup>                  | LG Chem Ltd.                                     | 220 to 275 ( $T_m$ )                                                   |

|                                            |     |        |                                                                                                |
|--------------------------------------------|-----|--------|------------------------------------------------------------------------------------------------|
| Polyamide- <i>b</i> -polyether<br>(Pebax®) | -65 | Arkema | Polyamide11 $T_m = 180\text{ }^\circ\text{C}$<br>Polyamide12 $T_m = 190\text{ }^\circ\text{C}$ |
|--------------------------------------------|-----|--------|------------------------------------------------------------------------------------------------|

Notes: <sup>a</sup>The values are for polyester and polyether. <sup>b</sup>Polyether is PEO or PPO or poly(tetramethylene glycol) (PTMG).

### 1.3 Importance of TPEs over Conventional Rubber or Thermoplastics

TPEs are the class of polymeric materials which display elastic behavior of rubber (Figure 3). Rubber have been of immense significance to our everyday life since the beginning of the automotive industry.<sup>36</sup> These days, plastics and rubbers are broadly utilized in various fields and thus it is called in some cases "*Plastic Age*". Because of the fact that these materials do not self-decompose easily, the disposal of their wastes causes a serious environmental problems.<sup>37, 38</sup> However, the reutilization of polymer wastes is challenging for our civilization. The most direct choice is, in any case, to mix elastic with a polymer material being able to stream under specific conditions (such as temperature and pressure) and then mold it into desired shapes at adequate expense. Next, an outline will be given on how ground tire rubber (GTR), with and without surface treatment, can be utilized in thermoplastic, thermoset and elastic plans.<sup>38-40</sup>

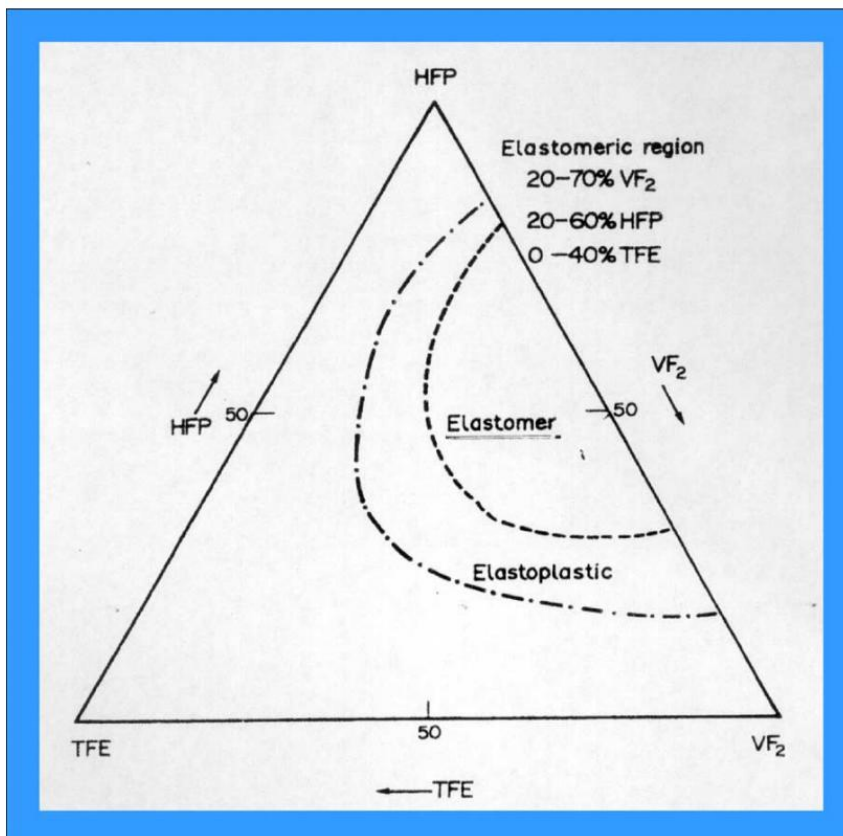


Figure 3. Ternary diagram showing elastomeric and elastoplastic regions of poly(VDF-*ter*-HFP-*ter*-TFE) terpolymers, the remaining part being thermoplastic. Reproduced with permission from Wiley.<sup>2136</sup>

## 1.4 Fluorocarbon Elastomers.

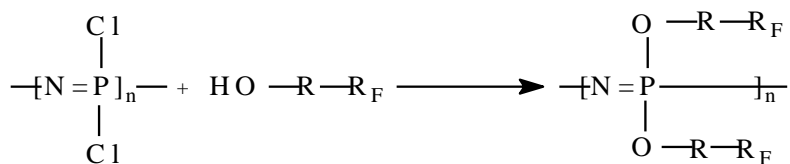
### 1.4.1 Fluorocarbon Elastomers.

These types of specialty polymers are usually prepared via radical copolymerization of different fluoroalkenes such as vinylidene fluoride (VDF), hexafluoropropylene (HFP), tetrafluoroethylene (TFE), perfluoromethylvinyl ether (PMVE), chlorotrifluoroethylene (CTFE) and pentafluoropropylene (PFP), followed by introduction of functional comonomers containing a crosslinking group.<sup>41-43</sup> Various examples of commercial fluorinated elastomers (FEs) are currently available.<sup>41-44</sup> Most of which are cross-linkable copolymers of VDF or TFE with few suitable fluorinated comonomers like HFP. In addition, researchers have developed several approaches for the synthesis of fluorinated multiblock copolymers using hydroxytelechelic perfluoropolyethers (PFPEs) as the precursor.<sup>45</sup> As an example, Tonelli et al.<sup>46</sup> synthesized original fluorinated polyurethanes containing a Fomblin®-based PFPE sequence.

Enhanced properties (chemical, thermal and mechanical stabilities) can be achieved when these fluoroelastomers are crosslinked. The crosslinking process has comprehensively been reported in books and reviews.<sup>41-44, 47</sup> Shimizu and coworkers<sup>48</sup> studied the use of various fluorinated dienes as cross-linking agents for perfluoroelastomers (mainly FKKM as a terpolymer based on TFE, PAVE and a cure site monomer) in order to bring two keys features: resistance to high-temperature vapour and cross-linking efficiency. These dienes were:  $F_2C=CF-R_1-CF=CF_2$  (where  $R_1$  stands for  $C_6H_4$  ( $CF_2$ ) $_6C_6H_4$  or bisphenyl) or  $H_2C=CH-(CF_2)_6-CH=CH_2$ .<sup>49</sup>

### 1.4.2 F-Phosphazenes.

Typically, F-phosphazenes (Scheme 1) are synthesized via nucleophilic substitution reaction of fluorinated alcohols with dichlorophosphazenes.<sup>6</sup>

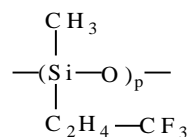


Scheme1. Synthesis of F-phosphazenes where RF stands for fluoroalkyl group

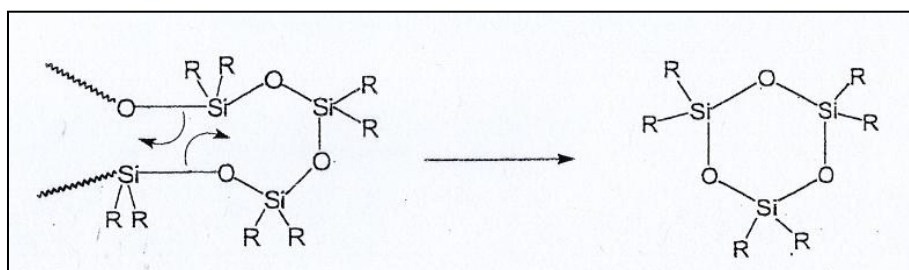
Firestone Polymers was the first company to commercialize F-phosphazenes by the name PNF<sup>®</sup>.<sup>50</sup> These polymers exhibit low  $T_g$ s (around  $-70$  °C). Gleria *et al.*<sup>51</sup> reviewed the synthesis, properties and applications of alkoxy and aryloxy substituted F-phosphazenes. Matyjaszewski<sup>52</sup> and Allcock<sup>53</sup> group also reported block copolymers based on such polymers by sequential polycondensation reaction on phosphazene.<sup>54</sup>

### 1.4.3 F-Silicones.

Dow Corning Corporation was the first company to commercialize fluorosilicones<sup>5</sup>: poly[methyl(3,3,3-trifluoropropyl)siloxane] under Silastic<sup>®</sup> trade name (Scheme 2). Interestingly, these polymers exhibited a  $T_g$  of  $-65$  °C. However, their thermal stability was not exceptional inducing a backbiting from 230 °C (Scheme 3).

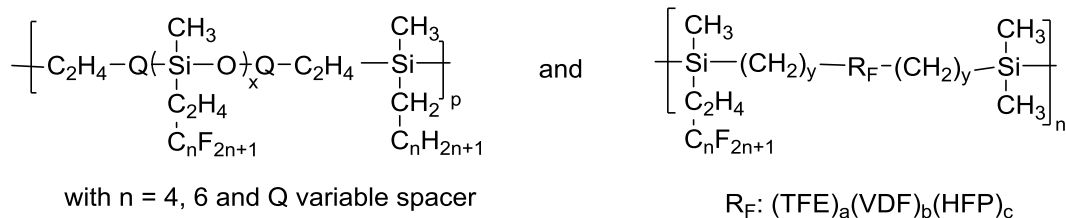


Scheme 2. Chemical structure of F-silicones.



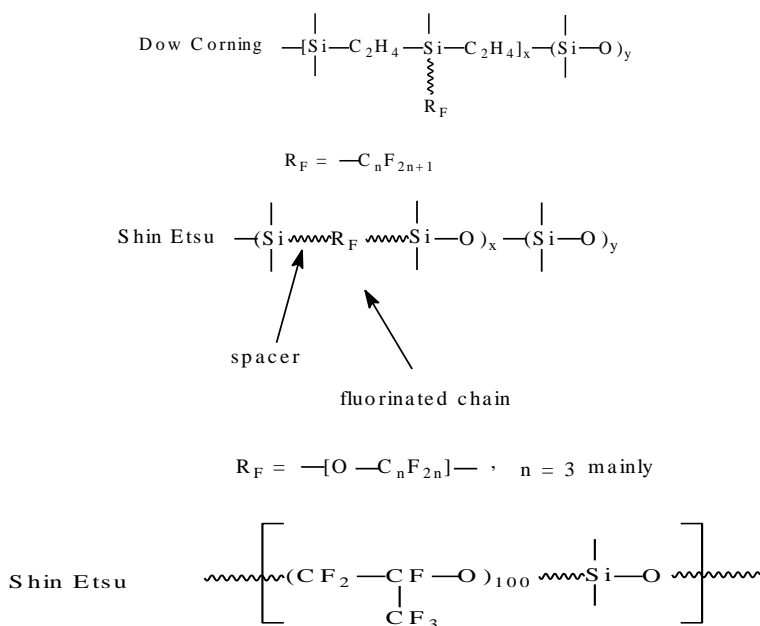
Scheme 3. Schematic illustration of backbiting occurring at  $T > 230$  °C in poly(dialkylsiloxane)s.

To increase such a thermal stability, one idea was to make further the silicon atoms and Kobayashi's<sup>55</sup> and Boutevin's<sup>56</sup> teams reported the synthesis of hybrid fluorosilicones containing polysiloxane and fluorocarbon moieties (Scheme 4). These unique hybrids exhibited improved oleophobic, hydrophobic, thermal and surface properties compared to conventional silicones or to Silastic<sup>®</sup>.



Scheme 4. Chemical structures of hybrid fluorosilicones ( $y = 2, 3$  and  $n = 3, 4, 6$ ).<sup>55, 57</sup>

Dow Corning and Shin-Etsu Companies<sup>58</sup> subsequently developed fluorinated-silicones as original hybrid silicones (Scheme 5) with very low  $T_g$ s. Additionally, for Sifel® material marketed by Shin-Etsu, the polymer contains only one dimethyl siloxane unit per ca. 50-100 hexafluoropropylene oxide (HFPO) units:



Scheme 5. Chemical structures of fluoro-silicones commercialized by Dow Corning or Shin-Etsu companies.

### 1.5. Fluorinated Thermoplastic Elastomers (F-TPEs)

Fluoropolymers<sup>1-7</sup> exhibit a unique combination of high thermal properties, chemical inertness (to acids, bases, solvents and petroleum), low dielectric constants and dissipation factors, low flammability and very interesting surface properties, in contrast to hydrocarbon TPE which fail in reaching such characteristics, as demonstrated by Andre et al.<sup>59</sup> The future prospects of

fluorinated polymers and H-TPEs depend on the possibility of successfully synthesizing new fluorinated TPEs possessing low coefficient of rubbing.<sup>20</sup>

### **1.6. FluoroTPEs vs HydroTPEs**

As mentioned in the section above, the presence of fluorine atoms in such copolymers<sup>7, 15, 60</sup> is the main reason of such high thermal, chemical, aging, and weather resistance, good inertness to solvents, oils. Along with these features, the presence of C-F bond resulted in high protection from oxidative and hydrolytic degradation. These unique properties open up more opportunities for applications of such copolymers in various emerging applications (see section 4). Thus, fluoroTPEs are preferred over hydroTPEs and have found specific applications for high technologies especially electronics, car and aerospace industries where the requirements are demanding regarding the chemical inertness and preserving their outstanding properties (including softness and resilience) on a wide range of temperatures.

### **1.7. Importance of Fluorinated Copolymer over Fluorinated Homopolymer**

Some of the well-known fluorinated homopolymers suffer from key disadvantages such as high crystallinity leading to poor solubility and the difficulty in cross-linking or tuning their properties. Fluorinated copolymers overcome these limitations if and when functional comonomers with tunable group (which favor the properties) are present in their backbone of the resulting material. This allows incorporation of functionalities required for the desired objectives and leads to interesting applications of these fluorinated copolymers in the field of functional coatings, separators/binders for cathodes in Li-ion batteries, membranes, seals, shafts, gaskets and specific items for automotive and aerospace industries, as well as biomedical applications.<sup>61</sup>

## **2. Synthesis of Fluorinated Thermoplastic Elastomers**

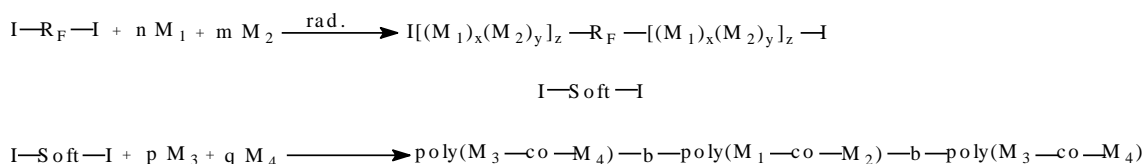
One of the main processes to develop high performance TPEs is based on the copolymerization of monomers of desired functionalities which may serve the purpose of building blocks. This approach provides the opportunities to combine the properties of the monomers of the diverse families and prepare a unique material with improved mechanical properties.<sup>62</sup> H-bonding serves the purpose of combining the properties of electron donor and acceptor monomers and thus may influence the mechanical properties of the final polymer.<sup>63</sup> Fluorinated TPEs are synthesized by one or multiple reaction steps to create each phase separately. The synthetic procedures are listed below.

## 2.1. Synthesis via Reversible Deactivation Radical Polymerization (RDRP)

Since mid 1990's, a major development on controlled radical polymerization (or RDRP)<sup>64</sup> has been witnessed, though the authors ignored the achievement of F-TPEs produced by sequential iodine transfer copolymerization discovered in the late 1970's (section 2.1.1). A successful RDRP procedure depends upon four factors: (i) lower concentration of the "active" (macro)radicals compared to the "dormant" chains; (ii) reversible fast exchange between living 'active' macro radicals and dormant chains; (iii) evidence of a linear molar mass versus monomer conversion relationship and (iv) possibility for chain extension for producing block or graft copolymers.<sup>65</sup>

### 2.1.1 Via Iodine Transfer Polymerization (ITP)

Iodine transfer polymerization (ITP) of fluoromonomers, pioneered in late 1970s by Tatemoto,<sup>66</sup> was projected as the first RDRP method to prepare fluoropolymers. In ITP, the control of the reaction is maintained by the terminal dynamic bond ("*pseudo-living*") of the propagating polymer chain which is generated from the iodine-containing chain transfer agent (CTA) and the monomer.<sup>67</sup> Interestingly, various combinations of synthetic block microstructures are possible<sup>20</sup> 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 applied by Daikin, Dupont Performance Elastomers and Solvay Specialty Polymers have led to commercially available block copolymers, regarded as the first fluorinated block copolymers produced in an industrial scale (Scheme 6).<sup>68</sup>

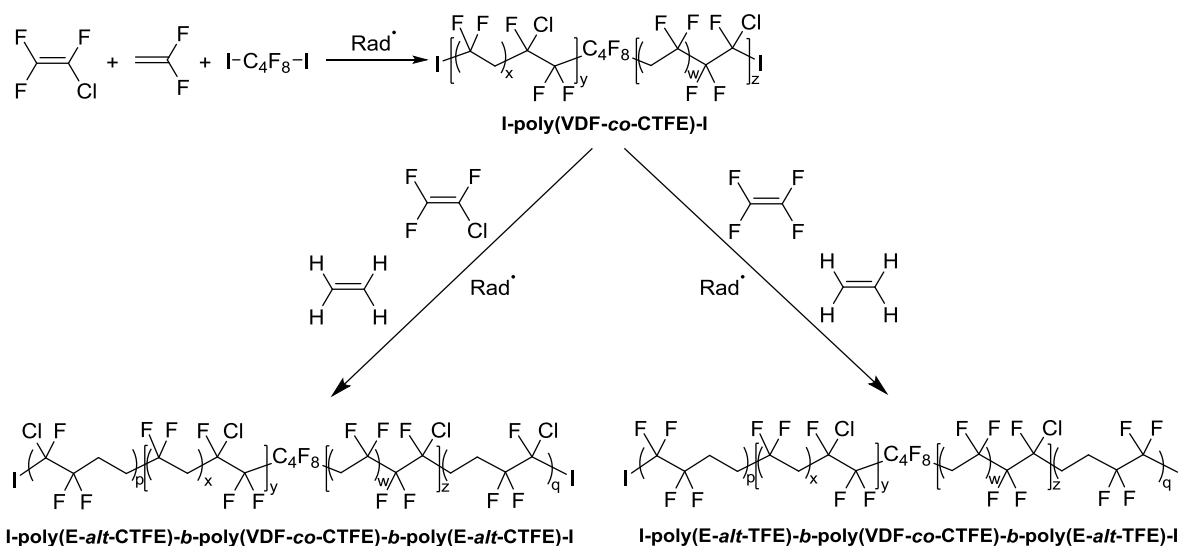


Scheme 6. Synthesis of Hard-Soft-Hard triblock fluorinated TPEs, where  $\text{M}_1$ ,  $\text{M}_2$ ,  $\text{M}_3$  and  $\text{M}_4$  fluoroalkenes can be well-chosen among TFE, VDF, HFP, PMVE, CTFE, ethylene (E) and propylene (P).

However, lowering their  $T_g$  values (as low as  $-50\text{ }^\circ\text{C}$ ) is still a challenge. Subsequently, researchers have improved on this aspect and reported the use of perfluoropolyethers crosslinked by triazine<sup>41</sup> yielding F-TPEs with improved properties.<sup>69</sup> Obtaining such materials required specific synthesis protocol, as demonstrated below.

Before F-TPEs, fluorinated telomers were produced since the 1940-1950's.<sup>4, 19</sup> Most relevant telomers were synthesized from fluorinated monoiodides ( $\text{R}_\text{F}\text{-I}$ ) or telechelic diiodides ( $\text{I- R}_\text{F}\text{-I}$ )<sup>4, 70</sup> which generate stable  $\text{R}_\text{F}\cdot$  radicals, induced by photo or thermal initiation. Scheme 7 describes a two-step strategy for the preparation of a fluorinated TPE bearing Hard-Soft-hard segment starting from a telechelic fluorinated soft polymer as an appropriate CTA (Table 2). Then, the second step inserts the hard end blocks (e.g. PVDF, PTFE, ETFE or ECTFE).

A typical example is shown in Scheme 7 where the soft block is an elastomeric poly(VDF-*co*-CTFE) copolymers,<sup>66, 68, 71</sup> (VDF mol.% ranging between 25 and 75%) while the hard sequences are either poly(TFE-*co*-E) or poly(CTFE-*co*-E) copolymers.



Scheme 7. Use of telechelic diiodo poly(CTFE-*co*-VDF) copolymers as a macro chain transfer agent in the radical copolymerization of ethylene with either tetrafluoroethylene or CTFE to achieve triblock thermoplastic elastomers. Reproduced with permission from American Chemical Society.<sup>71</sup>

Various other similar ITP strategies have been used to design F-TPE and Table 2 summarizes the thermal properties of F-TPEs, along with their composition molar ratio of Hard/Soft segment. From the result, it is clear that the composition of the copolymer significantly affects its thermal

properties.  $T_g$  is still high ( $T_g > -33$  °C) and a mix with F-silicone<sup>5</sup> or fluorophosphazene<sup>6</sup> or oligo(HFPO), PFPE<sup>45, 69</sup> would be valuable to approach values -60 or even -95 °C.<sup>72</sup>

The process can be emulsion, suspension, microemulsion, or solution. First, Daikin invented and protected such an innovation<sup>66, 68, 73-76</sup> and then almost one decade later, the DuPont Performance Elastomers Company (now Chemours Company)<sup>77</sup> and at Ausimont (now Solvay Specialty Polymers)<sup>49, 78, 79</sup> were inspired from it. A *quasi*-exhaustive summary of these investigations is given in Table 2 where  $M_1$ ,  $M_2$ ,  $M_3$  and  $M_4$  fluoroalkenes (Scheme 6) can be well-chosen among TFE, VDF, HFP, PMVE, CTFE, ethylene (E) and propylene (P). Typical combinations of comonomers by pair, trio or quartet enabled the authors to design both soft and hard sequences (Schemes 6-7).<sup>68</sup> In the case of the formation of blocks by the above co- or ter-polymerization of two or three olefins above, soft or hard segments could be synthesized by varying the comonomer amounts and taking into account their reactivity ratios. It is known that a poly(VDF-*co*-HFP) copolymers bearing less than 15 mol. % HFP is a thermoplastic (semicrystalline) while that containing an HFP content higher than 15 mol. % possesses elastomeric (amorphous) properties.<sup>43, 44, 60</sup> 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 TPE up to 1,000,000.<sup>80</sup>

As a consequence, original TPEs, composed of soft and hard segments, have been achieved in a living fashion by sequential ITP. They are endowed with a negative glass transition temperature,  $T_g$ , and high melting temperatures,  $T_m$ , sometimes higher than 250 °C (Table 2). Figure 4 represents typical structure of Dai-el<sup>®</sup> (marketed from Daikin)<sup>66, 68, 73, 80, 81</sup> or TPE supplied by Solvay Specialty Polymers (Tecnoflon<sup>®</sup>)<sup>49, 78, 79, 82</sup> or Chemours (Viton<sup>®</sup>)<sup>77</sup> in which both amorphous and crystalline zones coexist.

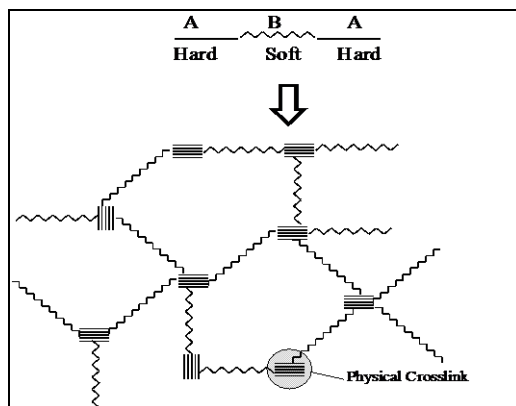
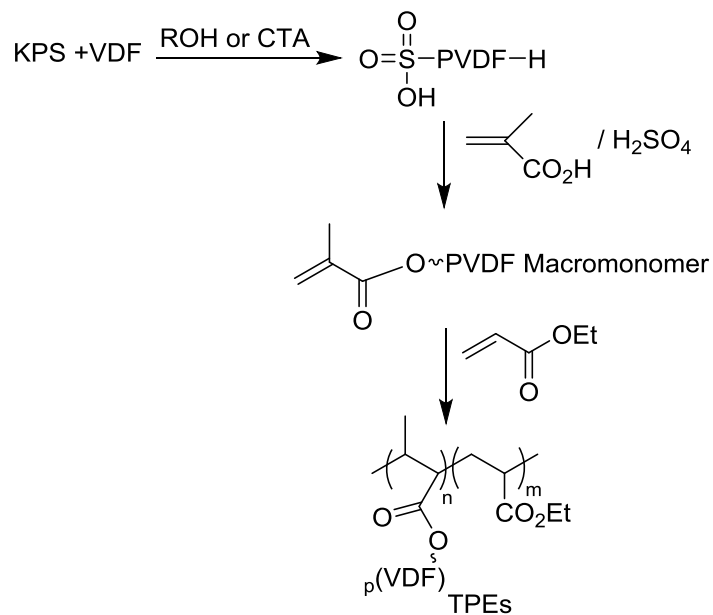


Figure 4. Schematic structural morphology of Hard-Soft-Hard thermoplastic elastomers that can be physically crosslinked.

The Daikin Company also reported the terpolymerization<sup>80, 81</sup> of VDF with HFP and TFE controlled by  $I-(CF_2)_4-I$  and initiated by bis(trichloroperfluorohexanoyl) peroxide to yield a soft  $I(HFP)_a(VDF)_b(TFE)_cI$ -diiodide containing a 30/50/20 molar ratio with a dispersity of 1.27. Further, this diiodide 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.

Another typical example deals with the hard sequence made of a poly(TFE-*ter*-HFP-*ter*-E) terpolymer (the comonomers having a 49:8:43 molar ratio in the thermoplastic block.<sup>80</sup> A similar approach was also adopted with a central soft sequence containing a poly(VDF-*ter*-HFP-*ter*-E) terpolymer in 50:20:30 molar ratio.<sup>83</sup> Additional advantages of involving ethylene as the comonomer deals on i) its low cost, ii) the livingness of the polymerization and iii) this monomer enables reducing the base sensitivity of VDF-containing copolymers.<sup>77</sup>

In addition, the Goodrich Company claimed the synthesis of original PEA-*g*-PVDF TPEs based on PVDF grafts and poly(ethyl acrylate), PEA (Scheme 8), and their mechanical properties (Figure 5) showed better stress-strain than the PVDF/PEA blend.<sup>32</sup>



Scheme 8. Synthesis of TPEs based on PVDF graft and poly(ethyl acrylate) backbone (where KPS stands for potassium persulfate initiator).<sup>32</sup>

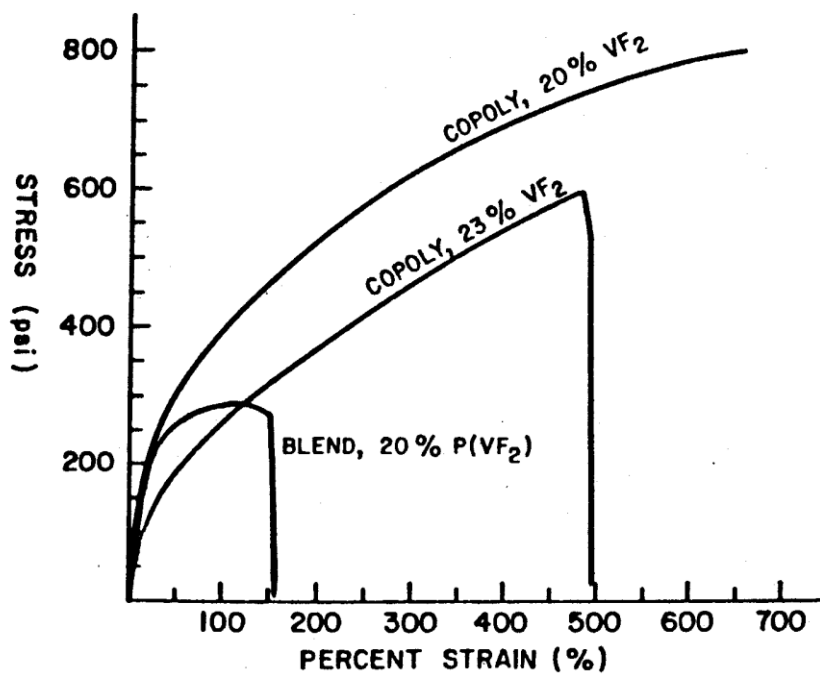


Figure 5. Tensile stress vs. strain curves for PEA-*g*-PVDF graft copolymers and physical PVDF/poly(ethyl acrylate) (PEA) blends with nominally 20% VDF (or VF<sub>2</sub>).<sup>32</sup>

Table 2. Iodine transfer polymerization of fluorinated alkenes for the synthesis of fluorinated thermoplastic elastomers: triblock copolymers based on hard and soft segments (n.d.: not given).

| Soft block                                                                 | %Composition of the block sample | Hard block                                | Mol ratio of Hard/Soft (wt%) | $T_g$ (°C) | $T_m$ (°C) | Reference      |
|----------------------------------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------|------------|------------|----------------|
| I[(VDF) <sub>x</sub> HFP] <sub>y</sub> I                                   | n.d.                             | PVDF                                      | n.d.                         | n.d.       | 160        | <sup>74</sup>  |
| I[(VDF) <sub>x</sub> HFP] <sub>y</sub> I                                   | n.d.                             | poly(E- <i>alt</i> -TFE)                  | n.d.                         | n.d.       | 220        | <sup>74*</sup> |
| I[(CTFE) <sub>x</sub> (VDF) <sub>y</sub> ] <sub>z</sub> I                  | 45/55                            | poly(E- <i>co</i> -TFE)                   | 85/15                        | -6         | 247        | <sup>80</sup>  |
| I[(CTFE) <sub>x</sub> (VDF) <sub>y</sub> ] <sub>z</sub> I                  | 45/55                            | poly(E- <i>co</i> -TFE)                   | 90/10                        | -8         | 252        | <sup>80</sup>  |
| I[(VDF) <sub>x</sub> (FVA) <sub>y</sub> ] <sub>z</sub> I                   | n.d.                             | PVDF                                      | n.d.                         | n.d.       | n.d.       | <sup>68</sup>  |
| I[(VDF) <sub>x</sub> P] <sub>y</sub> I                                     | 55/45                            | poly(E- <i>co</i> -TFE)                   | 80/20                        | -1         | 267        | <sup>77</sup>  |
| I[(VDF) <sub>x</sub> HFP(TFE) <sub>y</sub> ] <sub>z</sub> I <sup>b,c</sup> | 56/19/25                         | PVDF                                      | 80/20                        | -12 to -15 | 165        | <sup>49</sup>  |
| I[(VDF) <sub>x</sub> HFP(TFE) <sub>y</sub> ] <sub>z</sub> I                | 35/40/25                         | poly(E- <i>alt</i> -TFE)                  | n.d.                         | -8         | 222        | <sup>74</sup>  |
| I[(VDF) <sub>x</sub> HFP(TFE) <sub>y</sub> ] <sub>z</sub> I                | 50/30/20                         | poly(E- <i>ter</i> -HFP- <i>ter</i> -TFE) | 85/15                        | n.d.       | n.d.       | <sup>80</sup>  |
| I[(VDF) <sub>x</sub> HFP(TFE) <sub>y</sub> ] <sub>z</sub> I <sup>b</sup>   | 54/21/25                         | poly(E- <i>alt</i> -                      | 80/20                        | -13        | 266        | <sup>49</sup>  |

|                                                                           |          |                          |       |            |     |                   |
|---------------------------------------------------------------------------|----------|--------------------------|-------|------------|-----|-------------------|
|                                                                           |          | TFE)                     |       |            |     |                   |
| I[(VDF) <sub>x</sub> PMVE(TFE) <sub>y</sub> ] <sub>z</sub> I <sup>b</sup> | 62/19/19 | PVDF                     | 80/20 | -30        | 160 | <sup>49, 77</sup> |
| I[(VDF) <sub>x</sub> PMVE(TFE) <sub>y</sub> ] <sub>z</sub> I              | 73/17/10 | poly(E-co-TFE)           | 72/28 | -33        | 254 | <sup>77</sup>     |
| I[(VDF) <sub>x</sub> PMVE(TFE) <sub>y</sub> ] <sub>z</sub> I <sup>b</sup> | n.d.     | poly(E-co-TFE)           | n.d.  | -13 to -15 | 266 | <sup>49</sup>     |
| I[(VDF) <sub>x</sub> PMVE(TFE) <sub>y</sub> ] <sub>z</sub> I <sup>b</sup> | 57/23/20 | poly(E-ter-TFE-ter-PMVE) | 75/25 | n.d.       | 180 | <sup>84</sup>     |
| I[(TFE) <sub>x</sub> P(VDF) <sub>y</sub> ] <sub>z</sub> I                 | n.d.     | poly(E-co-TFE)           | 85/15 | -13        | 262 | <sup>77</sup>     |
| I[(TFE) <sub>x</sub> E(PMVE) <sub>y</sub> ] <sub>z</sub> I                | 45/19/36 | poly(E-co-TFE)           | 71/29 | -16        | 245 | <sup>77</sup>     |

a) CTFE : chlorotrifluoroethylene, E : ethylene, FVA : perfluorovinyl acetic acid, HFP : hexafluoropropylene, P : propylene, PMVE : perfluoromethylvinylether, TFE : tetrafluoroethylene, VDF : vinylidene fluoride

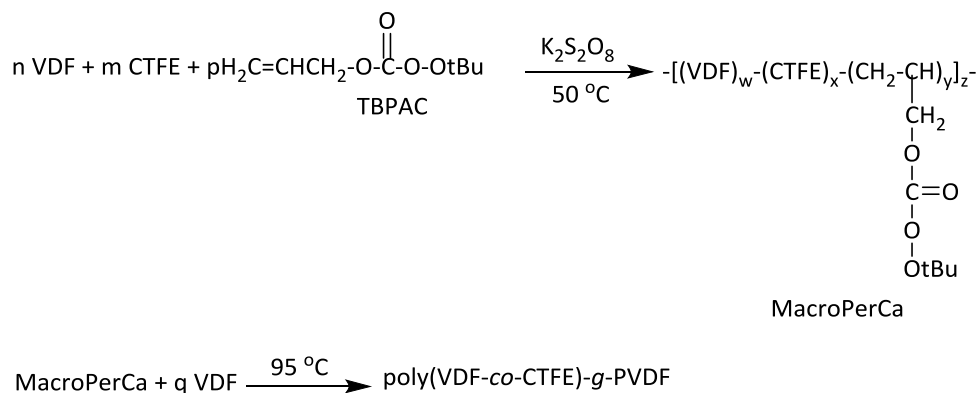
b) tetrapolymerization with less than 1 mol.% of H<sub>2</sub>C=CH-C<sub>6</sub>F<sub>12</sub>-CH=CH<sub>2</sub>.

c) tetrapolymerization with less than 1 mol.% of the mixture H<sub>2</sub>C=CH-C<sub>6</sub>F<sub>12</sub>-CH=CH<sub>2</sub>/H<sub>2</sub>C=CHC<sub>6</sub>F<sub>12</sub>C<sub>2</sub>H<sub>4</sub>/IC<sub>2</sub>H<sub>4</sub>C<sub>6</sub>F<sub>12</sub>C<sub>2</sub>H<sub>4</sub>I.

\*The composition of the soft segment is related to the mol% TFE or VDF (usually <80-85 mol%).

In addition, using  $\alpha,\omega$ -diiodofluoroalkanes favors the control of the (co)polymerization, as listed in Table 2 that shows the variety of chain transfer agents required in ITP of fluoroolefins. Although not all the reactions were carried out in the same experimental conditions, it is observed that dispersities of the final TPE as low as 1.73 could be produced from diiodides. In addition, when a fluorinated non-conjugated diene<sup>49, 79</sup> was chosen in the terpolymerisation of fluoroalkenes, *D* value was even lower (1.4). This improved control of ITP, called « *pseudo* living and branching technology », <sup>49</sup> has extensively been studied at Ausimont (in the 1990's) and enabled production of competitive thermoplastic elastomers. This is the case for example of Tecnoflon<sup>®</sup> FTPE XPL.

Table 2 also lists the  $T_g$ s and  $T_m$ s of these fluorinated thermoplastic elastomers. Even when PMVE was added in the soft block, the  $T_g$  could not be significantly lowered. Further, the introduction of a small non-conjugated diene amount slightly lowered the  $T_g$  and increased the  $T_m$  by a few degrees. Most of these TPEs could be utilized from  $-30\text{ }^\circ\text{C}$  to  $250\text{ }^\circ\text{C}$ <sup>74, 75</sup> and can be used in continuous service at  $200\text{ }^\circ\text{C}$  (in contrast to conventional elastomers that decompose at this temperature). F-TPEs can also be graft copolymers and an industrial example (Cefral Soft®<sup>81</sup> marketed by the Central Glass Company) is illustrated in Scheme 9. Thus, an unsaturated peroxide was terpolymerized at low temperature with VDF and CTFE to generate fluorinated copolymers bearing peroxide side groups which initiated the graft polymerization of VDF to yield original poly(VDF-co-CTFE)-g-PVDF graft TPEs.



Scheme 9. Synthesis of poly(VDF-co-CTFE)-g-PVDF graft thermoplastic elastomer (Cefral Soft® marketed by the Central Glass Company) in a two-step procedure from the sequential copolymerization involving an unsaturated peroxide-containing comonomer.<sup>81</sup>

Actually, the TPEs can be crosslinked by the peroxide / triallyl (iso)cyanurate system<sup>78, 82</sup> 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) than those characteristic of crosslinked fluoroelastomers. Tatemoto<sup>73</sup> 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) ;  $T_{dec} = 345\text{ }^\circ\text{C} <$  poly(E-*alt*-CTFE)-*b*-poly(VDF-co-HFP)-*b*-poly(E-*alt*-CTFE) ;  $T_{dec} = 379\text{ }^\circ\text{C} <$  PVDF-*b*-poly(VDF-co-HFP)-*b*-PVDF ;  $T_{dec} = 410\text{ }^\circ\text{C}$ .

Regarding their rheological properties, the above TPEs can easily be processed as gums.

Table 3. Thermal and mechanical characteristics of two commercially available block (Daiel®) and graft (Cefral® soft) 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       |
| $\epsilon_e$ (%)                | 650    | 1000 | 500          |
| $\sigma_R$ (kN/m <sup>2</sup> ) | 29     | 31   | 110-120      |

Table 3 compared the thermal and mechanical properties of block (Daiel®) and graft (Cefral Soft®) F-TPEs. Commercially available Daiel®<sup>74</sup> exhibit 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 ( $g_c \sim 19.6-20.5$  mN.m<sup>-1</sup>). These characteristics offer excellent resistance against aggressive chemicals and strong acids, fuels, oils, and ozone. In addition, their tensile moduli are close to that of cured fluoroelastomers. As a matter of fact, poly(E-co-M)-b-poly(VDF-co-CTFE)-b-poly(E-co-M) triblock copolymers (where M stands for TFE or CTFE) exhibit smaller transmittance than PMMA does in the UV range of 200 to 300 nm, while they had the same transmittance as that of PMMA in the visible range.<sup>80</sup> Hence, these A-B-A block copolymers can cut the UV light which is dangerous for eyes and can be successfully used in optics and contact lenses.<sup>80</sup> Other applications concern the compatibilizers for polymer blends composed of a hydrocarbon polymer and a fluorine-containing polymer, a dispersant for a fluorine-containing paint, a carrier for electrophotography, and an electrostatic charge adjusting or fusion preventing agent for toner particles or in high tech areas such as aerospace, aeronautics and engineering or in optics,<sup>80</sup> arising from their outstanding properties.

These TPEs are useful as O-rings,<sup>78</sup> pressure-sensitive adhesives, tough transparent films, sealants having good chemical and ageing resistance, protective coatings for metals, or even for

dental plates (since Daiel® T530 is claimed to show neither erythrocyte hemolysis nor cytotoxicity, and does not generate any harmful substances).

In addition, binary blends of TPE with fluoroelastomers or with thermoplastics,<sup>85</sup> and ternary blends two TPEs and one thermoplastics<sup>79</sup> have also been investigated. They can find applications as pressure sensitive adhesives,<sup>80</sup> sealants,<sup>80</sup> fuel hoses for engines,<sup>79</sup> O-rings<sup>79</sup> and shaft seals.<sup>79</sup>

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

### **2.1.2. via Atom Transfer Radical Polymerization (ATRP)**

Zhang and Russel<sup>86</sup> synthesized poly(VDF-*co*-CTFE)-*g*-PS and poly(VDF-*co*-CTFE)-*g*-PtBA graft copolymers by ATRP.  $T_m$  of the P(VDF-*co*-CTFE)-*g*-PS graft copolymer was found to be 165 °C while the  $T_g$  of PS grafts was 84 °C.  $T_m$  of poly(VDF-*co*-CTFE)-*g*-PtBA graft copolymer was determined to be 167 °C and  $T_g$  at 117 °C was observed, corresponding to PtBA dangling segments. Unfortunately, the authors failed to provide any evidence of grafting from the cleavage of C-Cl bond of CTFE. With the same strategy, Zhang et al.<sup>87</sup> produced proton exchange membranes by sulfonating the PS grafts (Figure 6). The resulting membranes showed higher proton conductivity than that of Nafion® 112 conditioned upon higher relative humidity (RH) (RH>60%) or low temperature (T<120 °C). The graft copolymers displayed  $T_m$  value of 163 °C. Tsang et al.<sup>88</sup> produced poly(VDF-*co*-CTFE)-*g*-SPS and poly(VDF-*co*-CTFE)-*b*-SPS (where SPS stands for sulfonated polystyrene) via ATRP and found that graft copolymers yielded membranes, tolerating much higher ionic contents. The authors further described the influence of morphological structures of such copolymers on the thermal properties of proton conducting membranes.

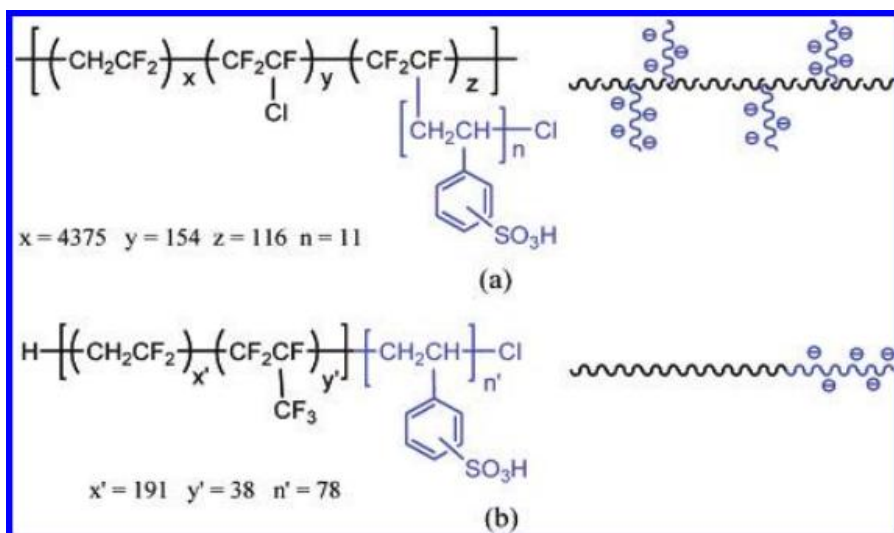
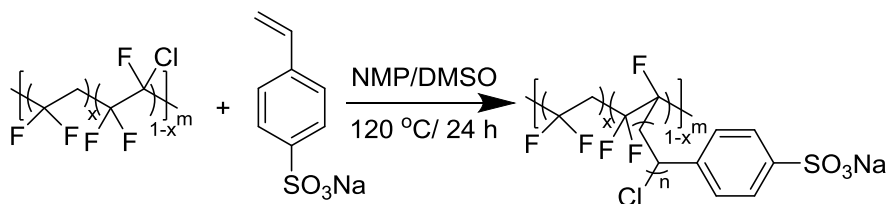


Figure 6. Chemical structures of (a) Poly(VDF-*co*-CTFE)-*g*-SPS graft and (b) Poly(VDF-*co*-HFP)-*b*-SPS diblock copolymers. Reprinted with permission from American Chemical Society.<sup>88</sup>

Different from the above-mentioned approaches, Patel et al.<sup>89</sup> synthesized poly(VDF-*co*-CTFE)-*g*-PSSA via ATRP (Scheme 10). The authors did not provide any  $T_g$  and  $T_m$  values of poly(VDF-*co*-CTFE)-*g*-PSSA graft copolymer but it is expected that the poly(VDF-*co*-CTFE) is crystalline to bring mechanical properties of the resulting membranes.

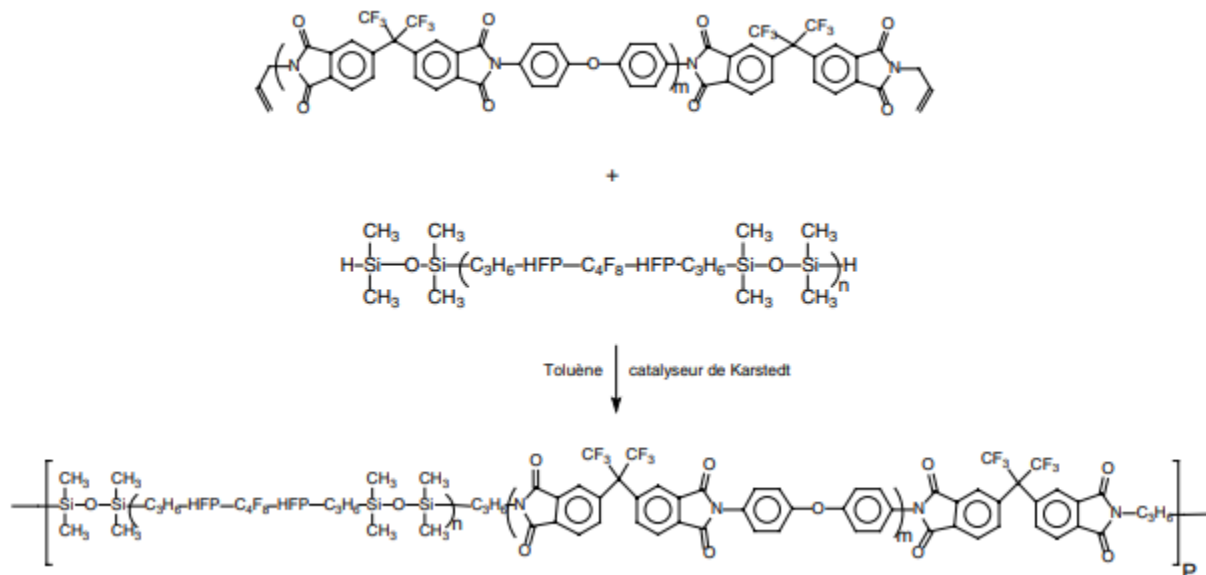


Scheme 10. Synthesis of poly(VDF-*co*-CTFE)-*g*-PSSA graft copolymer. Reprinted with permission from Wiley.<sup>89</sup>

## 2.2. Via Polycondensation

Like polyimides, poly(imide siloxane)s have good thermal ( $T_g$ ) and mechanical properties. The most widely used method for synthesis of such polymers is via condensation of a tetracarboxylic dianhydride with an  $\alpha$ ,  $\omega$ -diaminosiloxane. Andre et al.<sup>56, 59</sup> synthesized alternating fluorinated polyimide/fluorinated polyhybrid siloxane (FPI-FPHSX) block copolymers via

polycondensation (Scheme 11). The authors reported two  $T_g$ s: one corresponding to the fluorinated siloxane phase at  $-59\text{ }^\circ\text{C}$  while the other one was assigned to a fluorinated rich polyimide phase at  $239\text{ }^\circ\text{C}$ . The alternating sequence of soft polysiloxane segments and the hard polyimide sequences in such polymers induces a better phase segregation, thus altering their thermal and mechanical properties.



Scheme 11. General procedure for the synthesis of SiOH-FPHS alternating fluorinated polyhybridsiloxane (FPI-FPHSX) block copolymers via polycondensation. Reproduced with permission from Wiley.<sup>56</sup>

The same authors also investigated the thermal and dynamico-mechanical properties of such produced F-TPEs. Results revealed that the  $T_g$ s of the soft blocks ranged from  $-42$  and  $-6\text{ }^\circ\text{C}$ , while that of the hard segments from  $191$  to  $+237\text{ }^\circ\text{C}$ . Furthermore,  $T_g$  became higher when the length of the fluorinated group of the fluorosilicone materials increased. Compared to the properties of the commercially available TPEs, FTPEs exhibited higher  $T_g$  (Figure 7).<sup>21</sup>

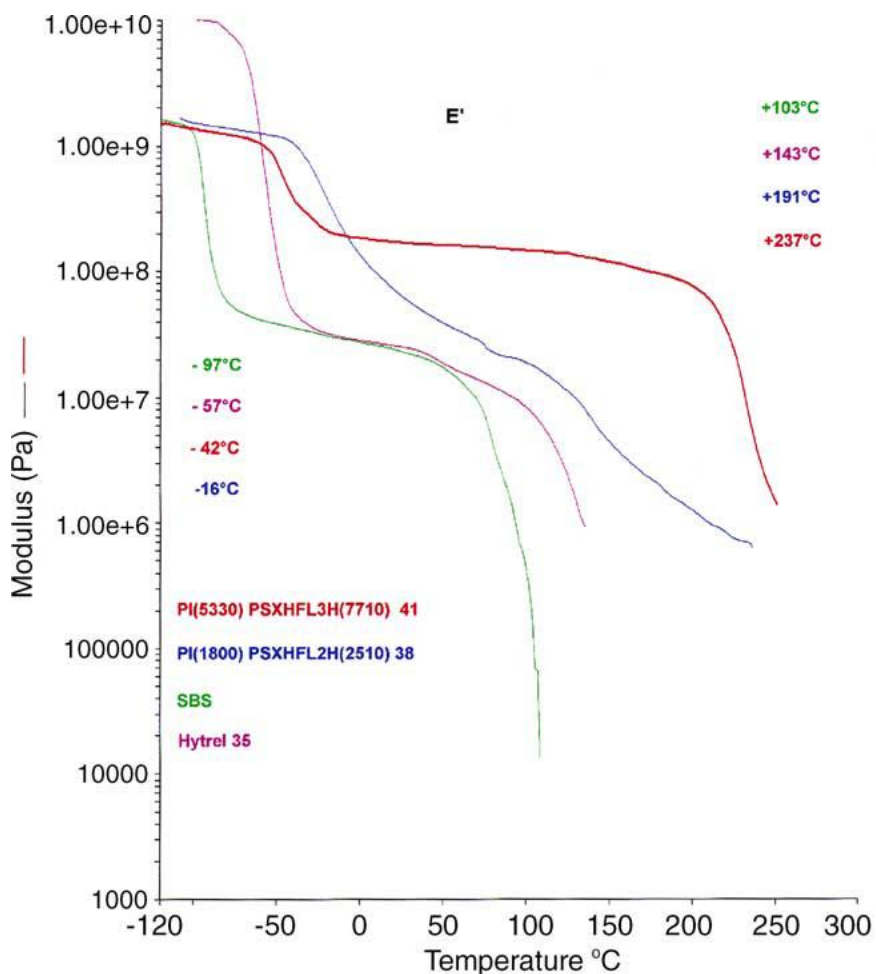


Figure 7. Dynamic-mechanical analyses of various thermoplastic elastomers (PI, SBS and Hytrel® stand for polyimide, polystyrene-*b*-polybutadiene-*b*-polystyrene triblock copolymers, and poly(ester)-*b*-polyether block copolymers, respectively). The figures indicated in the left part and in the right side correspond to the  $T_g$ s of the soft block and hard segments, respectively. Reproduced with permission from Wiley.<sup>56, 59</sup>

### 3. Properties of Fluorinated Thermoplastic Elastomers

#### 3.1. 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 nonrigid materials of modulus  $< 69$  MPa.<sup>90</sup> The FTPEs show elastomeric properties and are

considered nonrigid materials. Tensile strength in polymers is a type of mechanical property which can be enhanced by introducing rigid aromatic ring and fluorine in fluoropolymers.<sup>91</sup> Table 4 lists the physical and mechanical properties of such elastomers. Generally, fully fluorinated polymers exhibit about 1.5 times lower mechanical strength as compared to the fluoropolymers bearing hydrogen atoms in their structure.<sup>92</sup> On the other hand, perfluorinated polymers display higher maximum service temperatures and improved elongation.<sup>68</sup>

Table 4. Physical and mechanical properties of fluorinated elastomers. Reproduced with permission.<sup>92</sup>

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

### 3.2. Thermal Properties

The fluorinated TPE generally exhibits outstanding thermal properties. There are two types of fluorinated thermoplastic elastomers<sup>43</sup> such as i) if the fluorinated group is placed in the polymer backbone (i.e. most PTFE as in KALREZ® from Chemours, CTFE, VDF, homopolymer etc.) and ii) the other in which fluorinated group located in the dangling group [poly(acrylate)s or poly(styrene)s bearing per-fluorinated side chains]. The former one exhibits good thermal stability compared to the latter one. The fluorinated polymers display higher thermal stability so it can be used in gel polymer electrolyte in batteries, binders for electrode materials, gaskets, shafts, diaphragms as well as fluorinated additives for electrolytes.<sup>93-95</sup> Figure 8 suggests that the fluoroelastomers exhibit a higher thermal stability which is >250 °C but other materials like silicones, fluorosilicones, polyepichlorohydrin, and nitrile display thermal stability < 250 °C.<sup>5, 96</sup> The failure in thermal stabilities of silicones relies on the back biting releasing cycles (Scheme 3). Increase of fluorine content and making further silicon atoms lead to an enhanced thermal stability (Figure 8).<sup>5, 57</sup> In addition, the best candidates having the lowest swelling rate (in polar and non-polar solvents) are (per)fluorinated elastomers (Figure 8).

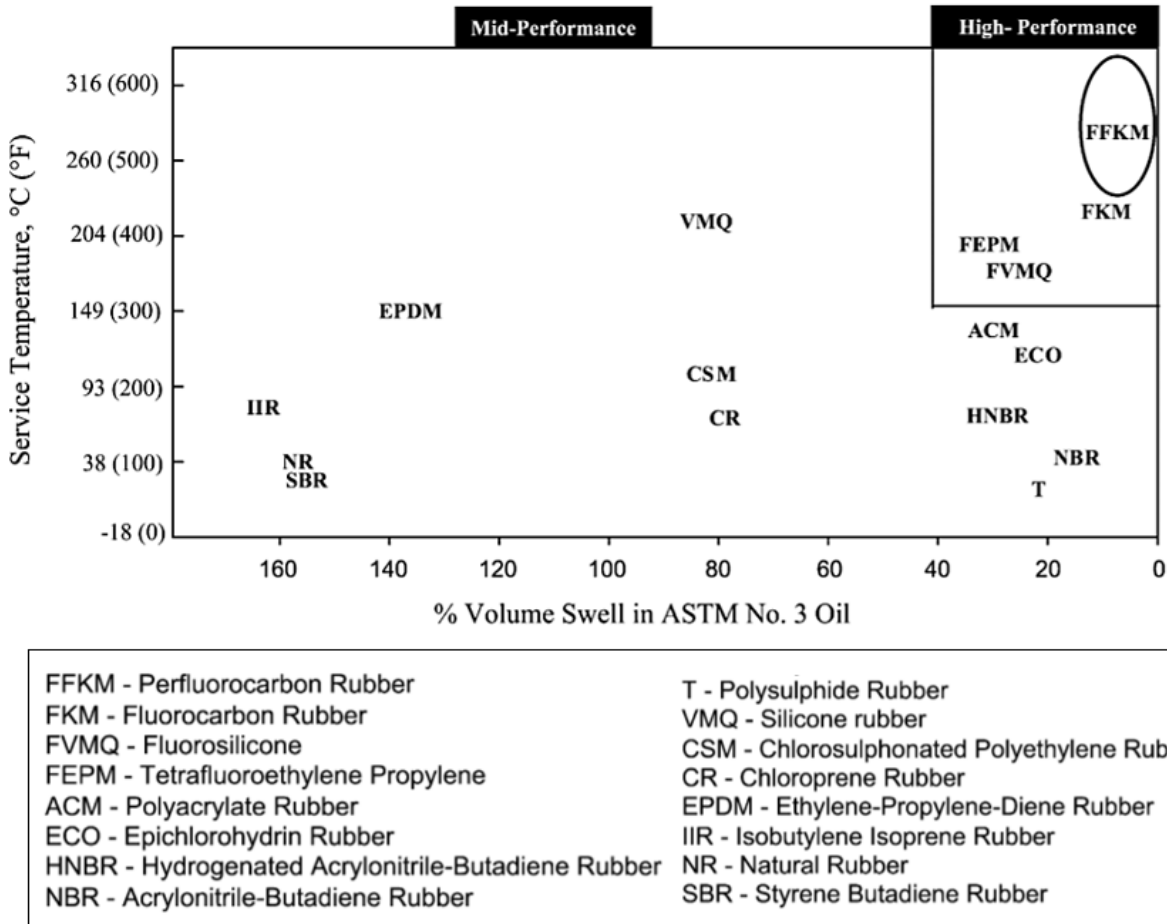


Figure 8. Relative heat and oil resistances of elastomers (ASTM D2000). Reproduced with permission from Elsevier<sup>96</sup>.

Perfluoropolyether elastomer exhibit excellent low temperature flexibility and heat resistance, together with improved performance in fuels, solvents, acids, and alkalis compared to standard fluoroelastomers.<sup>45, 69</sup>

### 3.3. Electrical Properties

The revolution of electrical and computer industrialization over the period has led to a drastic elevation in the need for safety and durable insulation for cabling and wiring. F-TPEs have emerged as a strong candidate for this purpose. To achieve optimum electrical properties of any fluoropolymers, polymerization reactions should be performed at high pressure because polymerization reactions performed at too low a pressure lead to voids.<sup>4</sup> The temperature also

plays an important role in fabrication of fluoropolymer for use in the electrical purposes because their electrical properties can be tuned by changing the temperature.<sup>4</sup> F-TPEs show properties such as low flammability, high flexibility, and show fuel, chemicals, and oil resistance. Due to all these interesting properties, iTPEs are mostly used in electrical and wire/cable industries.<sup>81, 85</sup>

### **3.4. Surface Properties and Adhesion**

Many research efforts focus on the development of strategies to increase the surface energy and adhesion properties of fluoroTPEs.<sup>78</sup> The wet-chemical modification methods with a reducing agent such as benzoin dianion in DMSO is primarily used.<sup>68</sup> The alteration of the chemical properties of poly(VDF-*co*-TrFE) copolymers has been only explored in designing and developing the crosslinking strategies. The adhesion properties of these materials can be very easily enhanced by adding groups such as carboxylic acid or phosphonic acid functions.<sup>97-99</sup>

### **3.5. Morphology**

Fluorinated polymers possess a wide assortment of conceivable morphological designs/physical states, going from totally indistinct to semi-crystalline and to TPEs.<sup>19, 100</sup> The structures are mostly based on the copolymers containing VDF.

### **3.5. Self-healing TPE**

Li et al.<sup>101</sup> prepared an original fluorinated polymer starting from low molar mass PFPAEs. The as-synthesized material demonstrated self-healing ability due to the hydrogen bonding. Simonin et al.<sup>102</sup> introduced a novel concept to produce a self-healing TPEs using a macromolecular additive that interferes with the hard segments of the TPE, accelerating chain dynamics and imparting self-healing properties to the resulting composite material. It is to be noted that this modification leads to only a limited detrimental effect on the mechanical properties. The authors utilized this concept to silicone-based elastomers and successfully prepared an autonomously self-healing material, exhibiting a relatively high elastic modulus.

## **4. Application of Fluorinated Thermoplastic Elastomers**

Many applications of these TPEs have been found in civil and engineering materials such as hot melts, gaskets, O-rings, diaphragms of pumps, pressure sensitive adhesives, medical contact lenses, electronic chemical items, coatings for food industries, and other devices involved in high-tech industries.<sup>4, 7, 43, 44, 68, 70, 103</sup>

### **4.1. Automotive and Aerospace**

Fluoro-TPEs having properties like chemical inertness, excellent thermal stability, and surface properties, are attractive materials for aerospace and automotive industries.<sup>1, 2, 104</sup> The materials should have some properties for the automotive and aerospace applications, low coefficient of friction, good mechanical properties, cryogenic properties, chemical resistance, low permeation properties, etc. Fluorocarbon-based polymers have been developed throughout the last 80 years, the most important of which are fluoroelastomers, fluorinated lubricants, and fluorosurfactants. These products make up 20% of the global fluoropolymer market. Fluoroelastomers are designed to maintain rubber-like properties and are used as O-rings, seals, shafts, and hosing, in the automotive and aerospace industries.<sup>43</sup> PFPEs are another important class of fluoropolymer composed of fluorocarbon units joined by ether linkages. Perfluoropolyethers (PFPEs)<sup>45</sup> are typically oils or greases depending on molar mass and are used extensively as high-performance lubricants for engines, machinery, and wherever surfaces and moving parts come in contact.<sup>45</sup> PFPE-based lubricants are thermally stable, non-flammable (even in liquid oxygen), chemically resistant, and non-volatile over a broad temperature range of -75 to 350 °C. They are also resistant to ionizing radiation, making them useful in the aerospace and nuclear industries. There are some risks involved while using fluoroelastomer in methanol and methanol containing fuels as methanol can swell VDF containing TPEs due to their high polarity nature. FTPEs swell or dissolve in some polar solvent like N,N-dimethylformamide (DMF) and methyl ethyl ketone.<sup>45</sup> To avoid such issues, it is essential to use TPEs which contain more than 69.5% fluorine atom to avoid swelling problems. The Kalrez®-type polymers contains 73% fluorine atom and show excellent resistance to methanol and methanol-fuel blends.<sup>68</sup> Consider these attributes, the TPEs are very useful in automotive and aerospace applications.<sup>104</sup> Recently, Banerjee and Bhowmick<sup>105</sup> reported the fabrication of a novel thermoplastic elastomeric blends from polypropylene (PP) and fluoroelastomer (FKM) via nanotailoring 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 9).<sup>106</sup>

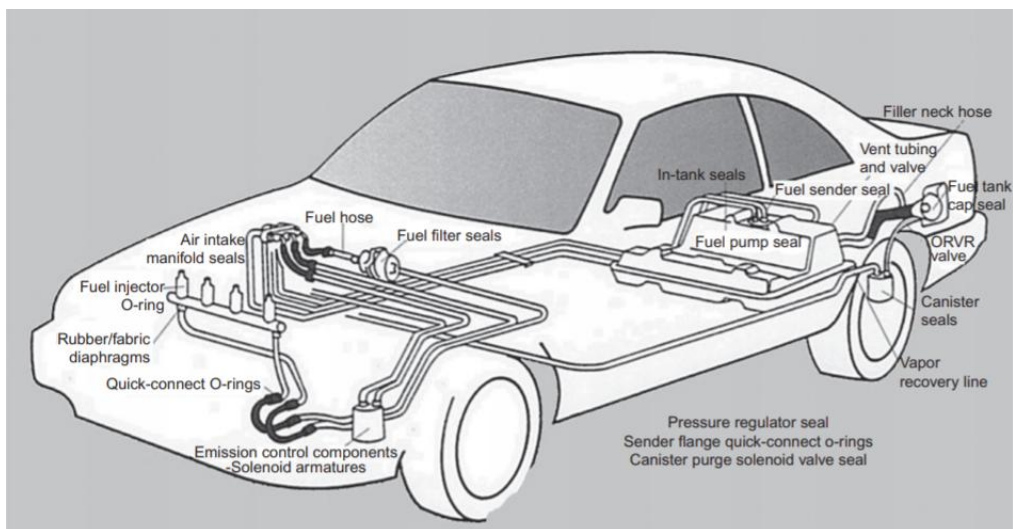


Figure 9. Fluoroelastomers used in fuel systems. Reproduced with permission from Elsevier.<sup>106</sup>

Regarding the aerospace FP market, the main aerospace fluoropolymer suppliers are 3M, AGC, Arkema, Chemours, Daikin, Dongyue, and Solvay (for the raw materials). Economically triggered by the increasing demand for durable materials to lower the maintenance cost, and thus avoid obsolescence, the global aerospace fluoropolymers market is forecast to reach US\$ 0.27 billion by 2026.<sup>107</sup>

Although the fluoropolymers market for the aerospace industry displays a growth over 2015-2018, a decline was noted in 2019, mainly due to: i) the grounding of Boeing737 Max, ii) the delayed deliveries of upcoming aircraft programs such as Boeing777x, iii) the adjusted production rates of key aircraft programs, and iv) the decline in passengers. Table 5 summarizes the use of FTPEs in aerospace applications.

#### 4.2. Medical Devices

Fluorinated thermoplastic elastomers also play a crucial role in medical devices. F-TPEs may be used to make liners in hoses to carry clean fluids. These F-TPEs should 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 F-TPEs have replaced chlorinated or hydrocarbon plastics to give higher yielding and higher virtue measures.<sup>61, 108-110</sup>

Table 5. Examples of fluorocarbon elastomers parts. Reproduced with permission from Elsevier.<sup>111</sup>

| <b>Automotive</b>                             | <b>Aerospace</b>                                   | <b>Industrial</b>                                                    |
|-----------------------------------------------|----------------------------------------------------|----------------------------------------------------------------------|
| Shaft seals                                   | O-ring in fuel, lubrication, and hydraulic systems | Hydraulic O-ring seals                                               |
| 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 liner                | Firewall seals                                     | Diaphragms                                                           |
| In-tank and quick connect fuel system seals   | Engine lube siphon hose                            | Electrical connectors                                                |
| Gaskets (valve and manifold)                  | Clips for jet engines                              | Flue duct expansion joints                                           |
| Balls for check valves                        | Electrical connectors                              | Valve liners                                                         |
| Heat-sealable tubing for wire insulation      | Shaft seals                                        | US FDA approved seals in food handling processes                     |
| Bellows for turbo-charger lubricating systems | Traps for hot engine lubricants                    | Industrial roll covers (100% FKM or laminates with other elastomers) |
| Lathe cut gaskets                             | Tire valve stem seals                              | Safety clothing and gloves                                           |
| Engine head gaskets                           | Heat-sealable tubing for wire and cable insulation | V-ring packers                                                       |

Clinical apparel, outfits, sheets, and shades are formed using or covered with F-TPEs to bestow oil, water, and stain opposition while F-TPEs is utilized to dry or humidify breath for sedation and respiratory consideration as for biomedical supplements. The F-TPEs are utilized for making surgical sutures, stent grafts and arterial grafts and they are also used to perform cosmetic facial

surgery. The other properties such as optical properties of fluoropolymers materials are also been utilized as materials of corneal inlays and contact lenses.<sup>80, 112</sup>

### 4.3. Electrical Applications

The electrical properties of polymers are relatively better if they have low dielectric constant values, high volume/surface resistivity, high dielectric breakdown voltage, flame resistance, thermal stability, and low refractive indices.<sup>102</sup> The polymers with all those characteristics would be utilized for wire and cable insulation, connectors, optical fibers, and printed circuit boards, etc. F-TPEs can be utilized in the cable insulation due to its high thermal stability, excellent properties, high limit oxygen index and because it produces relatively less smoke during combustion compared with the other polymers.

## 5. Summary and Perspectives

Although ITP was pioneered in the late seventies, more interest is noted from the mid-nineties when *pseudo*-living radical controlled polymerization (or RDRP) emerged. This explains why many investigations were carried out and also why Daiel® has become commercially available, although a few scientific articles (most of them from Tatemoto) have been published. The disadvantage arises from the cost of  $\alpha,\omega$ -diiodoperfluoroalkanes and environmental issues on perfluoroalkyl substances (PFASs).<sup>113, 114</sup> ITP is particularly well-adapted to fluoroalkenes, representing the only industrial method to enable RDRP of such halogenated olefins. Another advantage concerns the versatility of the process, which can occur in solution, suspension, emulsion, or microemulsion. More recent investigations carried out at Solvay Specialty Polymers from the branching and *pseudo* living technology have produced very interesting fluoropolymers. Other methods such as RAFT and MADIX require complex chain transfer agents (dithioesters trithiocarbonates, or xanthates) and sometimes the strong smell from these sulfur-containing derivatives cannot be avoided. In addition, CMRP of fluoroolefins is in its infancy. Nevertheless, both approaches are complementary in terms of the chosen monomers. However, few surveys have been developed and, to the best of our knowledge, none of them has been industrially scaled up.

In summary, fluorinated thermoplastic elastomers offer the unique opportunity to combine the properties of thermoplastic crystalline characteristics and elastomers or amorphous features. This combination offers new openings for emerging applications in engineering, high tech industries

and medical fields. However, successful transition of such fluorinated TPEs into industrial applications will require more research on the polymerization protocols/processes and generation of fluorinated TPEs with well controlled molar masses and macromolecular architectures. Once accomplished, this will lead to major shift in the potential applications of such materials in everyday life. To this end, several strategies have been developed to produce F-TPEs comprising of Hard (high  $T_m$ ) and Soft (low  $T_g$ ) segments. Among these techniques, ITP has emerged as the preferred and industrialized process. A successful synthesis of F-TPE with precisely placed hard and soft segments should lead to tunable thermal and mechanical properties. Along with this, these specialty polymers overcome the limitations of fluorinated homopolymers which suffer from lack of solubility and difficulty in crosslinking and functionalization. There is immense potential in the area of F-TPEs, especially in the field of sequence-controlled ones. The next Holy Grail in this area would be to be able to synthesize sequence-controlled F-TPEs with precisely placed hard and soft segments. Hence, still many investigations deserve to be confirmed in that emerging area, which should attract the interest of many academic and industrial researchers.

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