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Article

From Formulation to Application: Effects of Plasticizer on the Printability of Fluoro Elastomer Compounds and Additive Manufacturing of Specialized Seals

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Abstract: This work investigated material extrusion additive manufacturing (MatEx AM) of specialized fluoroelastomer (FKM) compounds for applications in rubber seals and gaskets. The influence of a commercially available perfluoropolyether (PFPE) plasticizer on the printability of a control FKM rubber compound was studied using a custom-designed ram material extruder, Additive Ram Material Extruder (ARME), for printing fully compounded thermoset elastomers. The plasticizer's effectiveness was assessed based on its ability to address challenges such as high compound viscosity and post-print shrinkage, as well as its impact on interlayer adhesion. The addition of the PFPE plasticizer significantly reduced the FKM compound's viscosity (by 70%) and post-print shrinkage (by 65%). While the addition of the plasticizer decreased the tensile strength of the control compound, specimens printed with the plasticized FKM retained 34% of the tensile strength of compression-molded samples, compared to only 23% for the unplasticized compound. Finally, the feasibility of seals and gaskets manufacturing using both conventional and unconventional additive manufacturing (AM) approaches was explored. A hybrid method combining AM and soft tooling for compression molding emerged as the optimal method for seal and gasket fabrication.

Keywords: additive ram material extruder (ARME); additive manufacturing; thermoset elastomers; voids and shrinkage; support for 3D printing; soft tooling; mechanical characterization; plasticizer in 3D-printed elastomers; additive manufacturing of seals



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1. Introduction

Among the vulcanized rubbers used for sealing and gasket applications, fluoro-elastomers (FKM) and perfluoro-elastomers (FFKM) are preferred because of their excellent heat and oil resistance [1]. The continuous drive for energy efficiency and reduced emission is continuously pushing the operating temperature of power-generating instruments upwards, and, in many cases, the end-use temperature for seals exceeds 200 °C. At such elevated temperatures, only FKMs and FFKMs provide meaningful sealing performance [2]. At lower temperatures, FKMs and FFKMs also remain highly relevant because of their broad chemical resistance [2]. The excellent properties of FKMs and FFKMs come from the C-F bond in their polymeric chains, which is the strongest bond in chemistry [3].

The predominant manufacturing techniques for FKMs and FFKMs are compression molding, injection molding, and transfer molding. As with any manufacturing industry dependent on molding processes for product manufacturing, a considerable gap in the timeframe exists between the product idea conceptualization and mass manufacturing of

products. Detailed design, prototyping, and testing are required to finalize the product design and specification before mass manufacturing starts [4]. As the rubber industry is heavily dependent on molding processes, the intermediate stages between conceptualization and mass production require considerable time and resources. In this context, additive manufacturing (AM) emerges as a crucial bridge between product conceptualization and mass production, dramatically reducing both costs and lead times. By minimizing or eliminating the need for tooling molds and dies during the prototyping phase, AM accelerates the process. Additionally, it facilitates the swift and cost-effective creation of prototypes for iterative design improvements and rigorous testing. This study is an attempt to combine the excellent properties of FKM with the design freedom and rapid prototyping attributes of AM to open up new application possibilities.

From the shoes beneath our feet to the tires meeting the road, from waterproofing gaskets for our homes to the precision seals of ultra-clean semiconductor chip processing chambers, vulcanized rubber is one such material class that seamlessly integrates into the fabric of our daily lives [5]. Key prominent vulcanizable rubbers are natural rubber (NR), nitrile butadiene rubber (NBR), styrene-butadiene rubber (SBR), ethylene propylene diene monomer rubber (EPDM), isobutylene isoprene rubber (IIR), isoprene rubber (IR), alkyl acrylate copolymer (ACM), ethylene acrylic elastomers (AEM), hydrogenated nitrile butadiene rubber (HNBR), and many others [6]. When these rubbers are mixed with specific additives and curatives to obtain desired properties, they are called fully compounded thermoset elastomer or rubber [5]. Although AM of different elastomeric materials using various methods has been discussed extensively in the literature [7–10], very few scientific articles can be found regarding AM of fully compounded thermoset elastomers or traditional rubber compounds. Recently, the literature reports have started to emerge demonstrating the fabrication of parts from several types of rubbers, such as NBR, HNBR, and silicones, using various AM processes [11–17]. However, we could find very little work in the literature discussing AM of FKM rubbers or FKM rubber compounds. Previously, we reported the feasibility of fabricating seals and parts from FKM and FFKM filaments via the fused filament fabrication (FFF) process [18]. One of the most critical challenges of printing FKM rubber compounds or any other traditional rubber compounds via the FFF process is the insufficient stiffness of the rubber filaments. This was solved in our previous work by in situ freezing the filament below its glass transition temperature using dry ice [18]. However, the FFF printing approach has demonstrated complications for manufacturing complex and specialized seals, gaskets, and other parts due to the narrow process latitude and reproducibility. In this paper, we report how the process latitude can be improved by employing a barrel-plunger material extrusion system.

Traditional rubbers are usually not used in the industry without some form of compounding to achieve the required end-use properties of the parts made from them. Compounding of rubbers usually involves mixing the rubber stock with various chemical additives such as accelerators, accelerator activators, anti-degradants, and processing aids; different reinforcing fillers such as carbon black, silica, clay, and glass fiber; and curing agents such as sulfur, organic peroxides, and metal oxides [5]. As a result, a rubber compound becomes a very high-viscosity material system. This elevated viscosity of traditional rubber compounds gives rise to critical challenges in fully compounded rubber AM, such as post-print shrinkage and limited time available for printing. In our previous work, a liquid NBR polymer was used as a viscosity modifier to fine-tune a traditional NBR compound for material extrusion additive manufacturing (MatEx AM) applications and to resolve the critical challenges associated with MatEx AM of rubbers [19]. The liquid NBR proved to be highly effective in resolving many of the challenges. In this study, we inspected the effectiveness of a plasticizer as a viscosity modifier and reported on its effect on the overall printability of an FKM compound.

Plasticizers are substances, usually liquids, added to polymers or polymer compounds to increase their flexibility, processability, and workability. They act as internal lubricants between polymer chains, reducing friction and making the polymer softer and easier to

shape. In the rubber industry, plasticizers are usually used as a processing aid to reduce shear during mixing, improve lubrication during processing, prevent sticking to the mold surface, and provide additional stability by increasing the internal adhesion in emulsions. Plasticizers can also be used to lower the viscosity of the rubber compound [20]. The use of plasticizers in material development for AM applications is not uncommon. Bajwa et al. [21] evaluated the effects of three different types of plasticizers on the mechanical and thermal properties of polylactic acid (PLA) filaments for AM. They observed significant improvement in elongation at break and reduction in ultimate tensile strength. Oz et al. [22] reported the effects of polyethylene oxide (PEO) as a plasticizer on the mechanical and joint properties of carbon fiber powder (CFP)-reinforced PLA filaments for AM. Their work concluded that incorporating the PEO plasticizer improved printed parts' ductility but reduced strength. Similarly, Menčík et al. [23] reported improved elongation at the break of printed parts using plasticizers in Poly(3-hydroxybutyrate)/Poly (lactic acid) filaments. Wasti et al. [24] evaluated the effects of two plasticizers (polyethylene glycol (PEG) 2000 and Struktol TR451) on the thermal and mechanical properties of bio-composite filaments made from lignin and polylactic acid for AM. They reported that the use of PEG as a plasticizer improved both tensile stress and elongation at break, whereas the use of Struktol TR451 as a plasticizer only improved the elongation at break. However, we could not find any information in the literature on the effect of plasticizers on the printability and mechanical behavior of additively manufactured parts from fully compounded FKM rubber compounds or any other thermoset elastomer compounds. This study employs the viscosity-modifying attribute of plasticizers to improve the printability of an FKM rubber compound. This article also intends to shed light on the effect of a commercial plasticizer on the mechanical properties of additively manufactured parts from fully compounded FKM rubber compounds.

The work presented in this article can be broadly divided into two sections. First, we evaluated the effectiveness of a plasticizer as a viscosity modifier and its effects on the printability of an FKM compound. In this regard, we compounded two FKM formulations. The first formulation, FKM-1, contained no plasticizer and acted as a control. The second formulation, FKM-2, had a commercial plasticizer for FKM rubber compounds. These two compounds were evaluated based on their viscosity, post-print shrinkage, tensile properties, and interlayer adhesion. Based on the performance of the FKM compounds on the parameters mentioned above, we drew a conclusion on their printability and reported in the first half of the result and discussion section (Section 3.1). Second, we evaluated the feasibility of rubber AM technology to fabricate FKM seals and gaskets for prototyping purposes. In this context, several conventional and unconventional AM approaches were evaluated and reported in the second half of the result and discussion section (Section 3.2).

2. Materials and Methods

2.1. Materials

The base fluoro-elastomer or FKM rubber stock was purchased as Tecnoflon VPL 45535 from Solvay (10 Leonard Ln, West Deptford, NJ, USA). FKM rubber cure package was obtained from R.T. Vanderbilt Company, Inc. (30 Winfield St, Norwalk, CT, USA), and silica filler was purchased from Fiberglass supply, Inc. (11824 water tank road, Burlington, WA, USA). The plasticizer, Fomblin M60, was purchased from Solvay (10 Leonard Ln, West Deptford, NJ, USA).

2.2. Preparation of Rubber Compounds

The formulations of the two FKM rubber compounds evaluated in this study are reported in Table 1. This study explores the printability of two custom FKM rubber formulations (FKM-1 and FKM-2) designed for applications such as seals and gaskets [25]. FKM 1 served as the control material. A 50 g batch of each compound was mixed using a Brabender Plasticorder Intelli-Torque Plus internal mixer (Model 01-55-000, Duisburg, Germany) with counter-rotating screws. The ingredients were incorporated into the mix

following the order in Table 1. First, the rubber was kneaded for 2 min. Fillers were then added and mixed for an additional 5 min to ensure proper dispersion. Next came the curing agents, adhering to the quantities listed in Table 1. To investigate the influence of a plasticizer on additive manufacturing and product performance, 5 parts per hundred rubber (PHR) of the plasticizer was included only in the FKM-2 formulation. For both compounds, mixing continued after the final ingredient addition until the mixing torque stabilized, indicating complete mixing. The total mixing time for all compounds was 18 min.

Table 1. Formulation of the two FKM compounds.

Compound/Recipe	Parts per Hundred Rubber (PHR)	
	FKM-1 (FKM w/o Plasticizer)	FKM-2 (FKM with Plasticizer)
Tecnoflon FKM (Tecnoflon VPL 45535-25 Mooney)	100	100
Filler and cure package for FKM	39	39
Plasticizer (Fomblin M60)	0	5

2.3. Additive Manufacturing

All 3D prints were conducted using a custom print head (shown in Figure 1) mounted on an Ender 5 pro with modified firmware. The printer (called ARME 3XL) shown in Figure 1 is an updated version of the Additive Ram Material Extruder (ARME) discussed in previous work [16], with a stronger stepper motor and lead screws on both sides of the barrel piston setup. Before printing, rubber compounds (formulated as outlined in Section 2.2) were loaded into the ARME 3XL barrel and heated under compression for a 5 min period. Then, the printing process of the desired geometry was started. All specimens were printed at 10 mm/sec print speed and 100 °C printing temperature. The bed was kept at room temperature. A nozzle with a 0.8 mm orifice diameter was used, and the layer height was kept constant at 0.4 mm for all prints. Completed prints were removed and transferred to an oven for curing. All specimens underwent a 15 min cure cycle at 160 °C.

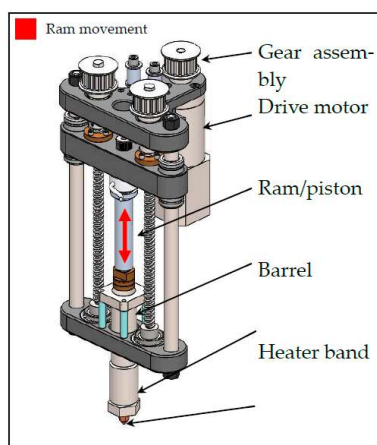


Figure 1. Three-dimensional model of the Additive Ram Material Extruder-3XL (ARME-3XL) printhead.

2.4. Characterization of Rubber Compounds

2.4.1. Cure Behavior and Formulation Viscosity

To analyze the rheological and cure properties of each rubber formulation, an oscillating disk cure meter (RPA 2000, Alpha Technology, Hudson, OH, USA) was used, following the guidelines of ASTM D2084 [26]. Moreover, 10 g uncured rubber samples were used as specimens to be tested with the RPA. Cure profiles were evaluated at both the print

temperature (100 °C) and the designated cure temperature (160 °C). All compounds were tested with a constant frequency of 100 CPM and a rotational amplitude of 1°.

2.4.2. Post-print Shrinkage

Post-print shrinkage was measured using a standardized rectangular test part (100 mm long, 15 mm wide, 1.2 mm thick). The direction of print was kept aligned to the longest arm of the rectangle, and a regular serpentine print pattern was used. Figure 2 illustrates the dimensions and printing pattern of the part used for post-print shrinkage measurement. Five samples were printed for each FKM compound. Dimensions of printed rubber samples were recorded before and after the completion of their thermal cure. From the dimensions of the fully cured printed part, their post-print shrinkage was measured as the percentage of reduction in length from the original length (or proscribed length).

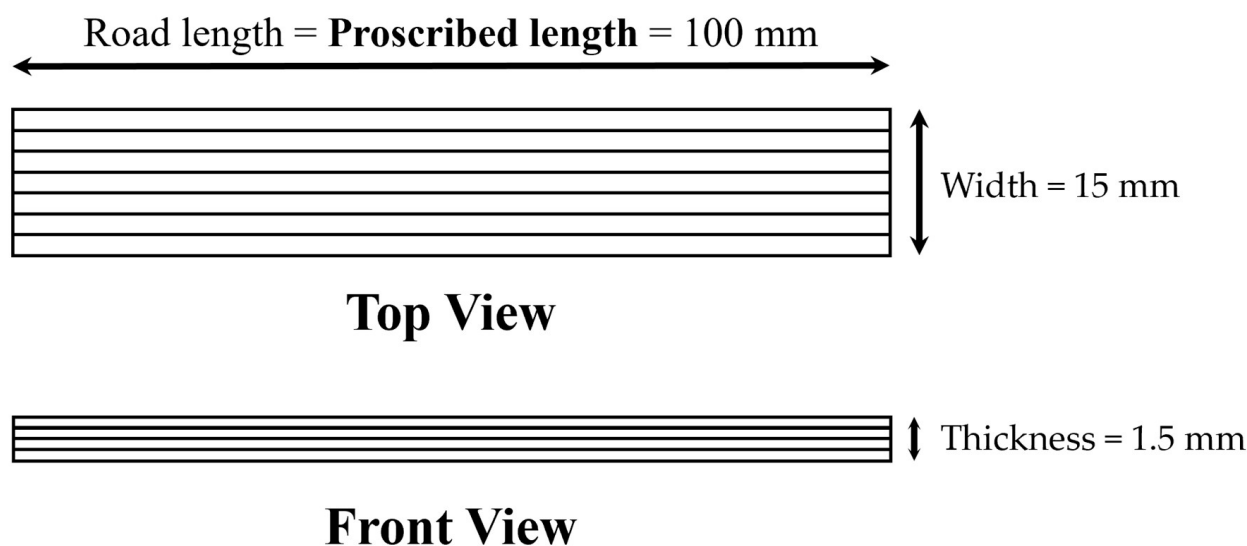


Figure 2. Schematic representation (not to scale) of specimen dimension and print pattern used for post-print shrinkage measurement.

2.4.3. Tensile Behavior

Tensile properties of printed specimens from the two rubber formulations were characterized. Three different types of printed specimens were evaluated in this study: printed (concentric) where the roads were parallel to the direction of applied force, printed (transverse) where the roads were normal to the direction of applied force, and printed (zigzag) where roads were at +45° / −45° angle with the direction of applied force. The tensile properties of printed specimens were compared against compression-molded specimens, which were die cut from a compression-molded sheet using the same die. Compression-molded sheets were formed using a 152 mm × 152 mm mold cavity with 1.5 mm thickness. To cure the elastomer compounds, the cavity was kept at a clamp force of 25 kN at 160 °C for 15 min. Tensile specimens were then die cut from the compression molded sheet using a half-scale ASTM D412-Type C die [27]. All tensile specimens were tested using a universal test machine (Instron 4466, Norwood, MA, USA) at a crosshead speed of 500 mm/min in accordance with ASTM D412. An extensometer (Instron 2603-086, Norwood, MA, USA) was used to record elongation of the specimens. Figure 3 shows the compression-molded, printed (axial), printed (transverse), and printed (zigzag) samples side by side.

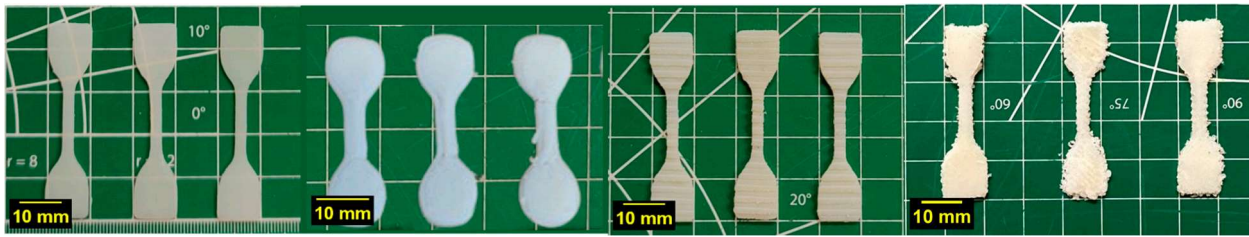


Figure 3. Compression-molded and three types of printed tensile specimens tested for each rubber compound. Sequentially from left to right: compression-molded, printed: parallel to applied force, printed: normal to applied force, and printed: zigzag (+45°/−45°). All tensile specimens were prepared following the ASTM D412—Type C tensile specimen at half-scale.

3. Results and Discussion

3.1. Effect of Material Formulation

3.1.1. Rheology and Cure Behavior of FKM Compounds

The presence of crosslinks in thermoset elastomers is the principal difference between a thermoplastic and thermoset material. Vulcanizing agents present in a thermoset compound, such as sulfur, organic peroxides, and metal oxides, form crosslinks with polymeric chains of the elastomer when the rubber compound is exposed to an elevated temperature and, in turn, yield more robust and thermally stable elastomers. This process of crosslink formation is called curing [28–30]. Vulcanization, as a process, comprises three distinct phases: the induction phase, the curing phase, and lastly, the overcure phase [5]. Rubber Process Analyzers (RPAs), a type of oscillating disk cure meter, are used extensively in the rubber industry to track vulcanization progress. This is achieved by measuring the torque needed to deform a rubber sample over time, generating a ‘cure curve’ [31]. Within the industry, torque values are broadly correlated with viscosity [32]. For this discussion, subsequent references to FKM compound viscosities will be in relation to Figure 4a,b, with units expressed in dN.m.

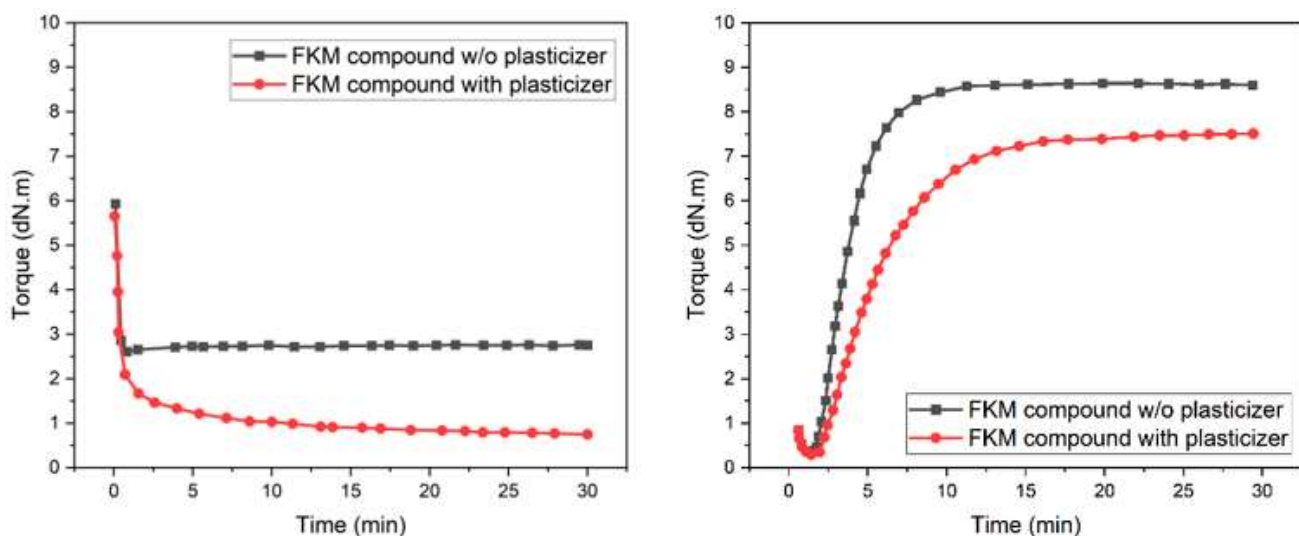


Figure 4. Cure curve of FKM compounds at printing temperature of 100 °C (left) and oven cure temperature of 160 °C (right).

When a rubber compound is exposed to an elevated temperature, the induction phase of vulcanization begins. As a result, crosslinks start to form, resulting in only a modest increase in the viscosity of the rubber stock. During this induction phase, the rubber stock remains processable and exhibits fluid-like behavior [31]. MatEx AM of the FKM rubber compound using the ARME 3XL printhead was conducted in this phase. Since one of the

most critical factors affecting the printability of a fully compounded thermoset elastomer is its viscosity, it is essential to evaluate the compound's viscosity during this stage at the print temperature. Figure 4a shows the viscosity of the FKM rubber compounds at the print temperature of 100 °C.

It is evident from Figure 4a that the FKM-2 compound with plasticizer showed lower viscosity than the FKM-1 compound without plasticizer. This behavior was expected and can be attributed to the small molecular size of the plasticizer. These small plasticizer molecules are located in between the long polymeric chains, acting like lubricants and increasing the spacing between the chains, known as 'free volume'. With more space, the polymer chains can slide past each other more easily, leading to less resistance to flow or lower viscosity [20]. It is also noticeable, from Figure 4a, that the viscosity of both compounds remained stable throughout the printing process, which lasted less than 30 min in all cases.

At the completion of the printing process, the printed parts were removed from the print bed and placed into a convection oven for curing at 160 °C. The cure curve is also used in the rubber industry to determine the optimum cure time for any compound at a specific temperature. The time required to reach 90% of maximum torque is considered the optimum cure time (t_{90}) [5,31,32]. It can be inferred from Figure 4b, showing the cure curve of both FKM compounds at the cure temperature of 160 °C, that the FKM compounds reach optimum cure around 15 min at 160 °C.

Last, the maximum torque value of a compound in a cure curve is usually used as an indication of the rubber compound's modulus in the rubber industry [32]. Figure 4b shows that the FKM compound with the plasticizer had a lower maximum torque value than the compound without the plasticizer. This suggests that the FKM compound with the plasticizer had a comparatively lower modulus than the FKM compound without the plasticizer. Again, such behavior was expected as the increased free volume contributed by the plasticizer would allow the polymer chains to move and slide past each other more easily, thus making the rubber compound more flexible and less deformation-resistant [20,33].

3.1.2. Post-print Shrinkage

When a strand of fully compounded rubber is extruded through the printer nozzle and allowed to relax, it shrinks in size in the direction of extrusion. This phenomenon is defined as post-extrusion or post-print shrinkage. Post-print shrinkage was found in this research to be one of the most, if not the most, critical issues in MatEx AM of fully compounded rubbers or thermoset elastomers. This phenomenon can be attributed to the inherent characteristic of polymeric chains to revert to their initial state of relaxation (random coil chain) after they have been stretched [34–36]. During the printing process, the FKM compounds were extruded through the small opening of the printer nozzle. This process induced stresses on the polymeric chains and elongated the coiled chains. Once the extruded road was laid on the print bed, the induced stress slowly dissipated due to the viscoelastic nature of rubber compounds. As the induced stress dissipated, the polymeric chains of the extruded road returned to their coiled state from the elongated state. This behavior of the polymeric chains gives rise to the post-print shrinking phenomena in MatEx AM of rubbers.

Post-print shrinkage is an important concern for rubber AM technology since this phenomenon results in dimensional inaccuracy. The severity of the dimensional inaccuracy depends on the degree of post-print shrinkage of the rubber compound used for printing. As a critical application of FKM rubbers are seals and gaskets for high-temperature and high-pressure applications for industries such as semi-conductor and oil drilling, achieving dimensional accuracy of the printed parts is very important to enable rubber AM technology to be a viable alternative manufacturing technique. In our previous work [19], we have demonstrated the efficacy of lowering the compound viscosity in reducing post-print shrinkage in MatEx AM of rubbers. In that work, a liquid NBR polymer was used as the viscosity modifier for the NBR compounds under examination. In this study, we focused on

evaluating the effectiveness of a plasticizer as a viscosity modifier for lowering compound viscosity and post-print shrinkage. Figure 5 shows the viscosity of the FKM compounds at the printing temperature of 100 °C and the percentage of shrinkage in printed parts after they were thermally cured.

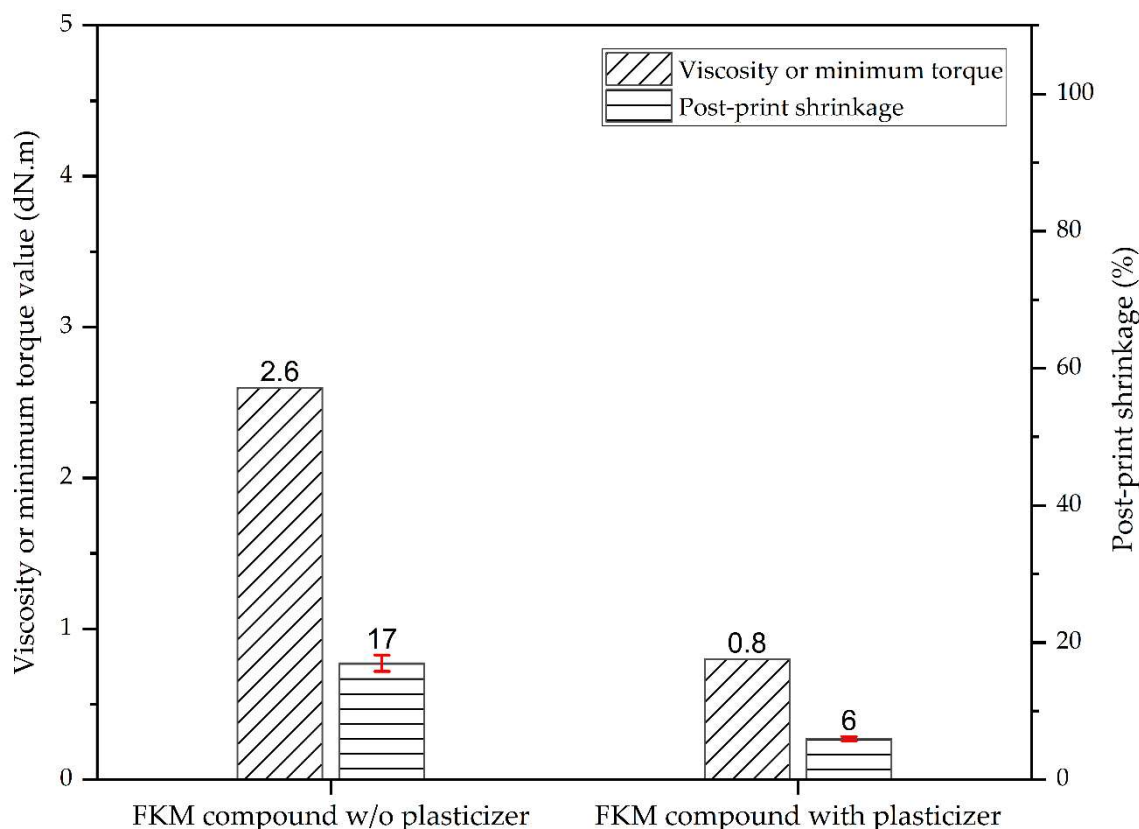


Figure 5. Correlation between the FKM compound viscosity and post-print shrinkage.

Figure 5 clearly shows that there was a direct correlation between the compound viscosity and post-print shrinkage. The FKM compound without plasticizer showed almost three-fold more post-print shrinkage (17%, post cure) compared to the FKM compound with the plasticizer (6%, post cure). Such behavior can be attributed to the lower viscosity of the FKM compound with the added plasticizer. Due to the lower viscosity, the FKM compound with plasticizer experienced less induced stress during the extrusion process compared to the FKM compound without plasticizer. The reduced stress experienced by the polymer chains during extrusion for the plasticized FKM meant they were less stretched compared to the FKM without plasticizer [34–36]. Consequently, upon relaxation to their coiled configuration, FKM with plasticizer displayed a lower degree of post-print shrinkage in comparison to FKM without plasticizer. Overall, the lowered post-print shrinkage of the FKM compound with plasticizer validates the effectiveness of plasticizer as a viscosity modifier in lowering the post-print shrinkage in MatEx AM of fully compounded thermoset elastomers.

3.1.3. Tensile Behavior and Interlayer Adhesion

An additively manufactured part can be described as a chain of roads with multiple interfaces since it is fabricated by joining materials layer by layer. These layers join one another by the process of diffusion of polymeric chains and weld healing [37,38]. As a chain is as strong as its weakest link, an additively manufactured part is as strong as the strength of the adhesion between layers. In the literature, tensile testing is a well-established method of characterizing the strength of interlayer adhesion and overall integrity of printed

parts [15]. In addition to studying the effectiveness of plasticizers on the viscosity and overall material printability, the effect on interlayer adhesion was also studied. As shown in Figure 3, three different types of printed tensile specimens, namely specimens with roads parallel to the direction of applied force, specimens with roads normal to the direction of applied force, and specimens with roads at $+45^\circ/-45^\circ$ angle with the direction of applied force were evaluated and compared against the compression molded samples. In Figure 6, the tensile properties of both FKM compounds are presented and compared. Figure 6 also provides a side-by-side comparison of the tensile strength of a compression-molded and printed specimen.

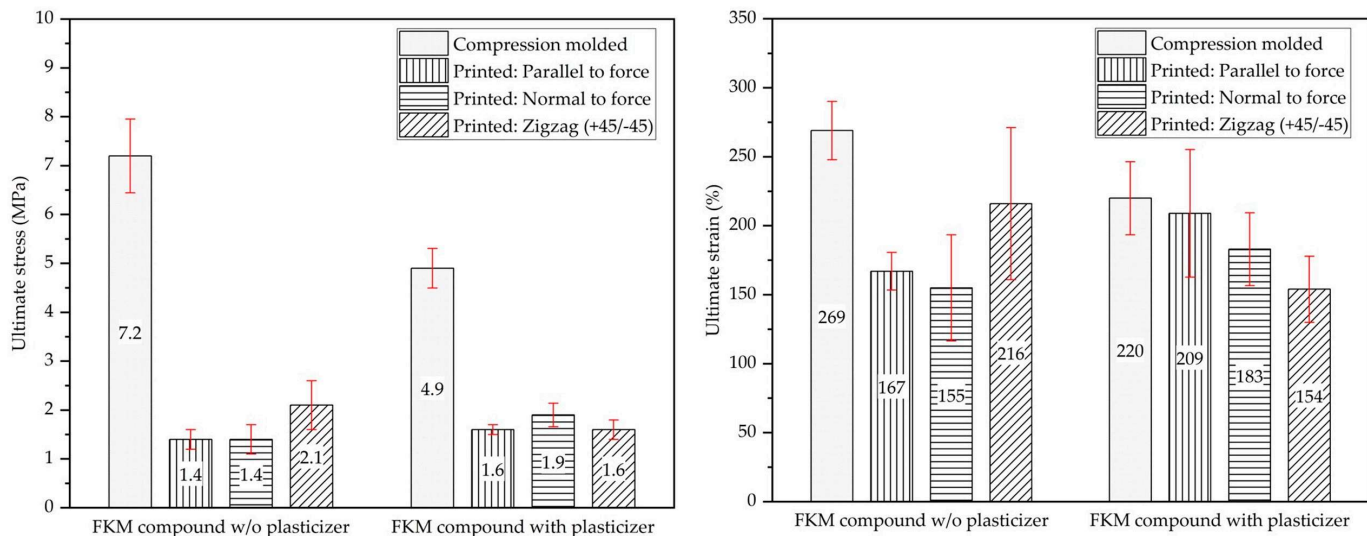


Figure 6. Tensile properties of compression-molded and printed samples of FKM compounds: (left) ultimate tensile stress and (right) ultimate tensile strain.

As can be seen in Figure 6, the compression-molded FKM compound with plasticizer is lower in ultimate tensile stress and strain by a noticeable amount when compared to the FKM compound without plasticizer. The effect of plasticizers on the mechanical properties is well known [21–24] and was expected. This behavior can be attributed to the increased free volume contributed by the plasticizer, making the rubber compound more flexible and less deformation-resistant [20,33].

Similarly, one expects printed tensile specimens from FKM-2 (plasticized) to show lower tensile strength compared to unplasticized 3D-printed tensile specimens regardless of direction. Therefore, to compare the tensile properties of the printed parts, the effect of directionality on the properties, and the effect of plasticizer on interlayer adhesion, the normalized stress at the break of the printed samples was calculated and plotted in Figure 7. Normalized stress at break was defined as the ratio of the ultimate tensile stress of printed samples to compression-molded samples for each respective formulation. Normalized stress at break provides a simple measure to assess how much of the strength of the compression molded sample was retained in the printed samples and, thus, indicates the strength of the interlayer bonds of the FKM compounds. Although printed tensile specimens from both FKM compounds showed similar tensile properties, printed parts with the FKM-2 compound (with the plasticizer) showed higher normalized stress at break compared to the FKM-1 compound (without the plasticizer). Such behavior of the FKM compounds suggests that the printed parts with the FKM-2 compound retained more of their mechanical properties as measured by the compression-molded specimens. Such behavior can be attributed to the lower viscosity of the FKM compound with plasticizer, which may have facilitated better interdiffusion between adjacent roads and, thus, stronger interlayer adhesion [37,38]. In conclusion, there might be a trade-off when adding plasticizers to FKM compounds for AM applications. On the one hand, the plasticizer favorably

affected the FKM compound's overall printability by lowering the material viscosity. The lower viscosity helped to reduce the post-print shrinkage substantially and facilitated better interlayer adhesion between adjacent layers. However, adding the plasticizer to the FKM compound dropped the overall mechanical properties of the FKM compound.

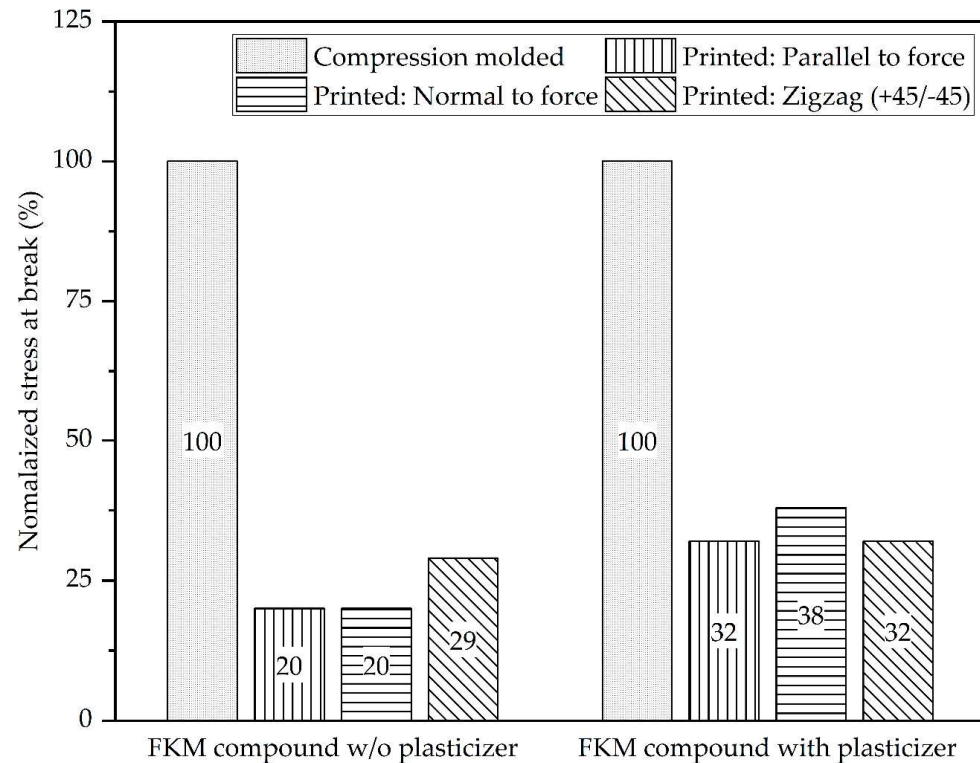


Figure 7. Normalized stress at break, an indication of interlayer adhesion of printed parts.

3.2. Different Approaches for Additive Manufacturing of FKM Seals

FKM rubbers are widely employed in high-temperature and high-pressure sealing applications [1–3]. Therefore, AM technology for FKM rubbers holds substantial potential for the streamlined fabrication of these seals, which are traditionally manufactured via compression molding. Optimizing the AM technology for this specific purpose could enable rapid, cost-effective FKM seal prototyping, low-volume manufacturing, the fabrication of complex multiplanar seals, automated preform deposition for compression molding, and even in situ seal fabrication. To explore the feasibility of these applications, we investigated several conventional and unconventional AM methods. The following sections discuss these methods in detail.

3.2.1. Traditional Additive Manufacturing of FKM Seals

In prior work, we demonstrated the feasibility of fabricating FKM- and FFKM-based seals and gaskets using the traditional FFF process by modifying a commercially available filament 3D printer and making filaments from FKM and FFKM compounds [18]. This work showed that the FFF process using FKM and FFKM filaments has a narrow process latitude, which caused reproducibility issues and shortcomings in meeting desired product specifications for very large and very small seals. In this work, the efforts were focused on increasing the process latitude to enable the printing of all types of seals ranging from large to medium and small seals. In the work, a large and complicated adapter seal was used due to its complicated design.

The first attempt to additively manufacture FKM seals involved the traditional AM technique, in which the desired geometry was fabricated by layer-by-layer deposition of material. The desired geometry, in this case, was the adapter seal. The adapter seal is a

static seal with a roughly 5 mm diameter circular cross-section. The seal geometry also had eight 90° sharp turns. Figure 8a provides the details of the seal geometry and its dimensions. Figure 8b shows the printed adapter seal at the end of the printing process but before the thermal cure of the FKM rubber. It can be seen from Figure 8b that the adapter seal fabricated using the conventional layer-by-layer AM method did not produce the desired shape. The most severe form of deformation occurred near the sharp turns. Post-print shrinkage of FKM rubber compounds resulting from the residual stress of extruded roads, as discussed in Section 3.1.1, can be attributed to these deformations. A closer examination of the cross-section of the printed adapter seal (Figure 8c) revealed the presence of a substantial number of voids. These voids, also known as pinholes, are typical characteristics of parts fabricated using the MatEx AM technique [39]. These voids are created when neighboring roads do not completely overlap with one another. Such voids usually weaken the printed part, but more importantly, in the case of sealing applications, these voids can lead to leakage and, eventually, failure of the seal [37]. Overall, the post-print deformation of the printed seal and the existence of characteristic pinholes in the cross-section made conventional layer-by-layer AM an unviable process for the fabrication of seals and gasket-like parts.

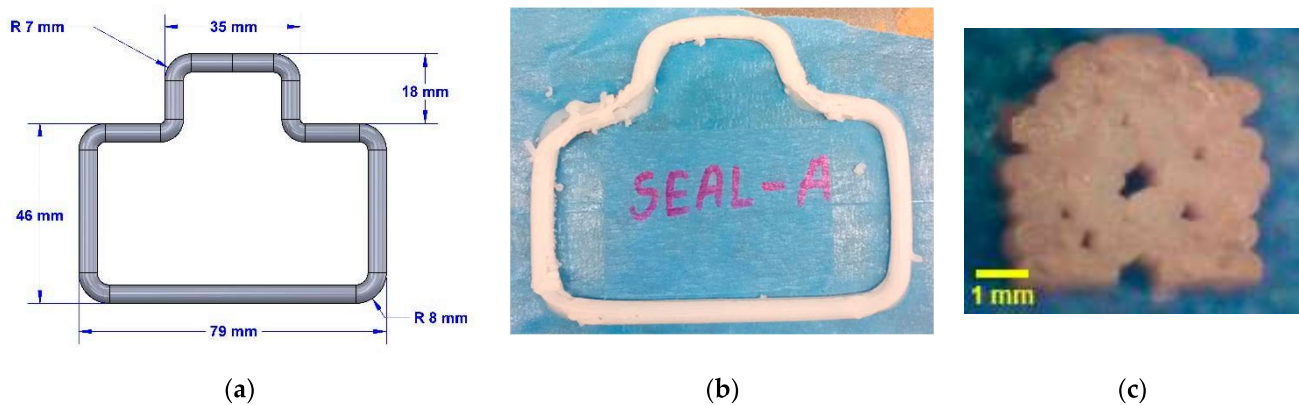


Figure 8. Conventional approach to additively manufacture a static seal from FKM rubber compound: (a) adapter seal geometry and dimensions, (b) printed adapter seal, and (c) cross-section of printed adapter seal.

To prevent the post-print deformation of the printed adapter seal and eliminate the pinholes, thermoplastic support structures and a larger nozzle matching the cross-sectional diameter of the seal were employed. Drossel et al. [40] previously reported the use of silicone rubber, molding sand, and plaster as media for dimensional stabilization of 3D-printed parts from rubber compounds. However, in their work, the printed rubber geometry is fully embedded in the media. Contrary to such an approach, in our work, as depicted in Figure 9a, thermoplastic support structures were placed around the inside perimeter and at selected locations on the outside perimeter of the adapter seal. The fixture-like thermoplastic structures were printed first with commercial PLA filaments using the thermoplastic extruder attached to the ARME printhead. After the PLA support structures were printed, the adapter seal was printed using the FKM rubber compound. The adapter seal was printed using a nozzle with a larger outlet (4 mm nozzle outlet diameter) than conventional nozzles used in MatEx AM [15]. This approach was used to print the adapter seal with a layer height matching the adapter seal's cross-sectional diameter. The reasoning behind such an unconventional approach was to eliminate the pinholes that were present when the seal was fabricated in multiple layers, which is the conventional approach of MatEx AM. Figure 9b shows the adapter seal printed in between the printed PLA support structures. It is evident from Figure 9b that the fixture-like PLA support structures prevented the extruded FKM rubber compound from deformation and allowed the acquisition of a substantially accurate printed part. Afterward, the adapter seal,

along with the support structures, were placed inside a convection oven to be thermally cured at 125 °C. After completion of the curing process, the seal was taken out of the oven, and the support structures surrounding the seal were removed. Figure 9c shows the printed adapter seal after the cure and removal of support structures. The fully cured seal retained its shape even after the support structures were removed, which justified the effectiveness of using support structures.

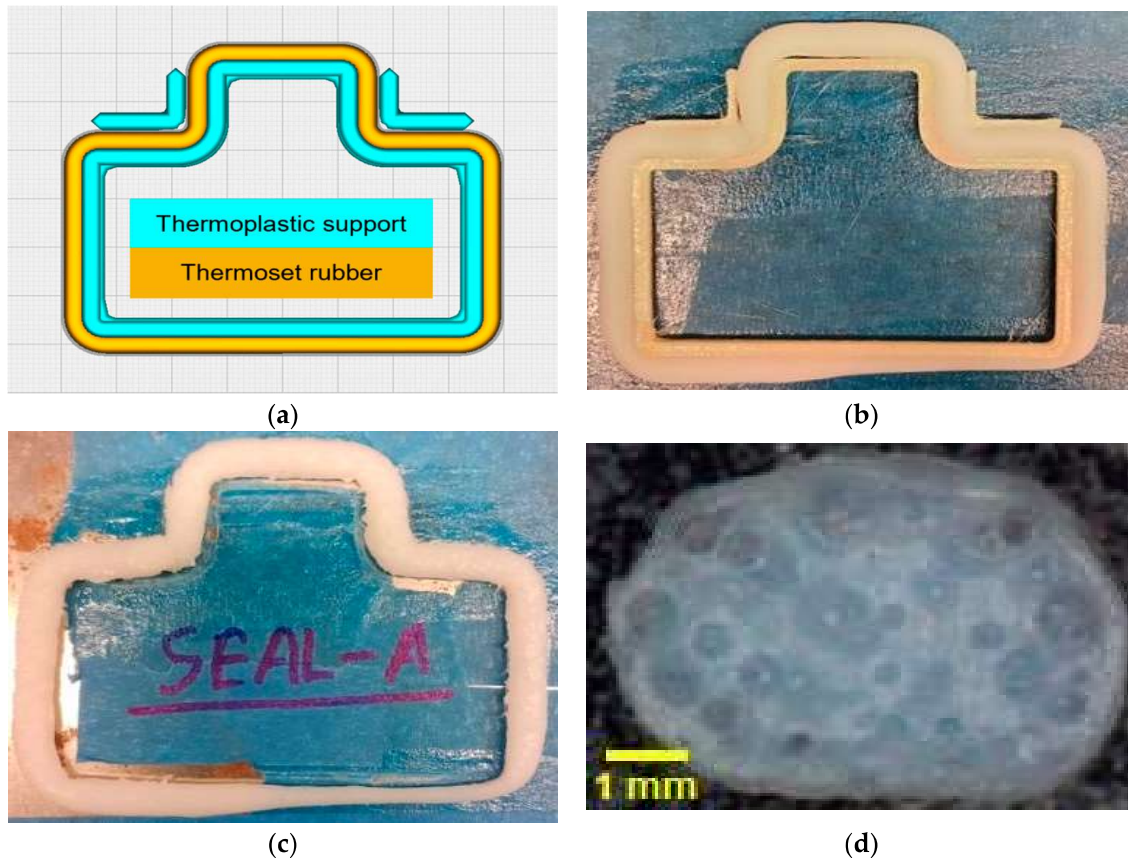


Figure 9. Traditional and direct additive manufacturing of an adapter seal with help of an enlarged nozzle and thermoplastic support structure: (a) 3D model of seal and thermoplastic support structure; (b) 3D-printed support structure and rubber seal; (c) 3D-printed rubber seal after thermal cure and removal of thermoplastic support structure; (d) cross-section of a 3D-printed FKM seal.

Additionally, the cross-section of the cured seal showed no presence of the pinholes, which was a result of using a large nozzle that matched the cross-section diameter of the seal. However, one drawback of employing a large nozzle matching the seal cross-section diameter was that there was only one seam where the nozzle completed the loop. This single seam was the weakest point of the seal and, as a result, was very prone to failure. Based on these results, a soft tooling approach to fabricating the adapter seal was employed to overcome the shortcomings of this approach and is discussed in detail in Section 3.2.2.

3.2.2. Soft Tooling Approach for FKM Seal Fabrication

Soft tooling is a manufacturing method that uses less durable and often more flexible materials to create molds, dies, or other production tools [41]. In this instance, the soft tool was a compression mold of the adapter seal additively manufactured with commercial acrylonitrile butadiene styrene (ABS) filament. In this approach, instead of printing on the print bed, the adapter seal was printed on the cavity of an ABS half mold, as shown in Figure 10a. The 4 mm nozzle matching the seal's cross-sectional diameter was used for printing. The walls of the half-mold cavity performed the same role as the PLA

support structures and prevented the extruded FKM rubber compound from shrinking and deforming. Once the seal printing process was completed, the other half of the mold was placed on top, and the setup was placed between a compression press. The mold was compressed with around 2 metric tons of force for 90 min at 100 °C. This method simulated the compression molding process and strengthened the seam situated at the point where the nozzle completed the loop. At the end of the compression cycle, the mold was removed from the press, the two halves of the mold were separated, and the flashed material was removed, as shown in Figure 10b,c, respectively. The adapter seal fabricated using this approach showed no post-print or post-cure deformation, as shown in Figure 10d. Upon closer inspection, no seamline was noticed, and the seal also retained its circular shape at its cross-section. Thus, using an additively manufactured soft tool, the adapter seal was fabricated through a hybrid process of AM and compression molding.

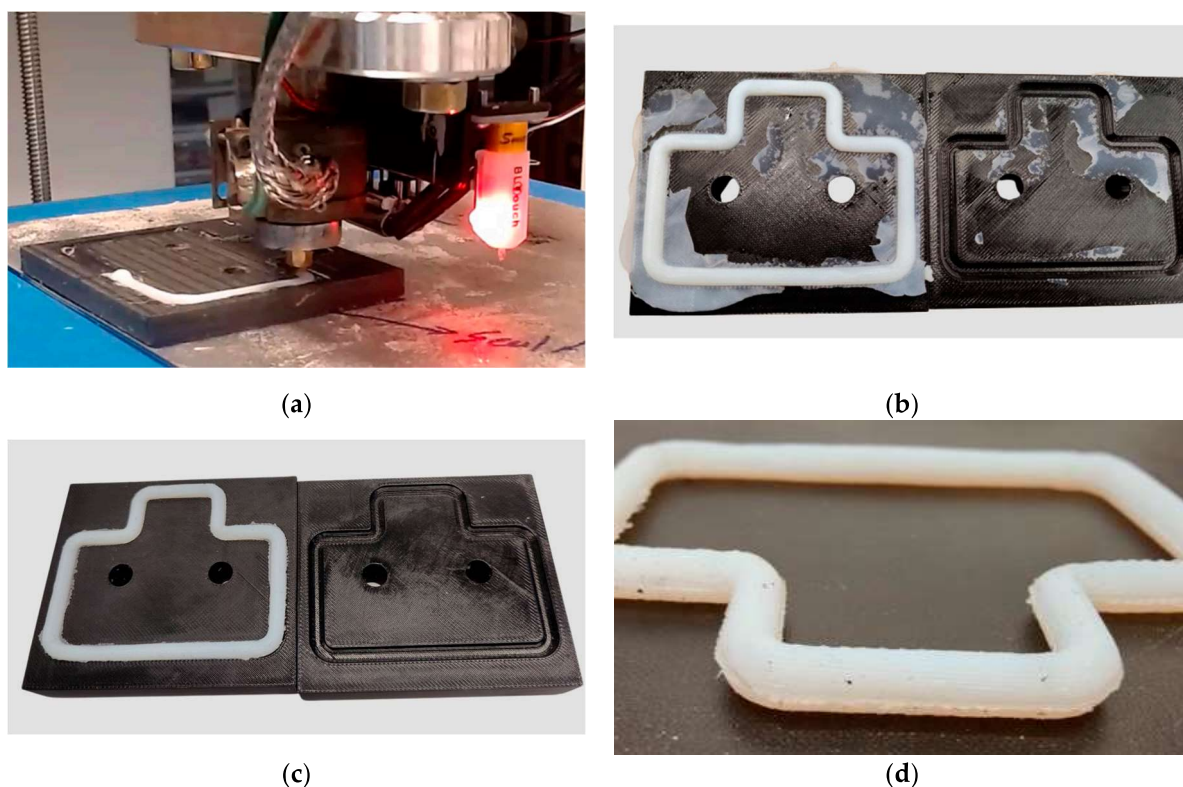


Figure 10. Soft tooling approach to fabricate seals: (a) deposition of uncured FKM rubber directly in the cavity of 3D-printed thermoplastic mold, (b) formed FKM seal with flash after completion of compression cycle, (c) FKM seal after removal of flash, (d) FKM seal after removal from 3D-printed thermoplastic mold/ soft tool.

3.2.3. Direct Printing of Molded-in-Place (MIP) Seals

As the name suggests, mold-in-place seals are formed by injecting the sealing material directly into the seal housing or groove. The sealing material creates a bond with the seal housing surface and, thus, forms a custom-fit seal. MIP seals offer superior sealing performance by reducing leak paths. They also offer enhanced environmental resistance as contaminants have no gaps to enter [42,43]. One of the significant advantages of MIP seals over conventional seals is their increased design flexibility, as they can conform to complex geometries. MIP seals find their application in numerous industries, such as automotive, aerospace, semiconductor, and consumer electronics [42,43]. MIP seals with FKM rubber as the sealing material are commonly used in the abovementioned industries where the seal needs to withstand high-pressure and high-temperature environments. Here, we have demonstrated the AM of an MIP seal directly into an aluminum metal housing

(Figure 11a) using an FKM compound with a single extrusion layer, as shown in Figure 11b. After extruding the FKM compound into the seal housing, the seal housing acted similarly to the thermoplastic support structures reported in Section 3.2.1. They prevented the extruded FKM material from shrinking inwards and helped retain the material in place. Figure 11c shows a MIP seal directly printed into the seal housing (after thermal cure). This demonstration exhibits the feasibility of rubber AM technology in forming MIP seals. It also demonstrates the prospect of using the ARME print head to deposit rubber preform directly into the cavity of a compression mold, a process that is currently the predominant method of manufacturing in the rubber industry.

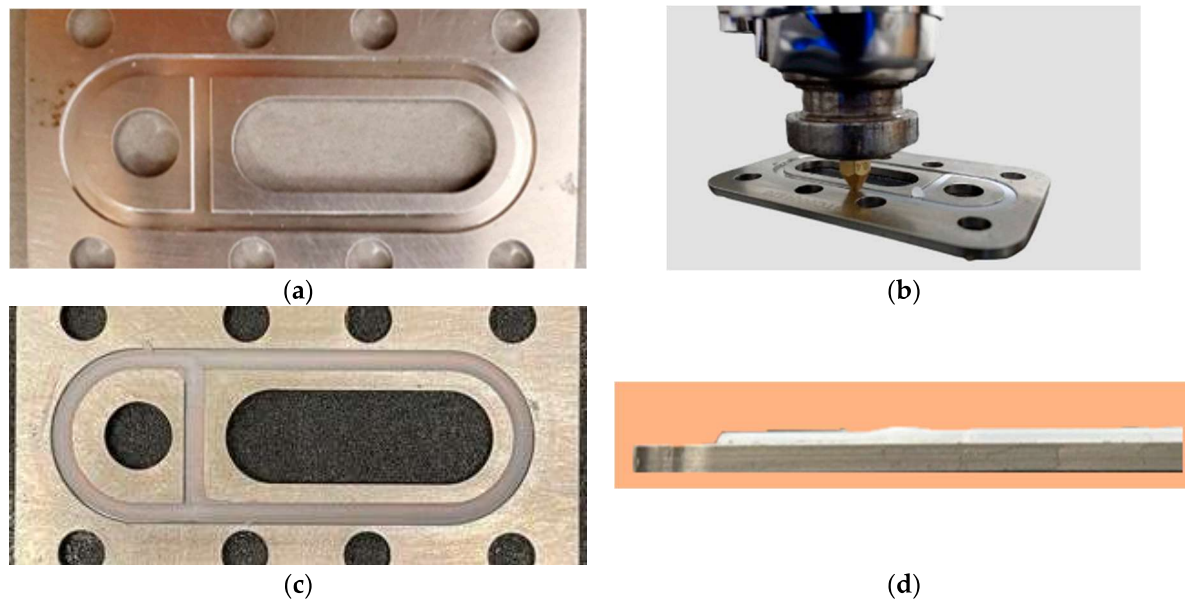


Figure 11. Additive manufacturing of bonded seal directly on seal housing: (a) metal seal housing; (b) deposition of FKM rubber compound directly inside of the seal housing; (c) printed seal after thermal cure (top view); (d) printed seal after thermal cure (right view).

4. Conclusions

This study successfully demonstrated the potential of material extrusion additive manufacturing of functional FKM rubber components. Precise FKM deposition was demonstrated with the ARME extruder designed to print fully compounded thermoset elastomers.

The aim of this study was to evaluate the effectiveness of a plasticizer as a viscosity modifier and its effects on the 3D printability of an FKM rubber compound. In this regard, two FKM compounds, with and without plasticizer, were formulated and evaluated based on their viscosity, post-print shrinkage, tensile properties, and interlayer adhesion. The addition of a PFPE plasticizer reduced the compound viscosity and, thus, lowered the post-print shrinkage. The addition of the plasticizer also lowered the overall modulus of the cured compounds. The normalized stress at break for samples printed transverse to the stress direction was higher for the plasticized FKM compound as compared to the unplasticized compound indicating potentially better interlayer adhesion for the plasticized FKM.

This study also evaluated the feasibility of rubber AM technology to fabricate FKM seals and gaskets for prototyping purposes. In this context, several conventional and unconventional AM approaches were evaluated. To better control the shape and dimensions of the printed parts, thermoplastic support structures were used. This approach was found to significantly improve the part quality. Last, a hybrid approach combining AM and soft tooling for compression molding was found to be the most promising fabrication method for FKM seals and gaskets.

These findings highlight the prospects of additively manufactured parts with tailored properties for various industrial applications. Future research directions could explore

optimizing AM process parameters to further enhance the mechanical properties of printed FKM parts while maintaining printability. Additionally, investigating alternative plasticizers or formulations tailored for AM could lead to superior performance. Overall, this study paves the way for the development of additively manufactured FKM seals, gaskets, and other functional components with improved efficiency and design freedom. The information reported in this paper is also included in the two pending patents by Greene Tweed & Company [18,25].

Author Contributions: A.M. and M.P. wrote the original manuscript, S.K. fabricated ARME printhead, S.K., A.M. and S.C. printed and tested parts, and D.O.K., J.L.M. and R.C. reviewed and revised the main manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are contained within the article.

Conflicts of Interest: Some information reported in this publication is included in two filed patent applications [18,25] by Greene Tweed & Company. Authors Mookkan Periyasamy, and Ronald Campbell are employed by the company Greene Tweed & Company LLC. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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December 2023

The American Chemistry Council's (ACC) Performance Fluoropolymer Partnership (hereafter "PFP") has developed a White Paper that focuses on the Infrastructure & Construction (I&C) end-use segments noted below. The PFP's members are some of the world's leading manufacturers, processors and users of fluoropolymers, including fluoroplastics, fluoroelastomers and perfluoropolyethers polymers.

The content provided here in this White Paper was submitted to the REACH Annex XV All PFAS Restriction Proposal in 2 parts. The submittal reference numbers are as follows:

August 27, 2023: Reference number 3eb5e616-f855-4393-abbc-e1eeb7c25ff4 and

September 24, 2023: Reference number 4cc4c0df-35b8-4354-a66c-37401d364694

These comments pertain to the use of fluoropolymers (fluoroplastics) in Infrastructure and Construction (I&C) applications. This is a commercial/industrial application/use segment with little to no direct consumer use. The fluoropolymers highlighted in this submission are listed in **Table 1**.

In this White Paper, we provide compelling case studies and technical data on the use of fluoropolymers in five (5) end-use applications that are often subject to continuous weather extremes based on the climate and/or their physical locations. Those uses are:

1. Building Facades and Protection - Metal Building Panels and Parts;
2. Roofing and Roofing Structures;
3. Bridge and Walkway Structures;
4. Water Towers; and
5. Solar Panels.

Please contact me if you or your colleagues have any questions.

Jay West
Executive Director
Performance Fluoropolymer Partnership

Table 1. Fluoropolymers highlighted in this White Paper

Polymer	PVDF	PVDF-HFP Copolymer	ECTFE	ETFE	FEVE
Name	polyvinylidene fluoride	vinylidene-fluoride, hexafluoro-propene copolymer	ethylene, chlorotrifluoro ethylene copolymer	ethylene, tetrafluoro-ethylene copolymer	fluoroethylene-vinyl ether copolymer
CAS Number	CAS 24937-79-9	CAS 9011-17-0	CAS 25101-45-5	CAS 25038-71-5	CBI
Structure	$-(CF_2-CH_2)_n-$	$-(CF_2-CH_2)_n-[CF(CF_3)-CF_2]_m-$	$\left[\begin{array}{cccc} F & Cl & H & H \\ & & & \\ -C & -C & -C & -C- \\ & & & \\ F & F & H & H \end{array} \right]_n$	$-(CH_2-CH_2-CF_2-CF_2)_n-$	contains fluoroethylene and vinyl ether segments

For a Glossary of Terms, see Appendix A.

For Testing and Reference Methods in the I&C End-Uses, see Appendix B. For each of the I&C end-use applications in this submission there are a set of exacting performance testing and reference methods. Appendix B contains a list of the critical test methods and what they measure. For the primary end-uses in this submission, designers, architects and builders have specific performance standards they must meet to achieve the desired long lasting coatings performance and surface protection.

Background on Fluoropolymers (Henry et al., 2018; Korzeniowski et al., 2022)

“Fluoropolymers are high molecular weight polymers with fluorine atoms directly attached to their carbon-only backbone” (Ebnesajjad 2017). The carbon-fluorine (C-F) bond is the strongest bond between carbon and another atom and imparts unique, outstanding and beneficial properties and extraordinary functional performance to fluoropolymers. (Banks et al. 1994, Scheirs 2007, Ameduri and Sawada 2017a, 2017b, Ameduri 2020, FPG 2021) These properties (fluoropolymers enable) include chemical, biological and thermal stability, heat and chemical resistance, unique dielectric properties and durability. Additional fluoropolymer properties include improved fire resistance, weather resistance, non-wetting and non-stick. Fluoropolymers are regarded as irreplaceable in many applications because their unique combination of specific properties, which are critical to help ensure optimal performance in many applications and cannot be achieved by alternative materials (FPG 2021, 2017; PFP 2020; Henry et al. 2018).

There is considerable media and public confusion and misunderstanding regarding PFAS, as the many different chemicals and groups are often not clearly differentiated under the broad term PFAS. PFAS, a large, diverse group of substances with vastly different properties, is too broad to enable effective, science-based assessment and regulation of chemical compounds as an entire group. This point has been raised in recent publications which suggest alternative approaches to effectively group PFAS for regulatory assessment (BDI 2021, Buck et al. 2021, Orgalim 2021, RSC 2021, Wallington et al. 2021, Amcham 2020a; Miller et al. 2020). PFAS must be assessed based on their chemical, physical, thermal and biological property differences and uses (Amcham 2020a, BDI 2021, Buck et al. 2021, RSC 2021, Wallington et al. 2021). As regulatory frameworks such as the subject EU REACH regulation continue to evolve, more work is needed to clearly distinguish among PFAS types, based on their properties to assure that regulations are appropriate in scope, proportional and based on science.

Fluoropolymers have material properties which help define their functionality. The unique properties of fluoropolymers include improved durability, mechanical strength, inertness, thermal stability and resistance to chemical, biological and physical degradation. Some can be classed as Polymers of Low Concern (PLC) to human health and the environment according to OECD criteria as they are chemically stable, biologically stable/inert, negligibly soluble in water, non-bioavailable, non-bioaccumulative; and non-toxic. (Henry et al. 2018, Buck et al. 2011, Korzeniowski et al 2022).

The PLC criteria were developed over time within regulatory frameworks around the world as an outcome of chemical hazard assessment processes which identified physical chemical properties of polymers that determine polymer bioavailability and thereby inform a polymer’s potential for hazard. For example, many of the physicochemical properties, such as molecular weight, limit the ability of a polymer to cross the cell membrane and therefore limit its bioavailability (Kostal 2016, USEPA 2012, Lipinski et al. 2001).

The results from the two PLC publications show that each of the 18 commercially manufactured fluoropolymers in these studies satisfy the widely accepted assessment criteria to be considered polymers of low concern and merit such designation. The study results add further evidence to show that fluoropolymers are demonstrably different and should not be grouped with other PFAS for hazard assessment or regulatory purposes.

For the purposes of this submission supporting the I&C end-use segments noted above, we will focus on uses of fluoropolymers. These are the fluorinated polymers on the left-hand side of **Figure 1** highlighted in light blue.

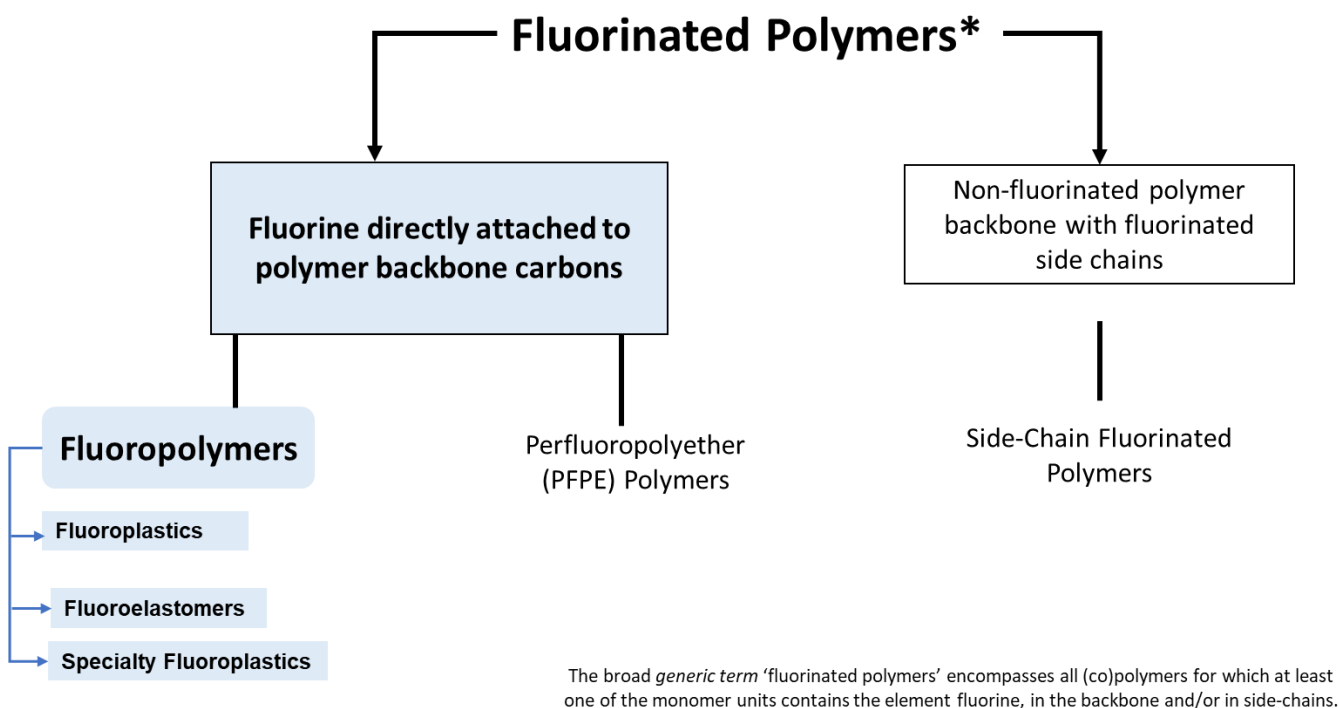


Figure 1. Fluorinated Polymers: Fluoropolymers, Perfluoropolyethers and Side-chain Fluorinated Polymers (Korzeniowski et al, 2022)

Table 2 below describes some of the core properties of the fluoropolymers that are covered in this set of comments. Some of the key critical properties noted here are increased mechanical strength, significant wear resistance, low coefficient of friction, barrier properties and improved resistance to chemicals and weatherability, among others. (Korzeniowski et al, 2022)

Table 2. Fluoropolymer Properties and Functionality.

Table zzz: Fluoropolymer Properties and Functionality Updated 19Apr

Properties		Durable				Inert - Stable					Functional						
Functionality		Mechanical strength	Wear resistance	Flexibility	Low coefficient of friction	Resistance to chemicals	Weatherability	Cryogenic properties (lower than -50°C)	High operating temperature range	High limiting oxygen index	Electrical insulator - high data transmission rate	Piezo-electrical properties	Barrier properties	Ultra High Purity grades for clean applications	Optical clarity	Low refractive index - used for optical effects	Polymer processing additive (PPA)*
Fluoroplastics	PVDF Homopolymer	•	•		•	•	•		•	•		•	•	•	•	•	•
	PVDF Co-polymer	•	•	•	•	•	•		•	•	•	•	•			•	•
	ECTFE Co-polymer	•	•		•	•	•	•	•	•	•		•				
	ECTFE Ter-polymer		•		•	•	•		•	•			•				
	ETFE	•	•		•	•	•		•	•	•		•				
	FEVE	•	•	•	•	•	•		•	•			•		•		

Polymer Processing Additives (PPA)*: also called Polymer Processing Aid, Extrusion Process Aids or Polymer Processing and Recycling Aids

Fluoropolymer Benefits, Features and Performance Properties Expected in I&C Coating End-Uses

The exceptional properties that fluoropolymers provide and/or enable in the I&C coating applications will be described more fully in the detailed end-use application descriptions that follow in this report. To help set the stage for these descriptions, we highlight below the critical parameters that determine how well a Fluoropolymer-Based Coating (FBC) and/or film functions and performs under various environmental conditions.

Flexibility is the ability of the material and its coating to bend without breaking and return to its original shape or position without damage to the exterior coating.

Wear resistance performance measures the ability of the coated surface to resist the aggressiveness of wearing medium.

Impact Resistance and Hardness is defined as the prepainted or coated metal surface's ability to withstand various impacts under the appropriate test conditions. There are various film hardness tests including the pencil test (ASTM D3363). Relative rankings for both impact resistance and hardness are often used when comparing organic coating films.

Color Retention is the ability of the prepainted or coated metal substrate to maintain its color and appearance over extended periods of time under exterior weather conditions and/or appropriate test methods simulating outdoor exposure.

Gloss Retention is a core exterior durability property that measures the retention of film gloss under UV exposure conditions.

Film Erosion is the degree to which paint films erode under harsh and/or weathering conditions. Film erosion of exterior paints and coatings is evaluated by comparison with photographic standards or reasonable facsimile. It can also be measured as a surface loss in $\mu\text{m}/\text{year}$.

Chalking Resistance is the evaluation of the degree of chalking on white or tinted exterior paint films.

Weather Resistance – Abrasion Resistance - is the combined ability of a material or structure to withstand, resist or endure harsh atmospheric weather conditions, such as extremely hot or cold temperatures, UV light, humidity, salt air or similar corrosive conditions.

Harsh Chemical Resistance is the ability of a substance to withstand, resist, or endure a chemical challenge for a specific period of time.

Corrosion Resistance is the ability of a previously painted or coated specimen to withstand accelerated and atmospheric exposure tests and subsequent evaluation with respect to corrosion, blistering as well as loss of adhesion.

Barrier Properties refers to the property of material when a specified permeable object transmits from one side to the other (from high density side into low density side).

Fire Retardancy/Smoke Suppression refers to how the painted metal materials and/or panels are evaluated, on a relative basis, for surface flame spread and smoke density measurements with that of a select grade of red oak and fiber-cement board surfaces. The property of limiting oxygen index (LOI) is the measure of the minimum concentration of oxygen in a mixture of oxygen and nitrogen that is needed to support the flaming combustion of a material. Limiting oxygen index (LOI) is the parameter most frequently used to characterize the improvements in fire retardancy.

Low Refractive Index for Optical Effects concerns the refractive index (RI), the ratio of the speed of light in a vacuum to the speed of light through a material. The lower the refractive index, the less the material bends the light, decreasing the focusing power, the reflective effect and the light dispersion. The material of an optical lens must possess a lower value of refractive index. The clarity or transmittance of a material usually increases with decreasing crystallinity, refractive index, compressibility and intermolecular interaction. Many of the optical properties of a material are related to the refractive index.

Reduced Dirt Collection or Dirt Pick-up Resistance is the ability of a coating to resist adherence of dirt over a defined period of time and avoid film darkening and an uneven appearance.

1. Building Facades and Protection - Metal Building Panels and Parts

Relevant Fluoropolymer Products Used: PVDF and FEVE

The information below is applicable to this end use as well as the metal and cool roofing end-uses.

General Introduction

Fluoropolymer-based coatings (FBCs) offer superior performance, service life, sustainability, appearance and value for applications on a wide variety of metal substrates used in commercial and monumental building projects.

These fluoropolymer-based systems include polyvinylidene fluoride (PVDF) and fluoroethylene vinyl ether (FEVE) resin-based formulations. These two fluoropolymers are the film-forming binder resins in factory-applied industrial and construction coatings used in settings where extreme durability and lifespan of several decades or more are needed to provide substrate protection. FBCs extend the lifespan of the underlying materials and are a critical specification for certain products and end markets.

FBCs are available in both coil and extrusion applications. Each type has specific uses for metal building products.

- Coil coatings are applied to large rolls or “coils” of steel and aluminum by a continuous, automated process that can run up to 700 feet per minute. The coil is unwound, cleaned, pretreated, primed, painted and thermally cured before being recoiled for shipment. This is also known as a pre-paint process.
- Extrusion coatings are spray-applied to aluminum, preformed extruded substrates in a vertical or horizontal line. The extruded product is cleaned and pretreated, then the coating is spray applied and thermally cured to set the system. This also is known as a post-paint process.

FBCs can be applied to a variety of components used in projects ranging from pre-engineered metal buildings to municipal arenas and skyscrapers (**Table 3**).

Table 3. Fluoropolymer Application Uses and Fluoropolymer Building Project Types

Fluoropolymer Application Uses	Fluoropolymer Building Project Types
• Canopies • Column covers • Curtain wall • Decorative accents • Doors and entrances • Façade systems • Fascia • Louvers • Perimeter trim • Rain and wind screens • Roofing • Skylights • Soffits • Storefronts • Sunshades • Wall panels • Windows	• Airports • Apartments and condominiums • Auto dealerships • Banks and financial service providers • Corporate campuses and office buildings • Courthouses and government centers • Hospitals and clinics • Hotels and resorts • Libraries • Museums and galleries • Performing arts centers and theaters • Recreation and community centers • Research laboratories • Restaurants • Schools and universities • Shopping and retail centers • Stadiums and arenas • Transportation stations and transit-oriented developments • Worship and spiritual spaces

Important properties that FBCs enable for construction include, but are not limited to the following:

- Adhesion, flexibility, formability, abrasion resistance, hardness and impact resistance;
- Resistance to chemicals, flame spread/surface burning; and
- Durability as demonstrated by UV-resistance, film integrity, low film erosion rate, humidity resistance and corrosion resistance.

We are unaware of another coating technology that enables the performance parameters of durability and product longevity that are the defining characteristic of FBCs.

Outdoor exposure testing provides data showing FBCs have an erosion rate approaching 50 percent less than other coating technology options used in I&C settings. This difference explains why FBCs have a life expectancy of 50 years or more in many settings compared to 20 years or less for some alternate technologies. This reinforces why FBCs are so unique and useful in the development of durable and essential building products.

Failure of the coating system will lead to the need to recoat the metal substrate or degradation of the metal substrate can occur, which may require its eventual replacement. The difference in coating performance is profound as FBCs can retain their protective properties for more than 50 years. Given the fact that exterior surfaces on infrastructure such as skyscrapers and monumental buildings cannot be easily repainted or replaced, coating performance and its subsequent substrate protection is key to overall sustainability. Driving towards less durable technologies would result in regrettable substitutions requiring field-refinishing and building component replacement leading to increases in waste and carbon emissions.

Even for buildings where repainting or replacement of metal panels is not as difficult as for skyscrapers or other monumental structures, reduced service life can present disruptions in the use of buildings housing areas such as education, medical, government and communications. In addition, field-refinishing brings with it potential release of VOCs to the atmosphere and the possibility of chemical releases to the environment.

PVDF-based Infrastructure and Construction Coatings

Prepainted metal is a high-quality product manufactured under strict quality control in the coil coating process. **Figure 2** illustrates the typical composition of a coated metal.

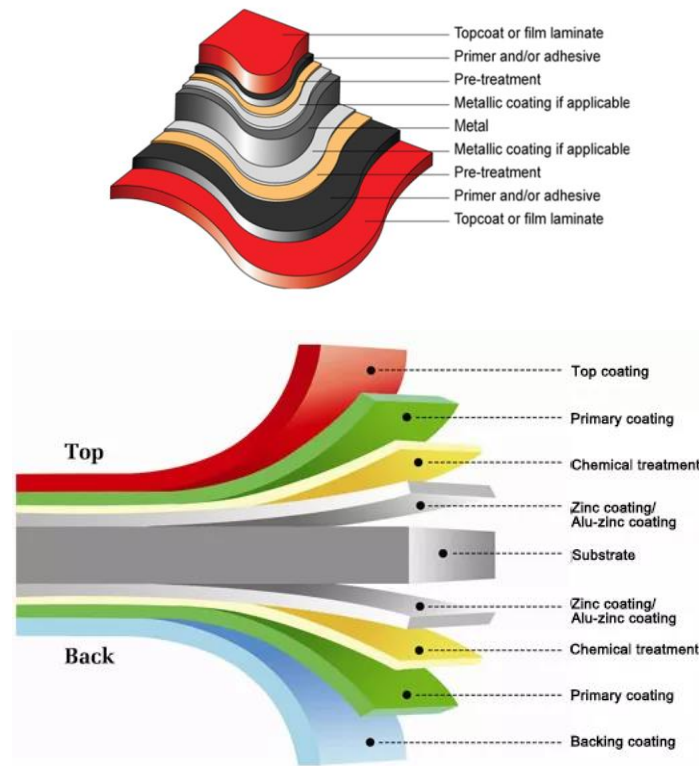
The thickness of coatings is usually quoted with a combination of top-coat and primer. In the majority of cases, the primer is a thin layer, of the order of 4 μm , the majority of the coating being the topcoat. For multi-coat systems, such as 3- or 4-coat PVDF-based coating, the total thickness including primer and 2 or 3 top-coats is usually quoted, the thickness of each layer being required for its individual function in the total system.

Liquid paints are made up of four main constituents:

- Pigments
- Binders
- Solvents
- Additives

The solvent is used as a delivery mechanism, allowing the paint to flow-out and give a smooth wet film before drying and curing. Solvents do not remain in the final, cured product. The function of the finished product is a combination of the binder, pigments and additives, but the industry standard is to refer to coatings based on the type of binder used.

Figure 2. Examples of the composition of a typical prepainted metal product.



Figures with permission from Arkema and www.yumisteel.com.

The binder is a polymeric material which gives structure to the paint. The main types of polymers used for coil coating paints are:

- Polyester
- Polyurethane
- Polyvinylidene fluoride (PVDF) and fluoroethylene vinyl ether (FEVE)
- PVC (plastisol)
- SMP (Silicone Modified Polyester)

PVDF forms a highly stable resin which is not cured in the paint in the same way as polyesters. Instead, it is fused into the paint film as a thermoplastic coating. Unlike other common coating polymers, the PVDF resins have been shown not to be susceptible to attack by UV radiation, leading to a coating that is very stable for long periods in sunlight.

FBCs tend to have coatings in the thickness range of 25 μm to 28 μm , although multi-layer systems can have higher thicknesses up to 55 μm . Unlike polyurethanes, high-build PVDF-based coatings are made up of up to 4 layers rather than the usual 2.

As mentioned above, PVDF-based film coatings have been shown not to be susceptible to attack by UV light, so the resin is highly resistant to degradation upon exposure to sunlight, unlike virtually all other polymers. This property provides a very high resistance to fading and chalking as well as very good long-term maintenance of gloss and color.

Apart from being highly resistant to UV light, the FBCs utilizing PVDF resin are also highly resistant to many chemicals and can have excellent stain resistance. Due to these superior qualities, FBCs also tend to carry a premium price compared to most other coating systems.

For this specific end-use, there has been a licensing program in place for over 50 years in order to help ensure that all specific PVDF-based coatings perform exactly at the expected level by architects and end users. All details are available online (Arkema 2022b).

Case Studies

Arkema Kynar 500® FSF® **PVDF Building Façade Case Studies:**

<https://kynar500.arkema.com/en/media/case-studies/>

Façade – Wall Panels Case Studies:

SEI Investments (PA, USA). Aluminum panel wall system meeting AAMA 2605 standards. PVDF Resin-based coating. 70% Kynar 500®FSF® system:

<https://kynar500.arkema.com/en/media/case-studies/sei-investments/>

The Valley View building on SEI Investments' North Campus in Oaks, Pennsylvania, features an aluminum panel wall system finished in 70% Kynar 500® FSF® PVDF based coil coatings. Along with these architectural coatings' vivid colors, these innovative finishes are formulated with solar reflective pigments. As with other specific 70% PVDF resin-based, high-performance, architectural coating systems, this particular application meets or exceeds AAMA 2605. It has been tested to meet or exceed the equivalent of 10 years south Florida weathering exposure conditions for color retention and resistance to fading, chalking and erosion.

DeWitt Family Service Center (Northwestern College, Iowa) Wall panel system. Coil Coatings PVDF-based system: <https://kynar500.arkema.com/en/media/case-studies/dewitt-family-science-center/>

Completed in 2019, this eco-friendly and state-of-the-art 61,000 square-foot facility creates a grand entrance to the campus of Northwestern College. It serves health science programs including biology, chemistry and the now on-campus nursing department. The building is brought to life with flat lock panels.

Appaloosa Library (Scottsdale, AZ) Wall cladding. Duranar® VARI-cool coatings:
<https://kynar500.arkema.com/en/media/case-studies/appaloosa-library/>

The one-story Appaloosa Branch Library in Scottsdale, AZ is a departure from libraries of the past that featured dark wood and dim lighting. As you approach the new Library, the building's metal skin-20,000 square feet (1,858 m²) of wall cladding changes colors. When applied and cured on properly prepared substrates, Duranar® VARI-Cool coatings offer brilliant color change along with exceptional color stability, chalk resistance, durability, abrasion resistance, chemical resistance and flexibility. The polychromatic coating utilized on the library is designed to help the structure remain beautiful for decades. The pearlescent pigments used in the coating reflect the sun's infrared [heat] energy, which helps the library stay cool and thereby consume less energy for air conditioning, even in the hot Arizona sun.

Stony Brook University (New York) Aluminum wall clad coil coating metal panels. Kynar 500® PVDF system: <https://kynar500.arkema.com/en/media/case-studies/stony-brook-university-student-c/>

An Aluminum Composite Material (ACM) was ordered in bold colors and installed as exterior cladding on an interconnected series of three buildings. The composite consists of two sheets of 0.020" aluminum thermobonded to a polyethylene core in a standard thickness in a continuous process. The composite material was pre-finished with Arkema's Kynar 500® PVDF resin-based coil coating. A wide spectrum of attractive standard and custom colors is available. Approximately 100,000 square feet of the ACM was installed on the buildings in a wide range of colors.

2. Roofing and Roofing Structures

Typical Products Used: PVDF FBCs

FBCs offer superior performance, service life, sustainability, appearance and value for applications on a wide variety of metal substrates used in commercial, monumental and other building projects. FBC systems often include polyvinylidene fluoride (PVDF) resin-based formulations. As previously discussed, PVDF is a film-forming binder resin in factory-applied industrial and construction coatings that is used in settings where extreme durability and lifespan of several decades or more are needed to provide substrate protection. FBCs extend the lifespan of the underlying end product and are a critical specification for certain end-use markets.

FBCs utilizing PVDF are typically only available in coil applications for the roofing end market. Coil-applied coatings over aluminum and steel substrates are used for metal roofing. Coil coatings are applied to large rolls or "coils" of steel and aluminum by a closed system, an automated process that runs up to 700 feet of coated material per minute.

Metal roofing can be incorporated into nearly any building type. Two typical metal roofing products are corrugated and standing seam. Additionally, metal roofing can be painted and stamped to look like other roofing substrates such as wood, shingles and slate.

Metal roofing has many inherent advantages compared to other traditional types of roofing, including:

- Better resistance to wind, hail and fire.
- Better energy efficiency, especially when incorporated with solar reflective pigment systems.
- Less weight than traditional types of roofing.
- Longer life spans (in some cases 50 years or greater) when utilizing FBCs.
- Higher circularity due to the common practices and infrastructure available for the recycling of steel and aluminum.

Important enabling properties of FBCs for metal roofing include, but are not limited to the following:

- Adhesion, flexibility, formability, abrasion resistance, hardness and impact resistance
- Resistance to chemicals, flame spread/surface burning
- Solar reflectance
- Durability as demonstrated by UV-resistance, film integrity, low film erosion rate, humidity resistance and corrosion resistance

As noted above, these fluoropolymer systems have been shown to provide numerous important benefits for both roofing and building facades. (Ref: <https://kynaraquatec.arkema.com/en/products/lower-lifetime-ownership-costs/>)

It is critical to understand that these many favorable attributes combine to provide a lower lifetime ownership cost:

- Lower energy usage from higher solar reflectivity and lower roof temperatures
 - lower carbon footprint
 - reduced dirt pick-up
 - significant mold and mildew resistance
- World-class UV resistance and long-life color retention
- Lower peak energy demand charge

- Longer lifespan of roof coating and longer lifespan of roof substrate
- Lower maintenance costs and less downtime
- Increased efficiency and longer lifespan of HVAC equipment
- Lower VOC emissions
- Support ability to seek tax credits, rebates and building codes
- Help enable Green Building credits applicability to buildings
- Versatile and can be applied to a wide variety of roofing types

Lower Energy Usage from Higher Solar Reflectivity and Lower Roof Temperatures

Higher Reflectivity (TSR value) throughout the roof's life results in lower cooling costs.

A properly formulated FBC can significantly reduce the surface temperature by reflecting the sun's rays. For roofs, it has been shown to reduce the roof's surface temperature by as much as 50°F (28°C) (USDOE) and interior temperatures by 6-9°F (3-5°C) (RCMA), which translates into reducing cooling costs by as much as 30% (CRRC).

Lower Carbon Footprint

Reduced air conditioning means less energy used, less carbon dioxide emitted and more comfortable building conditions. Lower energy bills mean less fossil fuels needed to generate electricity and so a lower carbon footprint. Add in less frequent roof cleanings and recoatings, and the carbon footprint of the project shrinks even further.

Furthermore, FBCs designed for roofing applications have shown the ability to maintain a 3-year Total Solar Reflectance (TSR) above 0.80 (Arkema 2022), well above industry standards for white roofs of 0.55 (as measured by the Cool Roof Rating Council, CRRC). This means a roof utilizing an FBC can reflect over 80% of the sun's rays. By comparison, a Modified Bitumen or Asphalt Shingle has a TSR of only 0.05 - 0.25 (CMR, 2015) (**Figure 3**). FBCs can reduce the "Heat Island Effect" of cities, where the difference between outside air temperatures in a city and its surrounding rural areas can be 5 - 9°C higher (9 -16°F) (Cool Roofs).

Figure 3. Sun's Radiation versus Solar Reflectance vs Thermal Emittance

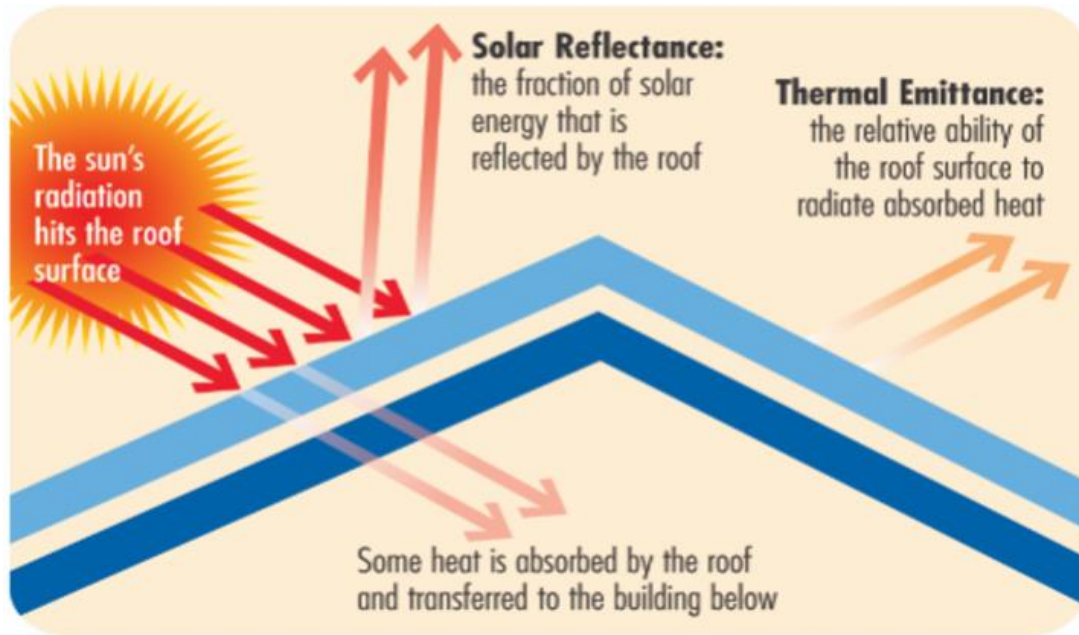


Figure with permission of Arkema.

Reduced Dirt Pick-up

An FBC topcoat's low surface energy promotes dirt shedding. The surface of a formulated FBC reduces dirt pick-up, keeping the building and other structural projects brighter and fresher looking. The pictures below show the results when a 1" square area of carbon black is applied to the paint surface and then is washed off. One can clearly see in **Figure 4** that the surface of the FBC is much easier to clean than the surface of the acrylic based coating.

Figure 4. Dirt Pick Up Study with Acrylic-Based Resin Coating vs Kynar Aquatec® Based System

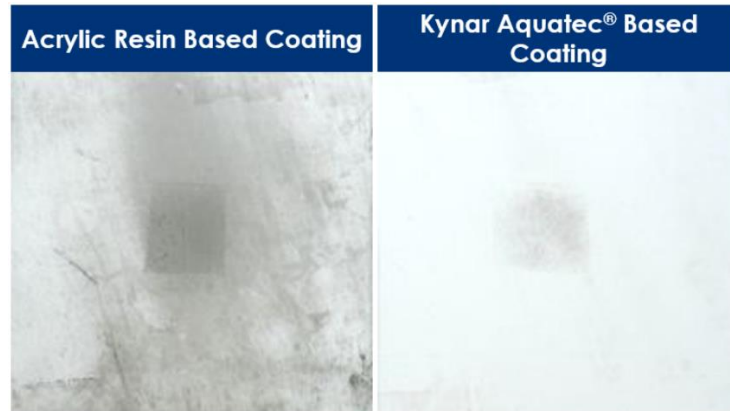


Figure with permission of Arkema

Mold and Mildew Resistance

An FBC topcoat has increased mold and mildew resistance. FBCs help to prevent mold and mildew growth. In the example below in **Figure 5**, the FBC stayed clean vs. the acrylic based coating after 19 months weathering in South Florida. No biocide was added to either coating.

Figure 5. Mold-resistance Study of Acrylic-based coating vs Kynar Aquatec® based coating

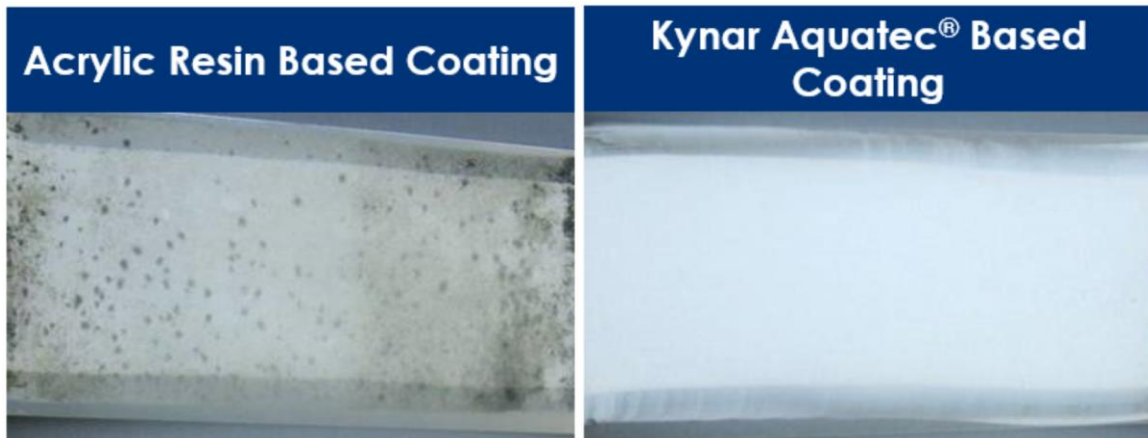


Figure With permission of Arkema.

World-class UV Resistance and Long-Life Color Retention

The FBC provides for long-lasting color retention. FBCs have been used on notable buildings since 1965. Using the same PVDF FBC technology, the FBCs have exhibited the same color fast performance. This picture (**Figure 6**) shows the color fastness after over 20 years of weathering in South Florida.

Figure 6. Twenty years of South Florida Exposure for Various Kynar Color Panels

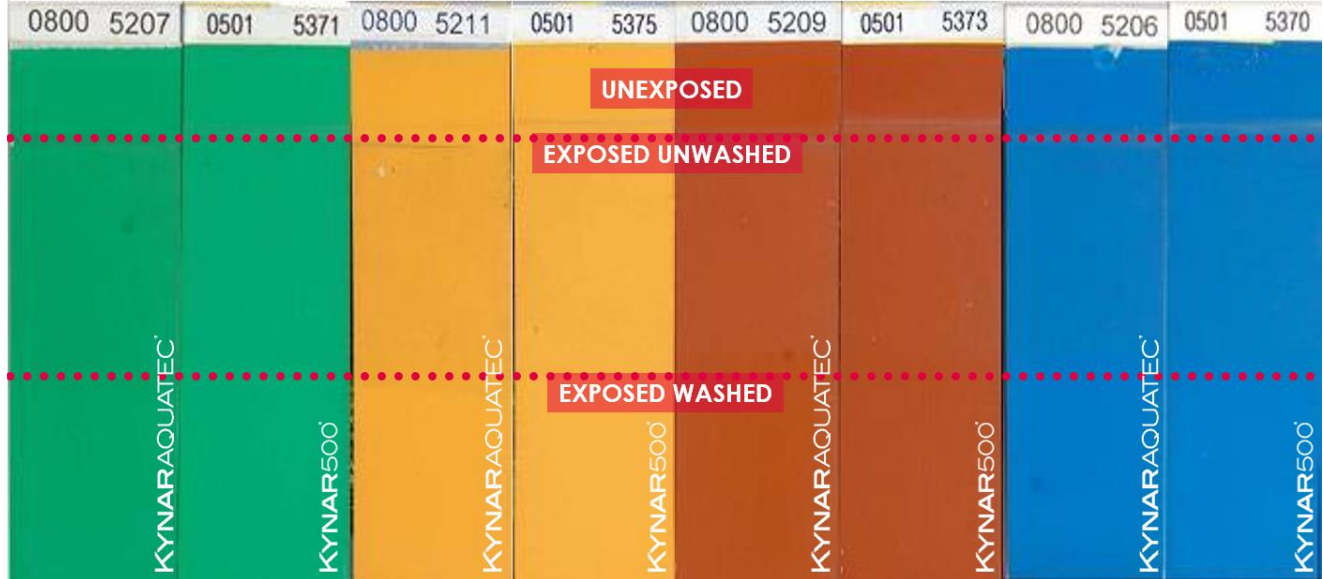


Figure with permission of Arkema.

Lower Peak Energy Demand Charges

Commercial Buildings are often charged peak demand fees by local utilities. Peak demand fees are a significant cost for commercial buildings, often greater than the electricity usage fees themselves (**Figure 7**). A 20-30% reduction in peak demand fees is common for Cool White Roofs (IRRC, 2016).

Figure 7. Kynar Aquatec® Cool Roof Energy Savings Calculator



Figure with permission of Arkema.

Longer Lifespan of Roof Coating and Longer Lifespan of Roof Substrate

Kynar Aquatec® resin-based roof coatings commonly last at least 20 years, much longer than the typical lifespan of an acrylic coating. The ability for the FBCs PVDF-based backbone to withstand the sun's UV ray is well demonstrated. This results in a longer-lasting roof coating. A lifespan of at least 20 years is expected for Kynar Aquatec®-based roof and façade coatings are quite common, well outpacing the lifespan of acrylic coatings which is low as 7 years. Additionally, the cooler surface temperature (by as much as 50°F/28°C) results in less degradation of the roofing substrate, extending the lifespan of the substrate.

Increased Efficiency and Longer Lifespan of HVAC Equipment

A cooler roof means less air conditioning (A/C) use and also means your existing equipment is more effective, extending the lifespan of your A/C unit. Alternatively, a smaller, less-expensive A/C unit could be adequate.

The cooler surface temperature (by as much as 50°F/28°C) of a Kynar Aquatec® resin-based roof coating results in several benefits: (1) less use and less wear and tear on the HVAC equipment, translating into longer service life for the equipment; (2) higher efficiency of rooftop units (due to lower inlet temperatures to rooftop air units) (Haverstic, 2016); and (3) for new construction, a small HVAC unit could be specified reducing the upfront HVAC investment.

Lower VOC Emissions

Kynar Aquatec® coatings are formulated to be low VOC. In addition, the FBCs long lifespan means less recoating (and less VOC's emitted during the recoating process) versus the other alternatives. Each time there is a recoating, volatile organic compounds (VOCs) are emitted into the atmosphere. Therefore, the less frequent coatings mean less VOCs over a defined period of time, or the lifetime of the structure. In fact, a study by Lawrence Berkeley National Laboratory showed a 30-40% reduction in VOC emissions. (CMR 2015)

No other coating technology enables the performance parameters of durability and product longevity that are the defining characteristic of FBC. Outdoor exposure testing provides data showing FBCs have an erosion rate nearly 50 percent lower than other coating technology options used in construction. This difference explains why FBCs can have a life expectancy of up to 50 years in many settings compared to less than 20 years for some alternate technologies in the same end uses. This also reinforces why FBC are critical in the development of durable and essential building products.

Failure of the coating system will likely lead to the need to repaint a metal roof or degradation of the metal substrate, which may require eventual replacement of the metal roof. The difference in coating performance is profound as FBC can last more than 50 years. Given the fact that exterior surfaces on metal roofing cannot be easily repainted or

replaced, coating performance and its subsequent substrate protection is key to meeting important sustainability objectives. Driving towards less durable technologies would result in regrettable substitutions requiring field-refinishing and building component repair and replacement, which in turn will lead to increased waste and a larger carbon footprint.

Reduced service life of metal roofing can present disruptions in the use of buildings housing areas such as education, medical, government and communication. In addition, field-refinishing brings with it potential release of VOCs to the atmosphere and exposure risks to people, animal life and the environment.

Case Studies (i.e., heat reflecting and temperature reductions).

FBCs PVDF Building Case Studies: <https://kynar500.arkema.com/en/media/case-studies/>

Florida Roofing and Sheet Metal Contractors Association (FRSA; Orlando, FL): Roof and Gutters: <https://kynar500.arkema.com/en/media/case-studies/frsa-case-study/>

This case study employed a water-based FBC PVDF resin that does not need to be baked at temperatures over 375°F, making it ideal for air-dry, field-applied coatings. The premium, weather-resistant coating can be easily applied to a variety of substrates, including metals, plastics, concrete, fiber cement, stucco, Exterior Insulation Finishing System (EIFS) and previously painted surfaces.

The use of this PVDF FBC resin and complex inorganic pigments gives the final coating system the ability to resist film erosion, chalking and fading caused by harsh UV exposure. For more information see the case study details:

https://kynar500.arkema.com/files/live/sites/hpp_kynaraquatec/files/downloads/literature-case-studies/Case-Study-FRSA-Durable-Exterior-Coating-Gets-New-HQ-Building-Ready-for-the-Long-Haul.pdf

Vinita Health Center (Tribal health center in Oklahoma): Metal Roofing. LEED Silver certified. FBC PVDF resin: <https://kynar500.arkema.com/en/media/case-studies/vinita-health-center/>

Cherokee Nation Health System, the largest tribally owned health care system in the United States, made plans to expand the 4,000 square-foot Vinita Health Center into a 92,000 square-foot building, making it 23 times larger than the original and the second largest center in the health system. With the overall inspiration taken from the community's past, historic materials like wood and stone were used as the primary construction materials. To help increase the durability and expand the lifespan of the center, a metal roof was installed on the structure. Furthermore, the use of a metal roof was selected to match surrounding community buildings, as standing seam roofs are commonly used on many other Cherokee Nation buildings. A standing seam roof, which required 43,500 square feet of Snap Clad panels finished in an FBC coating was installed.

Brandon Dunes Golf Resort (Brandon, Oregon): Metal Roof. Kynar 500®FSF® PVDF resin-based system: <https://kynar500.arkema.com/en/media/case-studies/bandon-dunes-golf-resort/>

FBCs based on PVDF resin were chosen to protect roofs of the clubhouse, snack bar and lodge against the rigors of the coastal weather.

Charles de Gaulle Airport (Paris, France). Cool Flat Roof:
<https://kynaraquatec.arkema.com/en/media/case-studies/charles-de-gaulle-airport/>
(Figure 8)

The airport has taken a step forward and chose to test the concept of saving energy linked to air conditioning thanks to passive cooling via cool roofing. A white paint that reflects the sun light waves during sunny periods was applied on the West Pier of Terminal 2G. Over 1,160 square meters were covered with the Cool Roof paint from the Cool Roof France Company. The application required 10 days and two people for the preparation of the roof/ coating application. The coating system included two layers of base coat formulated with an acrylic based paint and a topcoat based on an FBC latex.

The West (with cool roof) and East Pier (without cool roof) of Roissy airport were monitored by a consultant to estimate the efficiency of the cool roof paint system in lowering the temperature at the surface of the roof. The temperature at the surface of the roof, the temperature of the ceiling above and the ambient temperature were monitored from June 1 to September 30. A weather station also measured outside temperature (°C) and solar radiation (W/m²). During this period, the two Piers were air-conditioned and used in similar conditions with regard to passengers, traffic, etc.

Figure 8. Comparison of Cool Roof Surface Treatments at CDG Airport

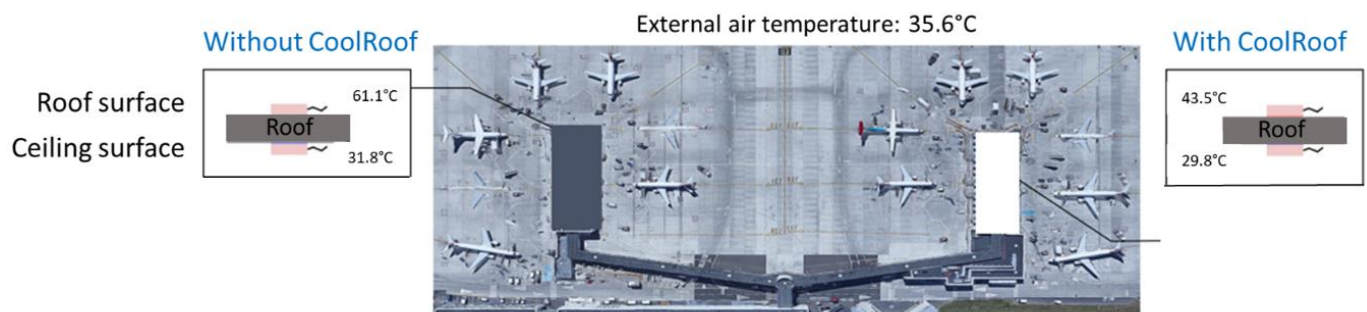


Figure with permission of Arkema.

The recorded data clearly displays the facts: the temperature of the passive cooled roof sharply lowered by 24.2°C and the energy consumption linked to air conditioning to reach desired settings inside building has seen a drop of 21% (6374 kWh, 5.5 kWh/m²). In addition, employees working all day long inside the Pier have reported a great improvement in thermal comfort during this period (as well as following years). A dark roof

absorbs most of the energy received by the sun, heating the roof structure and transferring most of heat flow to the underlying building or to the surrounding air: air conditioners that suck hot air and dump it outside can further exacerbate the cooling requirement of a building. The cool roof technology not only reflects as much of the sun's energy as possible, but also affects surrounding temperatures and offset carbon emissions.

Changwon Tunnel (S. Korea). Ceiling Coating:

https://kynaraquatec.arkema.com/files/live/sites/hpp_kynaraquatec/files/downloads/literature-case-studies/changwon-tunnel-case-study-2020.pdf See **Figure 9**

The light-reflecting characteristics of a ceiling finish enhance the overall efficiency and effectiveness of tunnel interior lighting systems. The presence of moisture and engine exhaust products in the tunnel - especially emissions from diesel power trucks - creates an atmosphere that can darken unfinished surfaces, detracting from their light-reflecting qualities and the aesthetic impression it leaves upon users. The evaluation and selection process for tunnel finish materials must therefore consider reflectivity, adaptability, cleanability, durability and public safety considerations. To improve illumination, visibility, cleanliness and safety within the Changwon Tunnel, the team responsible for maintaining the structure decided to paint the unfinished ceiling, which was dulling as a result of dirt and other airborne pollutants. Because the coating was to be applied inside the tunnel, the use of a low-VOC water-based coating was a key requirement. Other important coating performance characteristics desired were long-term durability; ability to resist dirt pick-up, biological growth accumulation and other weathering factors; and retention of reflective value and color.

Figure 9. Four-lane Changwon Tunnel in South Korea

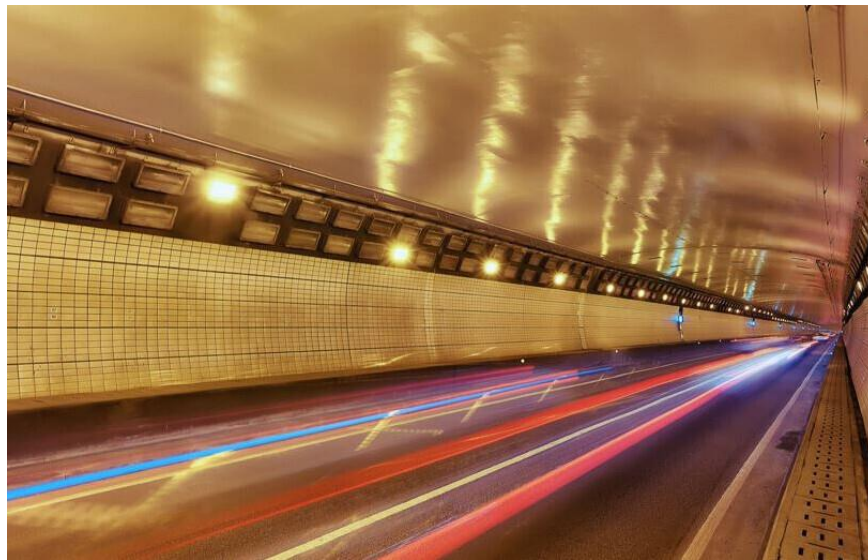


Figure with permission from Arkema.

3. Bridge Structures

Typical Products Used: FEVE

While the information in this section largely focuses on bridges, the general properties descriptions also apply to building facades and, in some cases, roofing.

Bridge structures clearly need durable coating performance to protect the painted metal substrate below and maintain the bridge's structural integrity. Any coating system must last a long time given how difficult, disruptive and expensive the recoat process is. Bridges are subject to highly adverse environmental conditions including high intensity sunlight, fog, rain, saltwater (coastal areas) spray and constant automobile exhaust among other stressor factors. The high weathering performance of FEVE allows the paint system to prolong the bridge's service life and protecting the substrate (or coated material), which subsequently decrease the number of re-painting cycles of the bridge infrastructure or building. This eventually contributes to a better (lower) Life Cycle Cost.

With its noted performance of water resistance and low oxygen permeability, a fluoropolymer-based coating systems that typically uses an FBC utilizing FEVE as a topcoat could protect the substrate (or coated material) by increasing the anti-corrosion ability of the substrate and coated material. This has the impact of prolonging the service of the paint system. Furthermore, it contributes to the reduction of CO₂ generation by extending the life of the protected material and delaying or postponing the time between re-coating the bridge structure. Less recoating is equivalent to lowering the CO₂ generated in paint system product manufacture and installation.

Oxygen Permeability Coefficient after accelerated weathering with a Sunshine Weather Meter (or weatherometer). See **Table 4**.

Oxygen contributes significantly to the ability of a substance to corrode. FEVE has demonstrated significant shielding effect under 5000 hours accelerated weathering test. Its permeability coefficient is unchanged after the 5000 hours test while the comparative alternative polyurethane film structure was deteriorated and broken after 2000 test hours.

Table 4. Permeability Coefficient for O₂ in FEVE and Polyurethane Coatings

Gas	SWM Exposure time (hrs)	Permeability Coefficient (cc • cm/cm • cm sec cm Hg)	
		FEVE	Polyurethane
O ₂	0	4.2×10^{-11}	2.6×10^{-10}
	5000	4.5×10^{-11}	Broken at 2000hrs

Data with permission of AGC.

Mechanical Properties

The FEVE coating film has almost the same mechanical modulus (E), complex modulus and attenuation rate even for 3,000 hours after sunshine weatherometer (SWM) irradiation. **Figure 10** shows retention of the ability to protect the underlying coating film and substrate over a long period of time. This means that the FEVE coating protects the base coating function as well as the substrate itself (i.e., bridge metal structure).

Figure 10. Mechanical Properties Graphs of FEVE Coating Film. In the legend, “SMW” stands for “sunshine weather meter.”

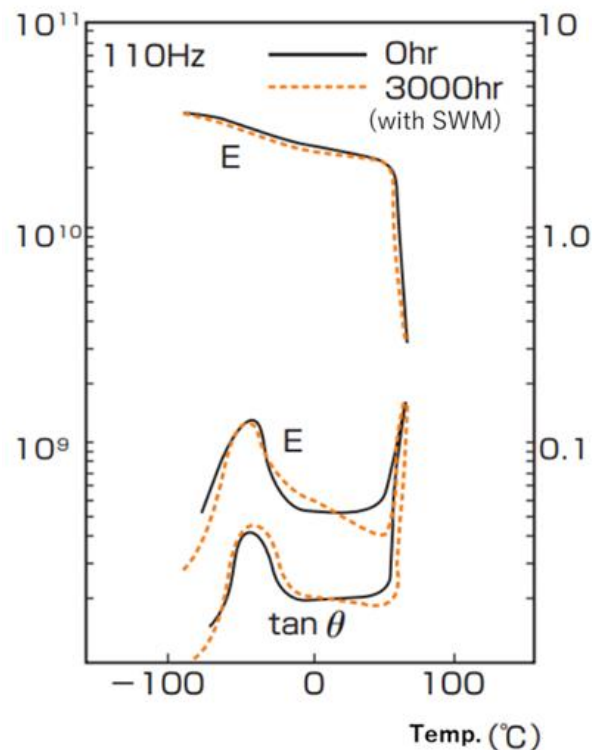


Figure with permission of AGC.

Comparison of weatherability and corrosion protection effects for four topcoat systems. FEVE was evaluated versus topcoats of polyurethane, chlorinated rubber and an alkyd system with a steel panel as the primary substrate. Each system also had a primer coating, an undercoat and an intermediate coat below the subject topcoats. These steel panels were evaluated initially by SEM (a scanning electron microscope) and then again after 2000 hours of accelerated exposure. While the alkyd surface structure was completely destroyed after the 2000 hours exposure and the polyurethane and chlorinated rubber systems also exhibited visible surface damage, the FEVE system was largely unchanged (**Figure 11**).

Figure 11. Comparison of weatherability and corrosion protection effects for topcoat systems. Picture of scanning electron micrograph for each of 4 systems along with data table for before and after exposure.

System	Topcoat	Fluoro-polymer	Polyurethane	Chlorinated Rubber	Alkyd
Substrate	steel panel				
Primer	zinc-rich primer				Wash primer
Undercoat	Epoxy resin	Epoxy resin	Epoxy resin	Chlorinated rubber	Anti corrosive Undercoating
Intermediate Coat	Epoxy resin	Epoxy resin	Epoxy resin	Chlorinated rubber	Alkyd
Top coat	Fluoro-polymer	Polyurethane	Chlorinated rubber	Alkyd	
Total Film thickness(μm)		255	255	245	170

Observation with SEM
(Scanning Electron Microscopes)

Initial surface

After Exposure surface
with SWM after 2000hrs

Results:

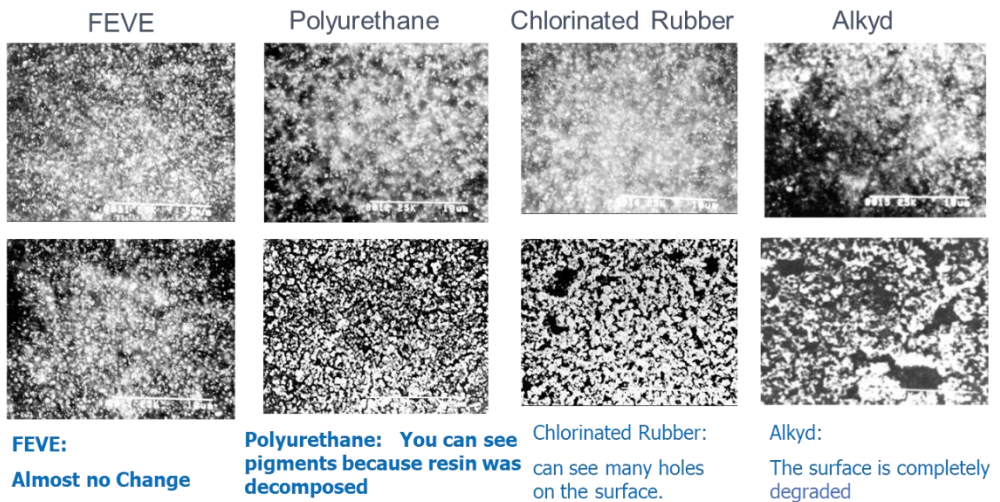


Figure with permission of AGC.

Molecular Weight Change for FEVE – Lumiflon® System vs Polyurethane. A study was conducted by the Honshu-Shikoku Bridge Authority (**Figure 12**) of the actual bridge and the test sample panel samples. **Figure 13** shows a Gel Permeation Chromatography (GPC) chart that can measure molecular weight. Molecular weight had been changed to about 1/6 for polyurethane within 3 years of offshore bridge exposure. On the other hand, FEVE has no change in the charts and little change in molecular weight. The polyurethane coating system has a broken polymer backbone. The FEVE system is intact.

Figure 12. Honshu-Shikoku Bridge Authority Coatings Study

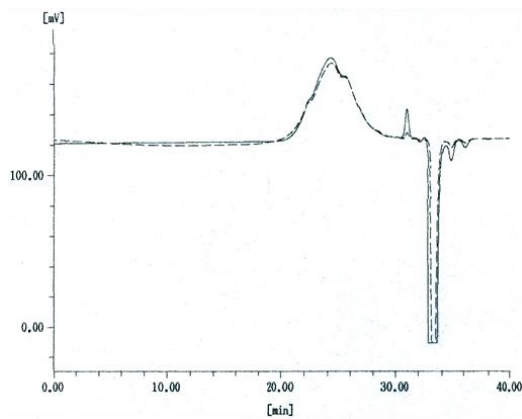


Figure with permission of AGC.

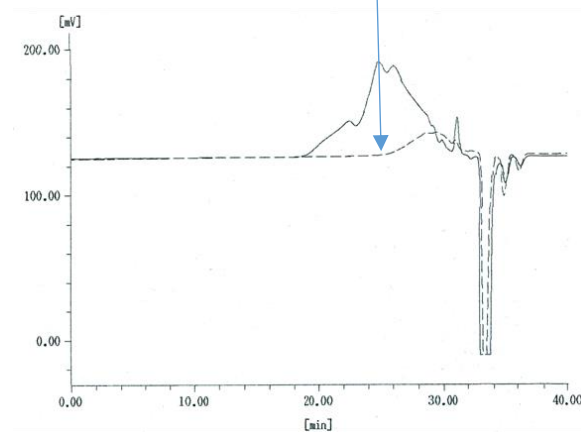
Figure 13. Molecular Weight Change Upon 3 Years Exposure in Two Bridge Coating Systems

solid line - initial coated year
dotted line - 3 years after exposure

FEVE Lumiflon ® System



PU System



Resin	LUMIFLON		Polyurethane	
Period	initial	3 years	initial	3 years
Molecular Weight	9,000	8,400	3,600	600

Data and graphs with permission of AGC

Film consumptions of FEVE vs Polyurethane including 20 years of data for 4 topcoat systems: Alkyd; Chlorinated Rubber; Polyurethane; FEVE.

This test was done as a Hiroshima rooftop exposure about 1 km (0.6 miles) from the Japanese coast. All the systems except the FEVE system exhibited chalking. It was noted that the film coating for both the polyurethane and chlorinated rubber were severely eroded. The coating thickness of the FEVE and polyurethane systems were then measured to determine yearly film exposure loss after a 15-year exposure period. The evaluation showed a 2 μm loss/year for the polyurethane and a 0 – 0.1 μm loss/year for the FEVE system (**Figures 14 and 15**).

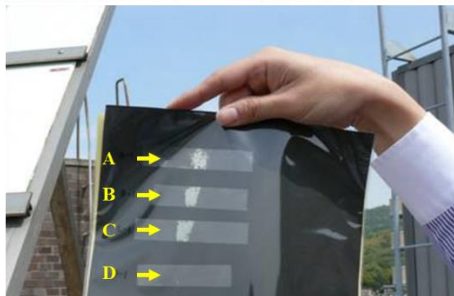
Figure 14. Film Erosion Study: 20-Year Rooftop Exposure of 4 Coating Systems.

When looking at the reflection of sunlight, everything except FEVE was chalking, and the coating film of polyurethane and chlorinated rubber was severely eroded.



20 Years Exposure

- A: Alkyd system
- B: Chlorinated Rubber system
- C: Polyurethane system
- D: FEVE system



Film Consumptions by Year
Polyurethane: 2 μm /year
FEVE: 0-0.1 μm /year

Figure and data with permission of AGC.

The ability of the anticorrosion effects depends on the coating's ability to prevent the diffusion of water and oxygen moving through the coating. Maintaining film thickness is fundamental to controlling the diffusion of corrosion substances. The fact that the topcoat of FEVE maintains its thickness for a long period of time is linked to the fact that the thickness of the middle and bottom coats is maintained, and the anti-corrosion function is maintained. On the other hand, epoxy resin, which is the under layer of polyurethane resin, loses film thickness each year due to sunlight. After the topcoat of polyurethane resin wears off, the overall coating film thickness decreases rapidly, resulting in a rapid loss of anticorrosion effects.

Figure 15. Film Erosion Study FEVE vs Polyurethane: 15-Years Rooftop Exposure

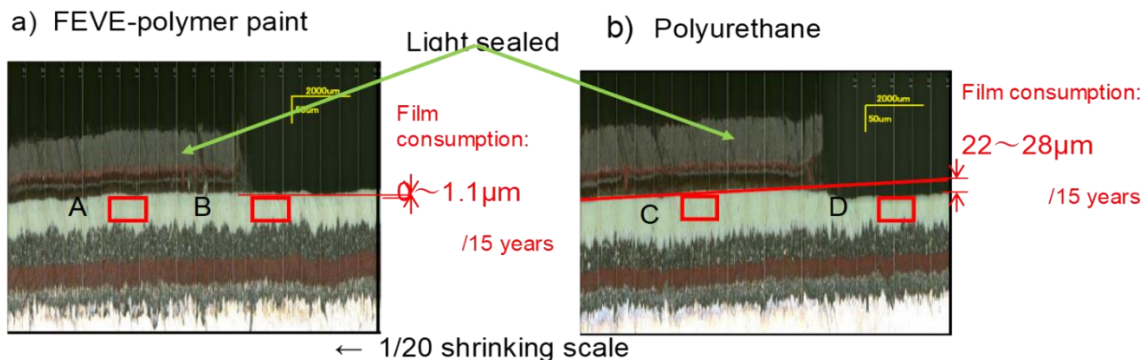


Figure and data with permission of AGC.

Polyurethane decreases by 22-28 μm in 15 years and about 1.5-1.9 μm per year. FEVE had a depletion rate of 0-1.1 μm at 15 years and less than 0.1 μm at 1 year. It can be seen that FEVE has much better weather resistance than polyurethane.

Isocyanate crosslinking retention of FEVE vs Polyurethane over a 15-year sunlight test exposure

Crosslinking in a film coating is often critical to the longevity and integrity of the film. The residual level of isocyanate cross-linking can be measured by Infrared (IR) spectroscopy. **Figure 16** shows the FEVE and polyurethane coatings in contrasting pictures, one of a light-sealed area and one in a light-irradiated area. It is quite clear that the isocyanate cross-linking in the polyurethane system was retained poorly, while the FEVE system provided good retention and will likely protect the substrate for several decades.

Figure 16. 15-Year Sunlight Exposure of FEVE polymer and polyurethane systems

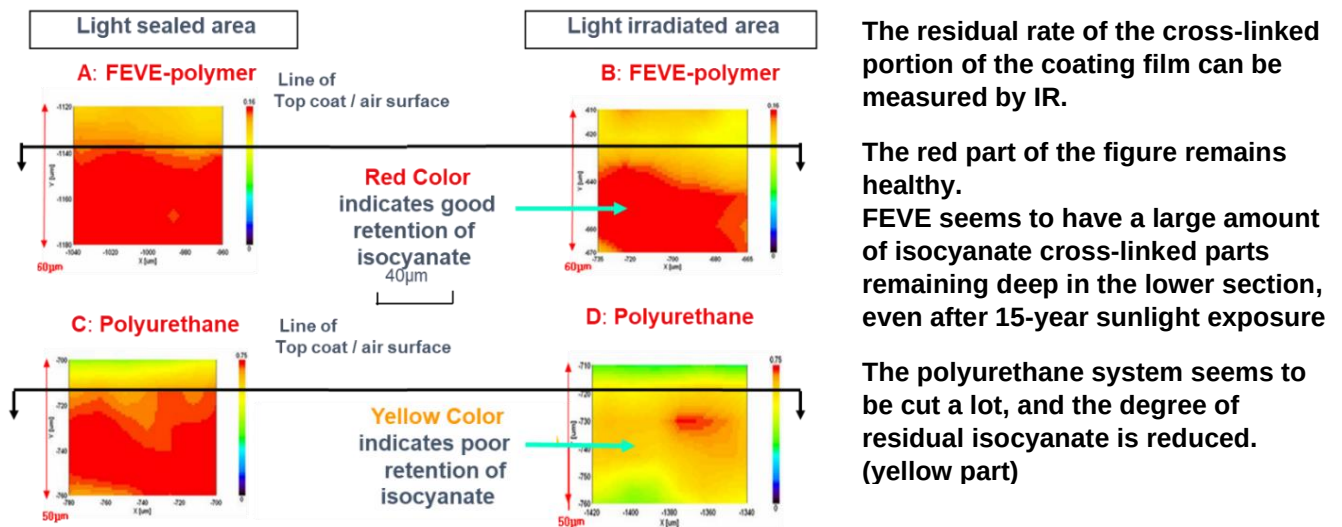


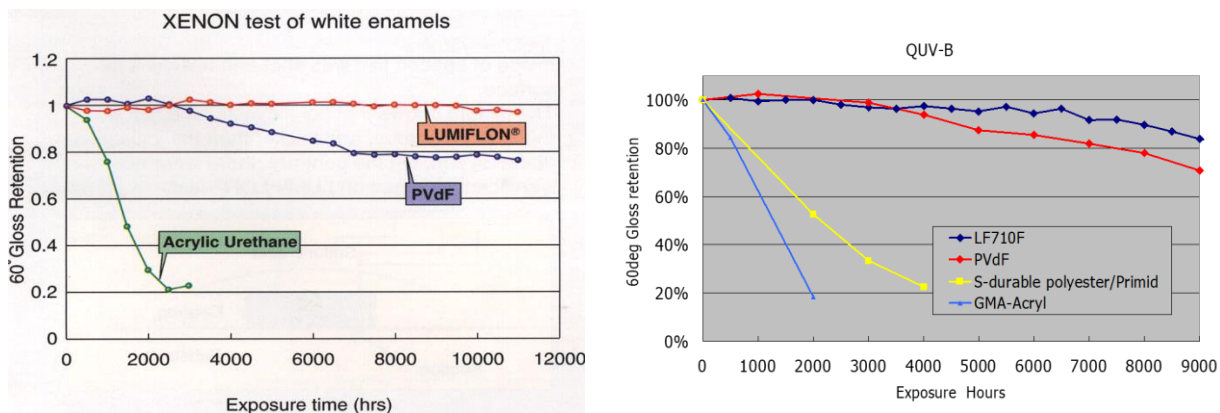
Figure with permission of AGC.

FEVE High Durability with Accelerated Weathering Tests – Gloss Retention

A standard method for evaluating exterior durability to sunlight exposure is by accelerated weathering tests. Two test types are via Xenon ARC and QUV-B. As shown in **Figure 17**, both the Lumiflon® FEVE and PVDF coatings on white enamel retained their gloss at >10,000 hours while the acrylic urethane lost about 80% of its gloss at 2,000 hours of exposure.

Similarly, both the Lumiflon® system and the PVDF coating retained their gloss even after 8,000 exposure hours in the QUV-B test. Both the Polyester and Acrylic systems suffered severe gloss retention loss at 2,000 exposure hours.

Figure 17. Fluoropolymer High Durability with Accelerated Weathering Tests



Figures with test data with permission of AGC.

FEVE low-dirt pick up systems (applicable to facades and bridges and other similar end-uses)

FEVE is compatible with many types of additives. In combination with inorganic low dirt-pick up agent such as silicate, it is possible to create hydrophilic low-staining surfaces. Façade stains are caused by dust deposited on the top, which is carried down the wall by rain and adheres to the wall. If the dirt is organic, such as black carbon, it is adsorbed by the paint film on its way down because it has a higher affinity for the same organic material than for water. Dust deposited at an angle at the top forms a strong stain on the wall with each rainfall. On the other hand, the silicate that bleeds from the silicate-added paint film onto the surface is hydrolyzed on the surface, and the silanol groups formed by hydrolysis are hydrophilic enough to adsorb water, so the surface is hydrophilic. Therefore, water forms a thin film between the paint films and dirt, and the dirt is washed away, preventing it from adhering to the paint film. Dust on the wall is washed away as water gets between the paint film. This means rain helps clean the coating system. Resin manufacturers have developed this system and shared it with paint manufacturers, making it possible to produce a much better low-dirt pick up paint film, or stain-free façade (**Figure 18**). The fact

that the surface stays cleaner may well mean improved roof aesthetics, improved solar reflectivity and heat resistance as well as less need for recoating, maintenance and cleaning.

Figure 18. Dirt Pick Up and Wash Off with Fluoropolymer-based systems

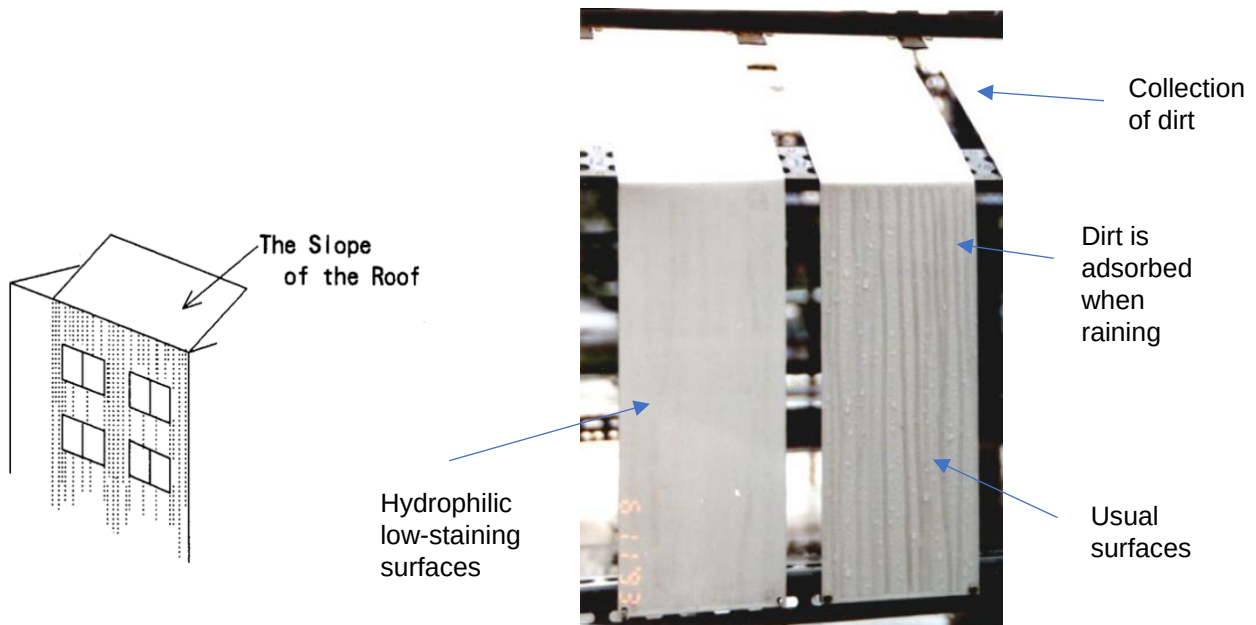


Figure with permission of AGC.

Estimation of Degradation Processes of Polyurethane System

To help visualize what occurs to a multicoat film system, a comparative FEVE versus polyurethane schematic was developed (**Figure 19**). This schematic covers a 60-year coating period for the two subject film systems. This report has provided significant information to show the longevity of the FEVE systems to indicate their useful life is in the 30–60-year range, if not longer. This schematic gives the 4-layer over substrate (steel) system – zinc rich primer, under coat, middle coat and topcoat. From the information that has been provided, it is clear that the FEVE top-coat system largely is intact throughout the study period. On the other hand, the polyurethane system exhibits marked degradation after 8-12 years and potentially catastrophic losses in the 30–60-year period of exposure.

Figure 19. Pictorial Schematic of degradation over time of FEVE vs Polyurethane

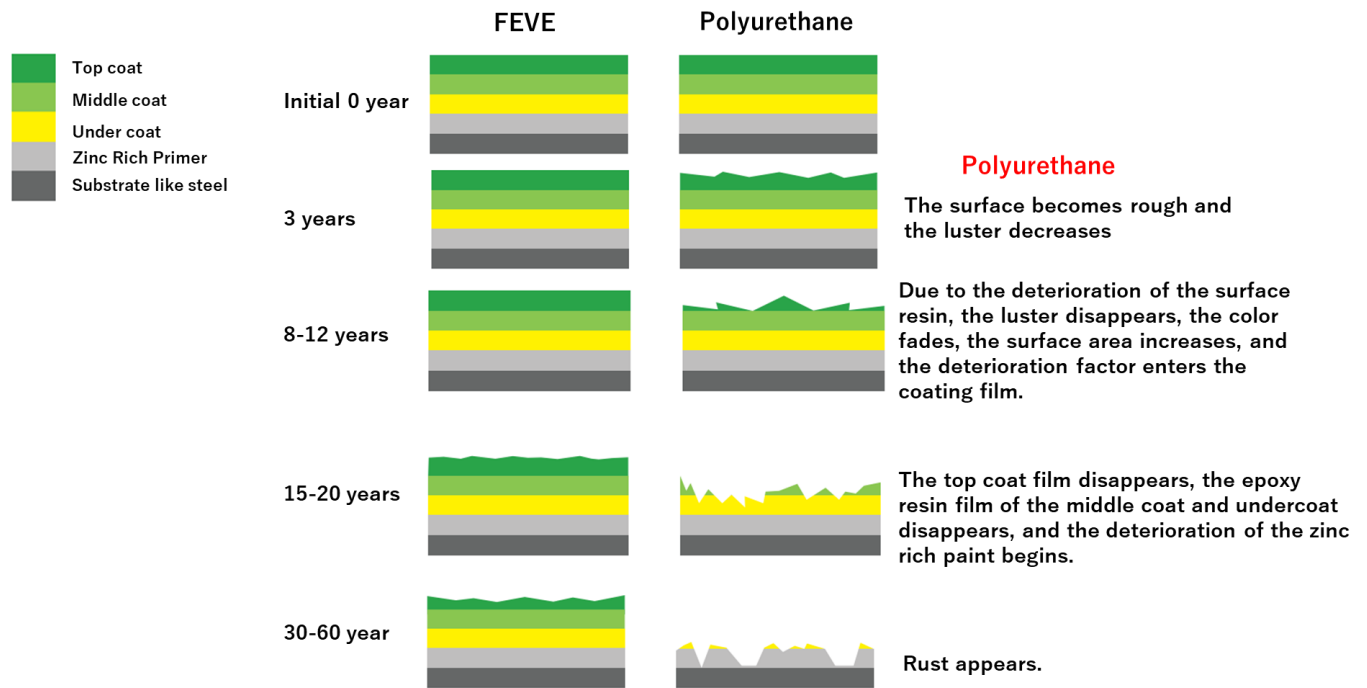


Figure with permission of AGC.

Chalking, Fading and Corrosion on Bridge Structures

Suigo Bridge Painting - 18 years of exposure for FEVE, Chlorinated Rubber and Alkyd Resin side-by-side painting comparisons.

The comparative pictures in **Figure 20** provide clear indications of the durability and long term FEVE film coating performance in terms of color fading, corrosion and chalking. A similar performance pattern can be seen when looking at the photos in **Figure 21** of the Daiichi-Mukaiyama Bridge (Mountainous area, Hiroshima). After 30 years of exposure, no chalking was evident. Gloss retention was excellent. The bolts, edges and abdominal plates were all in very good shape.

Figure 20. Suigo Bridge Paint Study



FEVE/Chlorinated Rubber rubber resin/Alkyd resin
Divided Painting

Chlorinated Rubber/FEVE



Fading

Chlorinated Rubber/FEVE



Fading



**Chlorinated
Rubber:
Chalking**

Chlorinated Rubber/Alkyd



Corrosive

Alkyd



Chalking

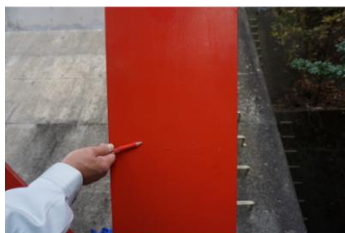
Alkyd



Corrosive

Figure with permission of AGC.

Figure 21. Daiichi-Mukaiyama Bridge (Mountainous area, Hiroshima): FEVE vs Alkyd Topcoats. FEVE topcoat after 30 years of exposure vs. alkyd topcoat after 16 years of exposure.



No chalking.
Gloss retention:
Good.
Bolts, edges,
and abdominal
plates:
Good

Alkyd section
16 years later,
peeling, rust,
With chalking

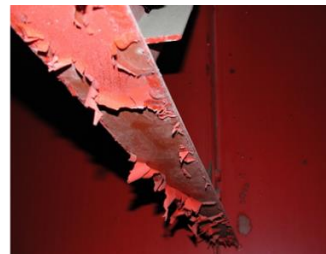
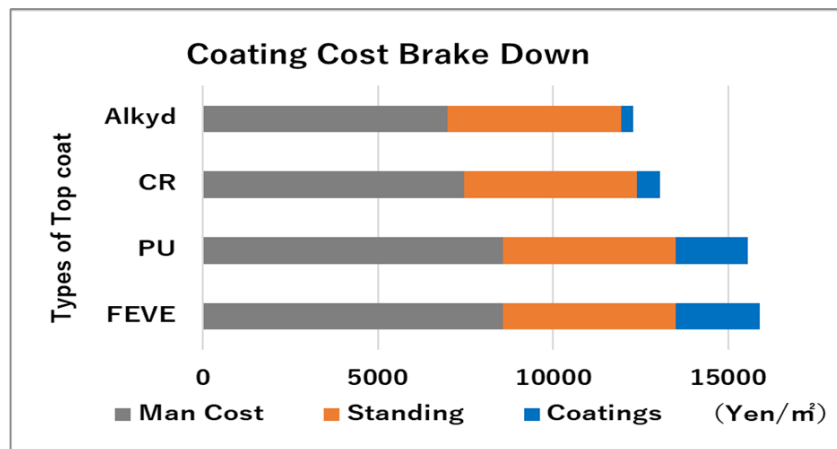


Figure with permission of AGC.

FEVE Service Life Estimated at >50 Years

Life Cycle Cost and Life Cycle Cost Reduction in Bridge Coatings using FEVE versus competitive materials such as polyurethane, chlorinated rubber and alkyd resin in **Figure 22**. It is important in creating a full picture to describe what it costs to paint a bridge structure. The estimated costs for the 4 subject topcoat systems are shown in the Cost Break Down Figure. In all 4 cases, the labor and scaffolding costs overwhelm the actual topcoat costs. The actual resin cost is only 3-15% of the total coating costs. And it is noteworthy that the FEVE system has only about a 6% price premium vs. the polyurethane system.

Figure 22. Coating Cost Breakdown for 4 Topcoat Systems. Life cycle total cost mainly consists of labor and scaffolding costs. The better the durability and the longer the repainting period interval, the lower the total cost.



Main cost (80% up) of painting cost are mainly Man - Labor and Standings (Scaffolders).
Resin cost is only 3-15% of total.
Only 6% difference between PU(Polyurethane) and FEVE system of total painting initial cost including man and scaffolder.

Figure and data with permission of AGC.

If a system is more durable and the recoat frequency is significantly lower (or extended), then the long-term ultimate maintenance costs can be significantly lower using the FBC system. Therefore, over time the costs can be lower, and the Life Cycle Costs (LCC) are greatly reduced with the FBCs.

In the Tokiwa bridge example shown in **Figure 23**, the study looked at an FBC FEVE-based coating system vs. a chlorinated rubber coating system over a > 30-year life span of the bridge coatings. The chlorinated rubber system needed repair every eight (8) years whereby the FBC FEVE-based system was intact even at >30 years. The pictures

show the visible performance of the FEVE system even after 30 years of exposure. The overall LCC savings can be significant even though the initial total coating costs were about 47% higher. Please take note that over the >30-year exposure horizon, the FBC system costs about 37% of the alternative chlorinated rubber system.

Figure 23. Tokiwa Bridge FEVE vs Chlorinated Rubber 30-Year Exposure Test

Tokiwa Bridge 30years

3y



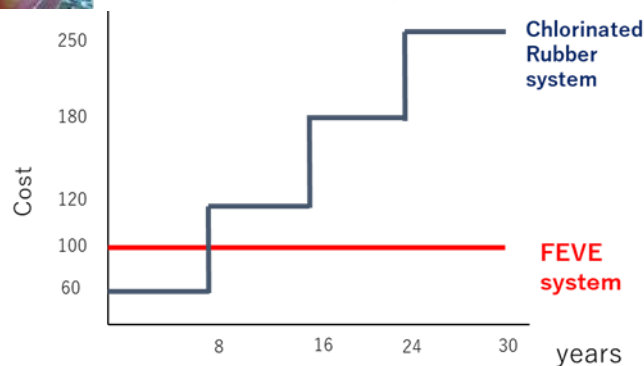
16y



30years



Item	Unit	FEVE System	Chlorinated Rubber	Ratio F/C
Top Coat	¥/m ²	502	101	500%
Pain total	¥/m ²	1,724	278	620%
Man Cost	¥/m ²	3,696	2,796	132%
Standing	¥/m ²	3,957	3,297	120%
Total	¥/m ²	9,377	6,371	147%
Durable Life	years	> 30	8	> 375%
Interval	time	Only initial	4 estimated	-
Total Cost	¥/m ²	9,377	25,484	> 37%



Actual Life Cycle Cost Reduction with FEVE

Figure with permission of AGC.

For clarity, the items in the table below include the standing cost which is the scaffolding. The Man cost is the labor. The Paint costs are the primer, under and intermediate layer costs. And the topcoat is either the FBC or the chlorinated rubber system. A relative comparison of the total cost ratio of 4 topcoat systems as well as the projected 100-year costs are shown in **Figure 24**.

Figure 24. Comparison of The Total Cost Ratio in 4 Topcoat Systems and the 100-Year Costs

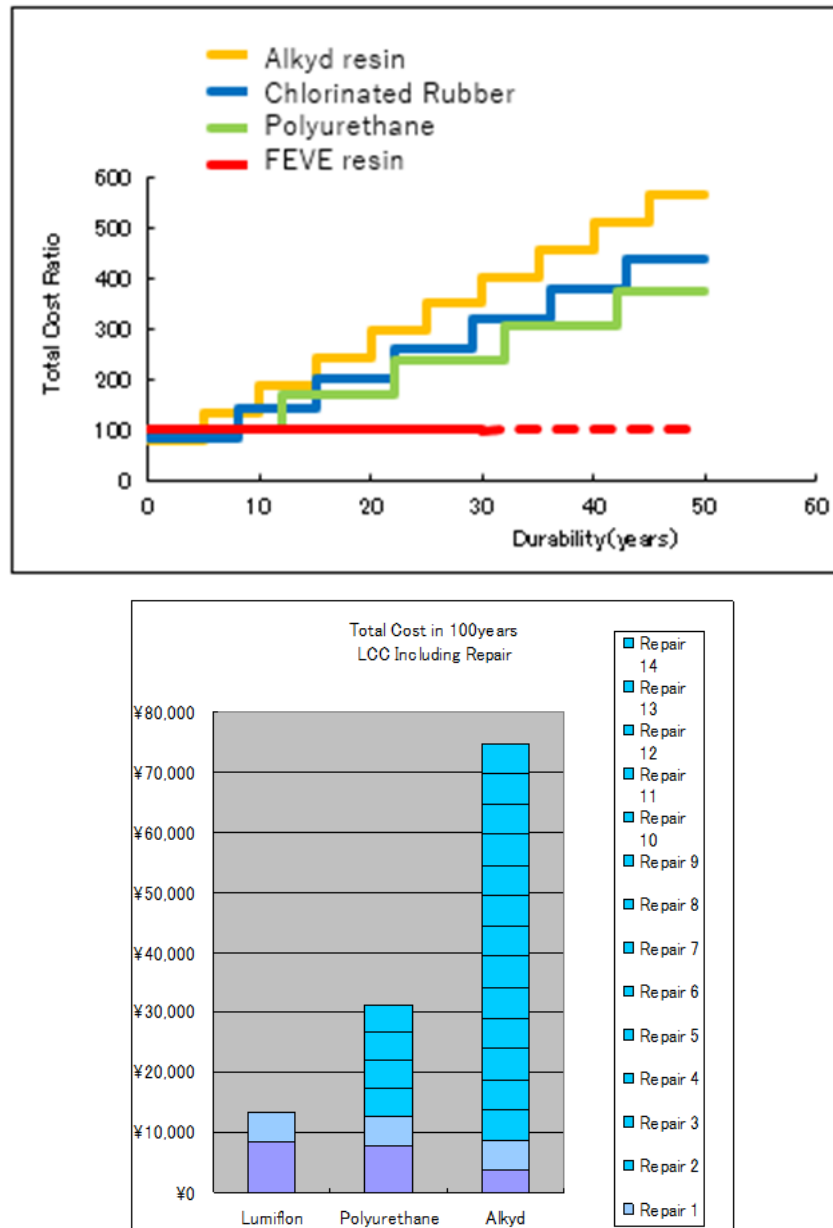


Figure with permission of AGC.

Expected Lifetime by Japan Paint Manufacturers Association (JPMA)

Table 5. Expected Topcoat Lifetime of an FEVE and a PU System

Authority	FEVE Top system	Polyurethane Top system
JPMA	60 years	18 years

Table with permission from AGC.

JPMA calculated the lifetime as the repainting time when the film thickness of the topcoat is reduced by 80% and rust has not appeared on the coating (**Table 5**; JPMA, 2002).

FBCs have a much longer durability when compared to more standards systems/chemistries, leading to a much lower impact on the environment (in kg CO₂). The extended durability and reduced need for both recoating and repairs can lead to a much lower overall LCC. By using an FBC as a topcoat, the overall cost over the lifetime of the system can be much lower, leading to more than 50% cost decrease (ECCA, 2023).

Life cycle and global impact assessment: Independent studies have been conducted by the European Council of the Paint, Printing Ink and Artist's Colours Industry (CEPE) leading to the following conclusions in building cladding panels (**Figure 25**).

Figure 25. Comparison of kg CO₂-equivalents Emissions Estimates for Various Cladding Panels

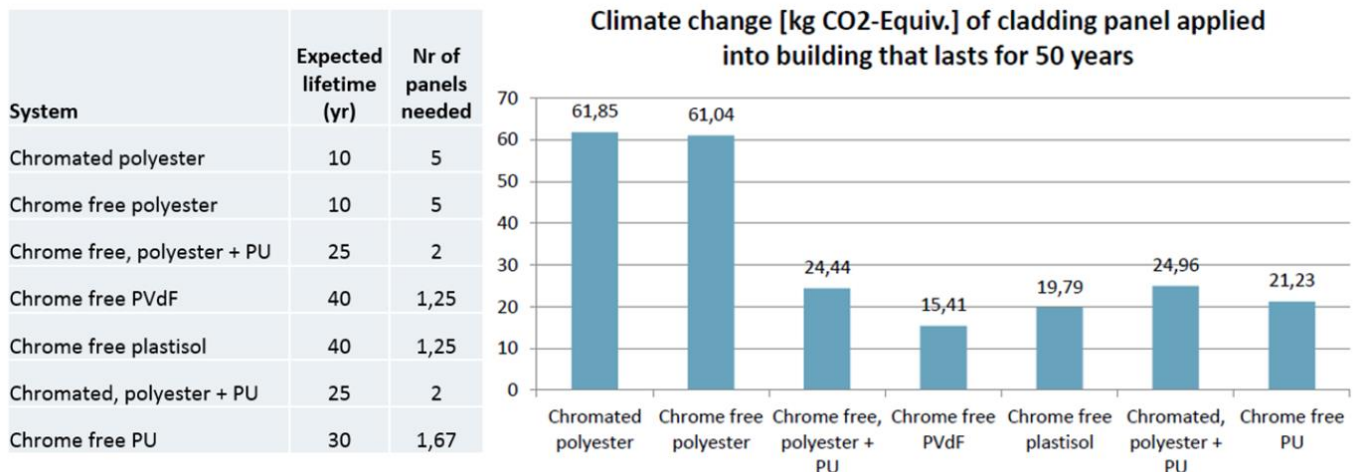
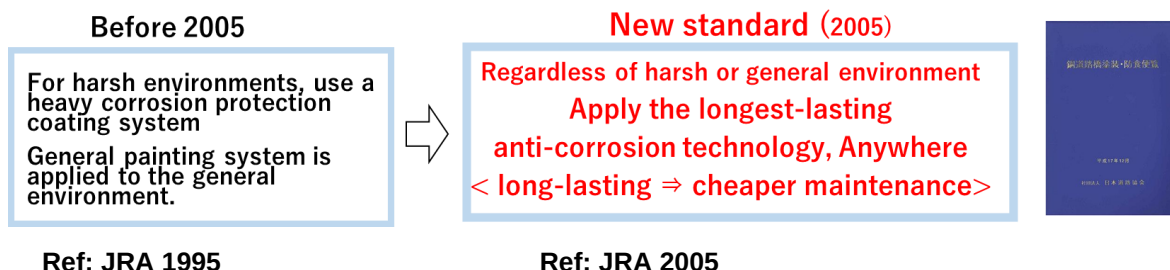


Figure with permission of CEPE.

Specification and Standards Discussions

Japan. Beginning in 2005, the only permitted topcoat system for bridges in Japan are the FBCs utilizing an FEVE-backbone. The other alternative systems, including polyurethane, chlorinated rubber and alkyd resins cannot be used as they have been withdrawn from the standards. The objective of the new regulation was life cycle cost reduction as well as sustainability. In summary:



ISO 12944-5

This ISO standard includes binders for the coating base that contain free hydroxyl groups (e.g., polyester, acrylic, epoxy, polyether, fluororesin (FBC)) which react with suitable isocyanate curing resin. In addition, there is a description of FEVE coatings noted as a special type of polyurethane based on fluoropolymers. **Table 6** lists some of the other global standards that include fluoropolymer systems like FEVE.

Table 6. Application, Specifications and Regulation in the World

No	Nation	Name (Organization /remarks)
ISO12944-5	Global	Paint and varnish – Corrosion protection of steel structures by protective paint systems
HG-T3792-2011	China	Standard for Cross-linked Fluoropolymer Coatings (Paint Industry Association)
HG-T4104-2009		Standard for Waterborne Fluoropolymer Paint (Paint Industry Association)
TBT 1527-2011		Protection Coating Standard for Railway Steel Bridges (Ministry of Railways)
TBT 3228-2010		Protective Coating Standard for Concrete on Railroads (Ministry of Railways)
JT T722-2008		Technical Standard for Steel Corrosion Protection for Public Road Bridges (Ministry of Highway)
13201-639、99-7.7	Korea	Anti-corrosion Coating Standard for Highway Bridges, Other 2 organization
TCVN11416	Vietnam	Fluoro resin paint for steel structure
	Myanmar	QUALITY CONTROL MANUAL FOR STEEL BRIDGE
Spec2911/2PU	Aus. N.Z.	Coating Organizations (including government)
D102-06	US	Water Tank (American Water Works)
BMS10-72		Boeing Standards
Mil-L5606,L7808		U.S. Air Force Standards
AAMA2605-05		AAMA (American Aluminum Manufacturers Association)
SSPC		
Qualicoat	EU	Class 3

Table with permission of AGC.

Numerous long-span bridges were built based using these standards. The following pictures provide real-world examples (pictures with permission of AGC).

- **Akashi Strait Bridge:** At the time of construction, it was the longest suspension bridge in the world. It is now the second longest bridge in the world.
- **Tokyo Gate Bridge:** This bridge was installed at the entrance and exit of Tokyo Bay.
- **Ping Tang Bridge:** After the FBC coated bridge standard was established, this bridge was built as a combined railroad and road bridge.

Akashi Strait Bridge (1998)



Tokyo Gate Bridge (2012)



Ping Tang Bridge (China)



VOC Reduction

Figure 26 shows the VOC emissions of solvent-based resin paints over time. The calculations are for the topcoat only. The calculations were made according to the JPMA (Japan Paint Manufacturers Association) service life for Alkyd, polyurethane and FBCs utilizing FEVE, which were calculated to be 7, 18 and 60 years, respectively. The longer service life of FBCs reduces the number of re-coats and significantly reduces the amount of VOC emissions. Since the middle and bottom coats are also protected by FEVE and have a long service life and do not need to be recoated, the overall coating system, including the middle and bottom coats, can achieve even greater reductions in VOC emissions than shown in the Figure.

Figure 26. VOC Emissions Over >100 Years Service Life for 3 Topcoat Systems

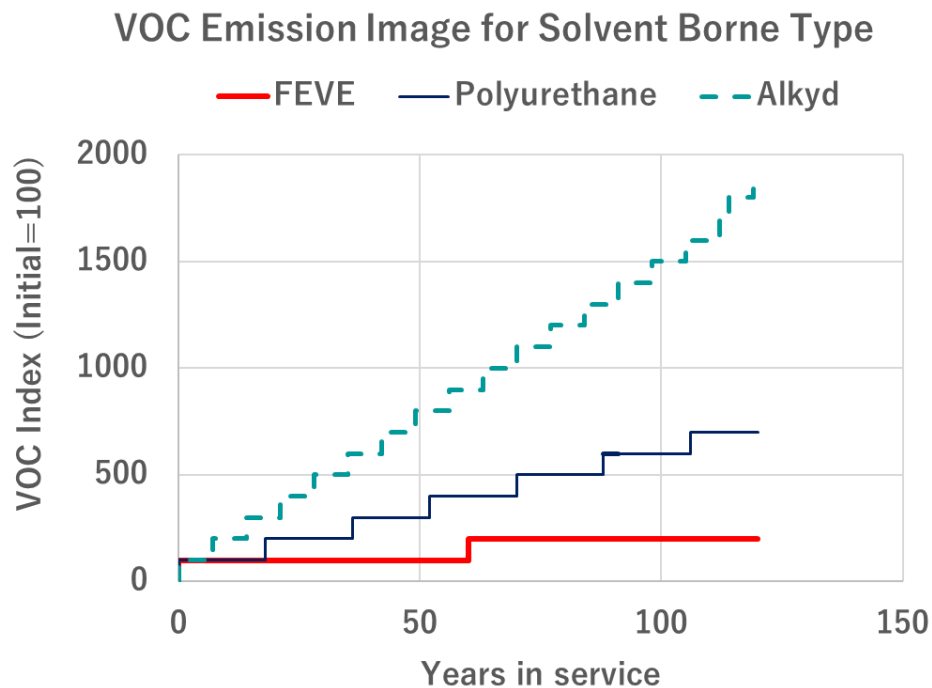


Figure with permission of AGC.

One also needs to consider the VOC reductions in powder FBCs utilizing FEVE Powder Coatings. The VOC emissions for the powder FBCs are essentially zero for the several decades of service life for the façade-wall panels or roofing panels. **Figure 27** compares the VOC index for the FEVE-Powder Coating to both a polyester-water based system and a polyester-solvent based system. The VOC reduction is significant with the powder FBCs utilizing FEVE Powder Coatings.

Figure 27. VOC Emissions Index for 3 Coating Systems over 50 Years

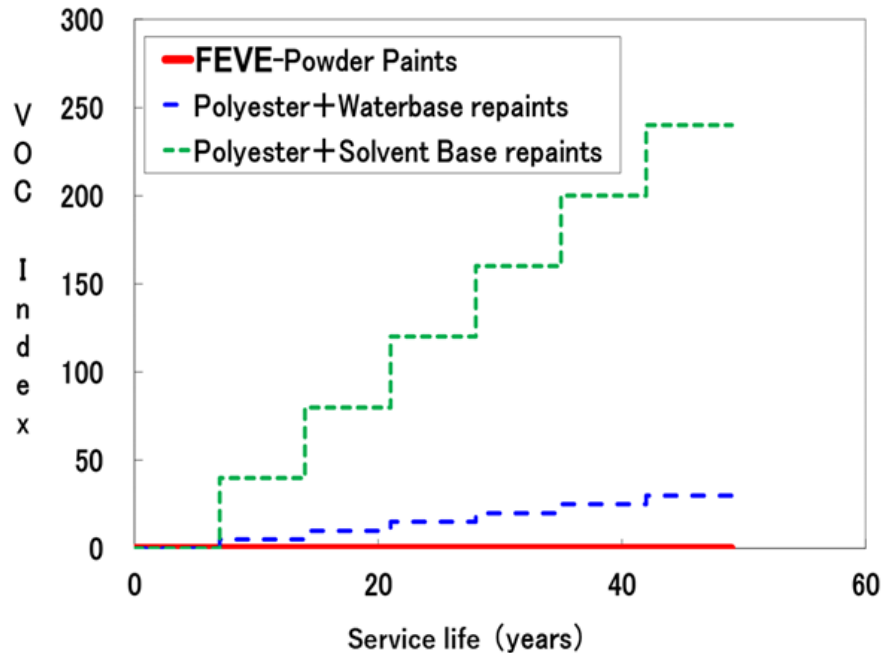


Figure with permission of AGC.

Powder FBCs utilizing FEVE ultra durability reduces VOC emissions over decades.

CO2 Reduction in the field for Façade and Building Panel Life Cycle

The CO2 emissions of paint systems using panels painted with the powder FBCs utilizing FEVE save CO2 - significantly more than polyester paint system in architectural fields over a 100-year structure evaluation.

The powder FBCs utilizing FEVE have a significantly lower life-cycle CO2 emissions than the polyester powder paint system by 47%. For emissions during the initial coating phase, the FEVE powder paint system emits more CO2 than the polyester powder paint system. However, overall emissions are lower due to its higher durability and lower number of repaints over the 100-year life of the building. Note that the repainting system is usually done twice with epoxy/polyurethane. At the time of these calculations there was no inventory of epoxy resin, so polyurethane was substituted. However, it is estimated that there is no significant difference between the two recoat systems (**Figure 28**).

Figure 28. CO₂ Reduction Over 100-Year Life of Building Façade-Panel

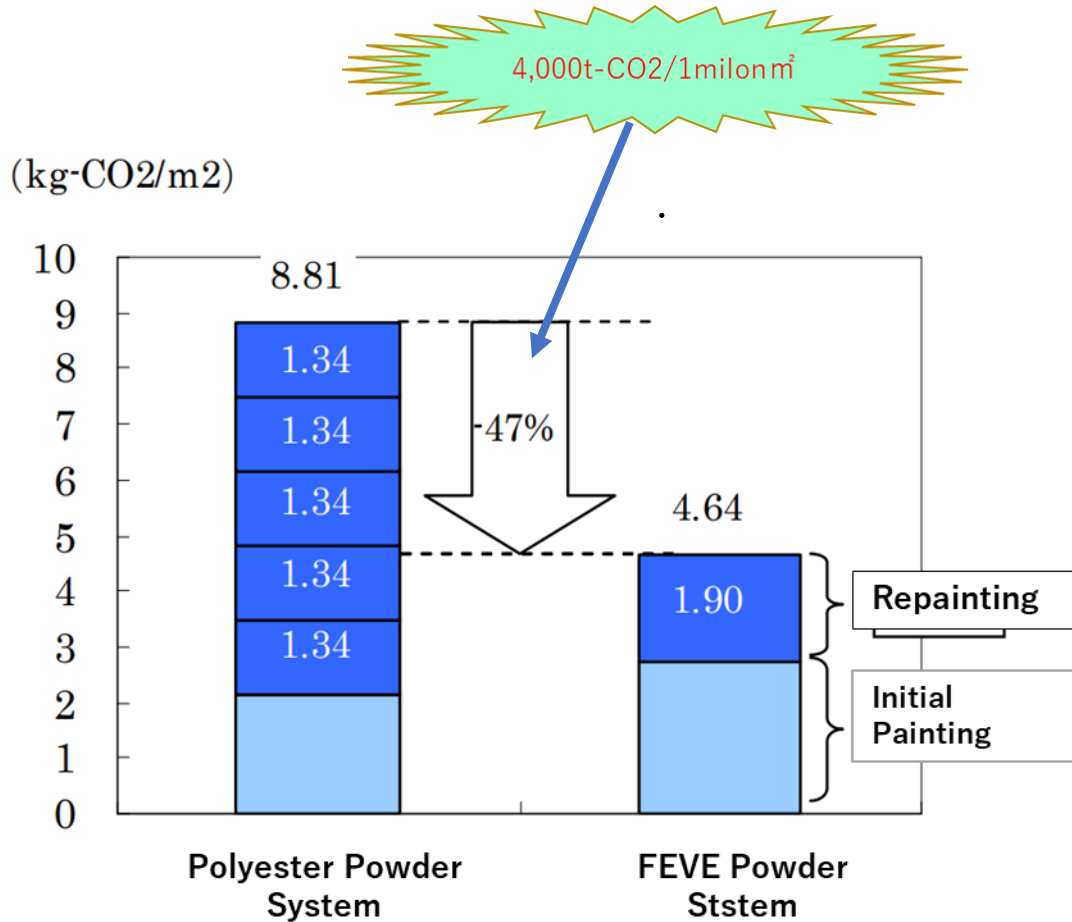


Figure with permission of AGC.

CO₂ Reduction in the field for bridges LC (Life cycle)

The FEVE protective coating system saves approximately 38% more CO₂ than a polyurethane protective system in 100-year life evaluation of bridges (**Figure 29**). As is the case above with facades and panels, the initial CO₂ emissions during the first coating were higher than the polyurethane system. Predictably, overall emissions are expected to be lower due to the FEVE system higher durability and lower number of repaints over the 100-year evaluation life of the bridge.

Figure 29. CO₂ Reduction Over 100-Year Life of a Bridge

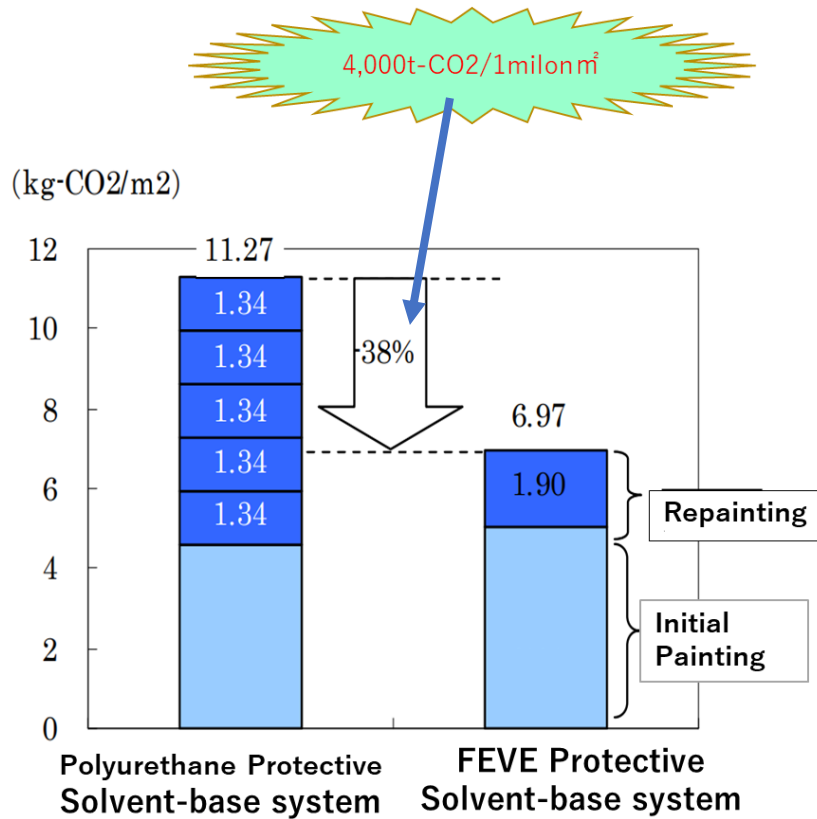


Figure with permission of AGC.

Green Building Certification

An important recent certification for CO₂ reduction and VOC reduction is green building certification. The certification is an important point of appeal for ESG (environmental, social, governance) investment. FEVE powder- and water-based grades earn green points with the paint maker's declaration. In New York City, the 10 Hudson Yards building achieved LEED Platinum, while 30 Hudson Yards achieved LEED Gold.

Photo of 10 and 30 Hudson Yards, NY, NY



Permission obtained from Carlos David/Shutterstock.com.

Examples of LEED-certified buildings:

[LEED Platinum Office Building Revitalized Downtown Pittsburgh with High Performance Energy Efficient Façade – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[Architects Design First LEED Platinum Government Building in Maryland – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[Architects Design Award Winning Multi-Family Housing Complex with Stunning Exterior Designs – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[NBBJ Designs Facebook Spring District In Washington With Sustainable Design – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[Architecture – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[Award Winning Hudson Yards Lobby Features Mixture of Tactile Materials – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

Figure 30 (photos with permission of AGC) shows three different types of low-to-no VOC concrete skyscraper coatings, including:

- a. FBC utilizing FEVE which can be applied at ambient temperature and on-site solvent coating;
- b. FBC utilizing FEVE which is water-based, where there is less concern about VOCs and solvent odors; and
- c. Concrete panels which can be coated with FBCs utilizing FEVE in the factory at temperatures below 100°C and installed on site.

Figure 30. Three Types of Concrete Building Coating Systems Illustrated by Office Buildings in Tokyo

a. Painted on site



b. Water-based repainting on site coating



c. Low temperature coating panel in factory



Water Towers

Products Used: FEVE

FBCs utilizing FEVE have become more common for water tank coatings (in the US). These FBCs utilizing FEVE do have a price premium for the initial cost of application. As discussed below, there are considerable coating and applications cost savings over the life of the FBC utilizing FEVE-coated water tank. Therefore, coating costs are lower over the lifetime of the tank. There is also a reduced environmental burden in terms of lower solvent emissions as well as surface preparation and blast media for removing the old coating and materials disposal.

One of the most important advantages of an FBCs utilizing FEVE is that it can be cured at ambient temperature. Therefore, it is possible to apply the coating outdoors and/or on site. This would include not only newly constructed water tanks, but also existing water tanks with deteriorated coatings that can be refurbished on site and given a longer service life.

This FEVE fluoropolymer-based system can be used to coat the exterior of the water tank at the same time the tank interior is repainted with an epoxy or related system, thus reducing overall down time. The interior coatings are not subject to the exterior harsh environment of the tank itself therefore an epoxy-type system is appropriate. The interior and exterior coating life can be closely matched so they are repainted at the same time and cut down time by up to 50%. For towns and water districts with limited budgets or future budget uncertainties, lowering infrastructure costs is helpful and often necessary.

Another advantage that an FBC utilizing FEVE product has is that it can produce very beautiful and vivid colors on the exterior of the water tank. Using an FBC protects this investment. See the water tank images at <https://lumiflonusa.com>

These familiar designs could be used as a community amenity or landmark. It is possible for them to become one of the region's representative infrastructures. An FBC utilizing FEVE has a longer life expectancy with the expectation of not fading for decades. This has not been shown with conventional polyurethane resins that fade in a few years.

Water tanks are high above the ground and therefore have an increased safety risk to paint and repaint, and they require scaffolds for a clean finish. Painting work other than paint is usually expensive. As was noted in the bridges section, the cost of paint is less than 20% of the total coating process costs. The major costs largely consist of scaffolding and labor costs. The long-life cycle of the fluoropolymer-based paint system (extended over several decades) has not been shown with polyurethane coatings. The several decades life cycle can be realized with FEVE fluoropolymer-based resin system. The Life-Cycle Cost is reduced due to the reduction in the number of recoatings required over the life of the water tank. With fewer repainting cycles there is less tank downtime.

FEVE thus serves as a stable technology for the long-term maintenance and management of water tanks as an important infrastructure that supplies the life-giving water that is essential to human life. The FEVE Coating system has been incorporated into the water tank painting standards (AWWA, 2007).

Solar Panels

Products Used: ETFE; PVDF; Zeffle®; FEVE; PVF

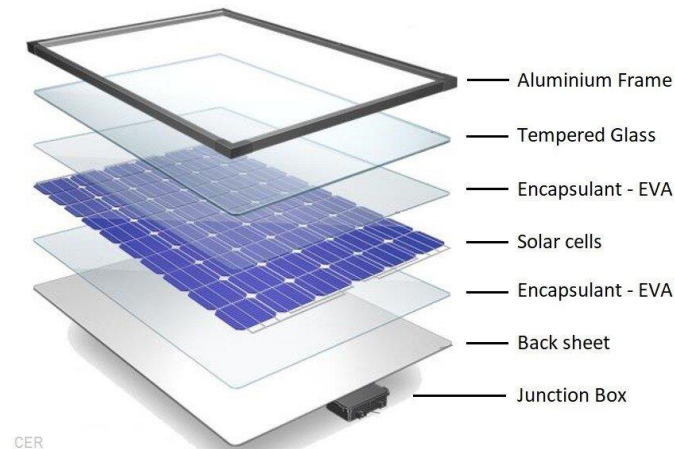
Fluoropolymers are often used as back sheets (films) in photovoltaic solar panel construction (**Figure 31**). Materials used in this end-use should have significant UV resistance and stability, corrosion resistance and flexibility. Fluoropolymers are light in weight and have extended durability in full exposure to a variety of environmental conditions, including intense sunlight and heat. Other materials used in back sheet applications are polyamides, polyethylene terephthalate (PET), glass and polyesters. A number of studies have been conducted to evaluate these materials and viable alternatives. (DuPont PV Study, 2020; OECD, 2022; GSPI, 2021)

Numerous uses of fluoropolymers are documented in solar panel manufacture and use. Fluoropolymer coatings or films may be incorporated into the glass top layer of panels, the encapsulant film that surrounds the solar cells and the back sheet. Fluoropolymers reportedly increase durability, transparency, UV-resistance, heat-resistance, mechanical strength, dirt-repellency and energy production, and they are lightweight. Halar® (ECTFE), Tefzel® (ETFE) and Lumiflon® (FEVE), as well as polyvinyl fluoride (PVF) and PVDF, are among the fluoropolymers used for solar panels. (GSPI, 2021; AGC, 2021)

Back sheets are used on solar panels to help protect the solar cell from weather, humidity, loads, and impact damage. It has also been noted that they also help provide electrical isolation for safety purposes. The proper choice of the back sheet can increase the panel life and reduce the cost of electricity generated from the panel over the solar panel cell's life. Requirements for the back sheet include opacity and high reflectivity.

Back sheets as shown in **Figure 31** are typically laminates often consisting of PVF, PET and poly (ethylene-vinyl acetate) (EVA or PEVA) films. For example, PET films are used in applications where increased UV stability is desirable. These applications include back sheets on solar panels as well as architectural and automotive protective films. It should be noted that PET will degrade over time reducing its ability to protect the desired substrate. PVF and Lumiflon® FEVE have been used as a weather resistant topcoat layer that helps protect the PET and EVA from degradation, especially from UV light.

Figure 31. The 6 main components used in the construction of a solar panel



From: <https://www.cleanenergyreviews.info/blog/solar-panel-components-construction>

To demonstrate the benefits of the fluoropolymer coating on the non-fluorinated film layer, two examples are provided below for illustrative purposes. The first is a xenon arc accelerated weathering test. In this test, the FEVE polymer-coated PET film was subjected to 3,000 hours in a weatherometer, a device used to evaluate UV aging. The results were compared to the uncoated PET film and the Color change (ΔE) was measured. Results are shown below in **Figure 32**. After 3,000 hours, the PET film coated with the FEVE-based topcoat shows no change in color, while the uncoated film has a visible decline in appearance.

Figure 32. Xenon Arc Weatherometer Test Results of FEVE-coated and Uncoated PET Film

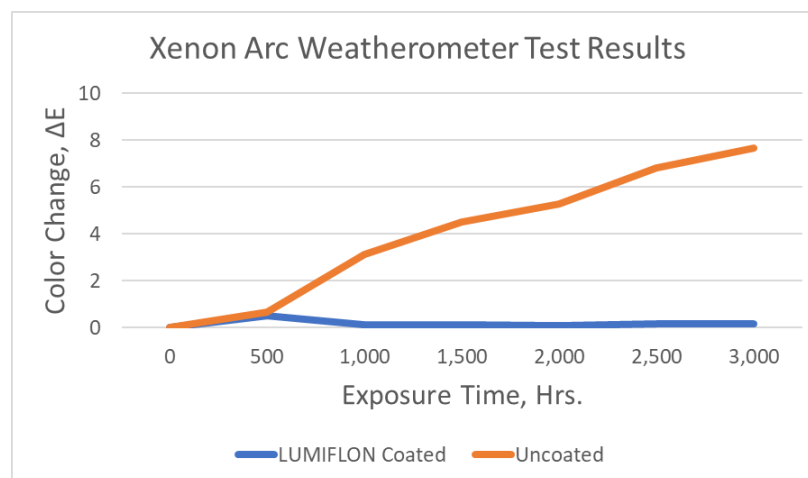


Figure with permission of AGC.

In the second test to evaluate UV stability of the Lumiflon® FEVE-based fluorourethane coating compared to that of PVF-based coating, panels were placed in the Xenon Arc Weatherometer for 5,000 hours. When color change of polymers is measured, B* is an indicator of yellowing. B* was monitored over the duration of the test; results are shown in **Figure 33** below.

Figure 33. Xenon Arc Weatherometer Test of PVF and FEVE Laminate Films

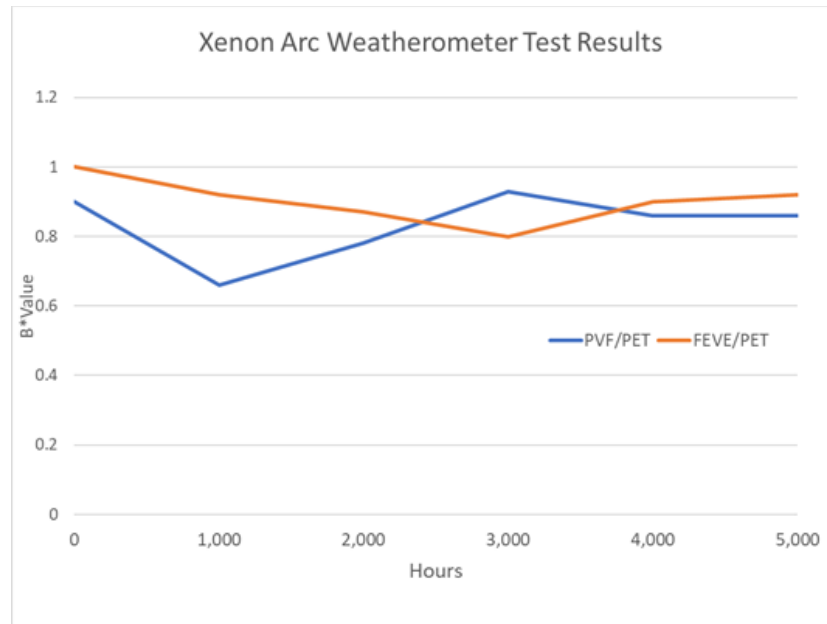


Figure with permission of AGC.

Both the FEVE-based fluorourethane coating and the PVF-based topcoat film performed extremely well in this test by preventing yellowing of the PET film over the 5,000-hour duration of the test (Madico, Inc., 2013).

Conclusions

Fluoropolymers are high molecular weight polymers with fluorine atoms directly attached to their carbon-only backbone. The carbon-fluorine (C-F) bond is the strongest bond between carbon and another atom and imparts unique, outstanding and beneficial properties along with extraordinary functional performance. These properties include chemical, biological and thermal stability, heat and chemical resistance, unique dielectric properties and durability. Additional fluoropolymer properties include increased fire resistance, weather resistance, non-wetting and adhesion resistance.

Many fluoropolymers, including the fluoropolymers used in the I&C end-uses, have been shown to meet the "polymers of low concern" (PLC) criteria, and as such, do not present a notable concern for human health or the environment (Henry et al. 2018, Korzeniowski et al. 2022). As discussed in those references, fluoropolymers are negligibly soluble in water, non-mobile, non-bioavailable, non-bioaccumulative and non-toxic.

Fluoropolymers are regarded as irreplaceable in many applications because their unique combination of specific properties, which are critical to ensure optimal performance in many applications and cannot be achieved or guaranteed by alternative materials. In the particular I&C end-uses covered in this document, there are a number of specific properties that enable the unparalleled performance fluoropolymers provide versus a number of major alternatives such as polyurethanes, chlorinated rubbers, alkyds and polyesters.

The exceptional properties that fluoropolymers provide and/or enable in the I&C coating applications are:

Flexibility;	Abrasion Resistance
Wear resistance;	Harsh Chemical Resistance
Impact Resistance and Hardness	Corrosion Resistance
Color Retention	Barrier Properties
Gloss Retention	Fire Retardancy and Smoke Suppression
Film Erosion	Low Refractive Index for Optical Effects
Chalking Resistance	
Weather Resistance	Reduced Dirt Collection

The unique combination of these properties in the subject I&C end-uses provide several significant benefits that include:

- VOC reduction due to extended service life and longer (less frequent) recoat time intervals;
- CO₂ reduction due to improved functioning of building HVAC systems as a result of lower peak and regular energy demands;
- Lower energy demands lead to lower carbon footprint;
- Life Cycle Costs (LCC) that are significantly reduced due to the extended service life of the end product, requiring less recoating, better color and gloss retention as well as little to no surface chalking;
- Dirt pickup is reduced and the surface in question is easier to maintain and is less susceptible to environmental damage;

- Mold and Mildew resistance is improved with FBCs; and
- And finally, help in qualification for Green Building Certification.

We are unaware of another coating technology that meets the performance parameters of durability and product longevity that also provides the cited benefits that are the defining characteristic of FBCs.

The five (5) I&C end-use applications described in this submission are:

1. Building Facades and Protection – Metal Building Panels and Parts

Fluoropolymer-based coatings (FBCs) offer superior performance, service life, sustainability, appearance and value for various applications which are used on a wide variety of metal substrates for commercial, monumental and other building projects. These fluoropolymer-based systems include polyvinylidene fluoride (PVDF) and fluoroethylene vinyl ether (FEVE) resin-based formulations. These two fluoropolymers are the film-forming binder resins in factory-applied industrial and construction coatings used in settings where extreme durability and lifespan of several decades or more are needed to provide substrate protection. FBCs extend the lifespan of the underlying materials and are a critical specification for certain products in the building and construction markets.

FBCs are available in both coil (roll-applied) and extrusion (spray-applied) applications. Each type has specific uses for various construction and architectural metal building products. Coil coatings are applied to large rolls or “coils” of steel and aluminum by a continuous, automated process that typically occurs in a controlled factory environment. Extrusion coatings are spray-applied to aluminum preformed extruded substrates, in a vertical or horizontal line also in a highly automated factory environment. FBCs can be applied to a variety of metal components used in projects ranging from pre-engineered metal buildings to municipal arenas, skyscrapers and many others.

2. Roofing and Roofing Structures

Roofing that incorporates a fluoropolymer-based topcoat system has significant advantages versus conventional roofing. These fluoropolymer-based systems have been shown to provide numerous important benefits for both roofing and building facades. Many favorable attributes combine to provide a lower lifetime ownership cost including lower energy usage from higher solar reflectivity and lower roof temperatures. This leads to lower carbon footprint, reduced dirt pick-up and improved mold and mildew resistance. Other important benefits from using these fluoropolymer-based systems include:

- World-class UV resistance and long-life color retention;
- Lower peak energy demand charge;
- Longer lifespan of roof coating and longer lifespan of roof substrate;
- Lower maintenance costs and less downtime;
- Increased efficiency and longer lifespan of HVAC equipment; and
- Lower VOC emissions.

3. Bridge and Walkway Structures

Bridge structures need durable coating performance to protect the painted metal substrate and maintain the bridge’s structural integrity. Any coating system must demonstrate through rigorous testing to be reliable and last a long time given safety considerations and how difficult, disruptive and expensive the recoat process is. Bridges

are subject to highly adverse environmental conditions including, but not limited to, high intensity sunlight, fog, rain, saltwater spray (in coastal areas) and constant automobile exhaust. The high weathering performance of the subject fluoropolymer-based resin allows the paint system to prolong the bridge's service life and protect the substrate (or coated material), which subsequently decrease the number of re-painting cycles of the bridge infrastructure or building. This eventually contributes to a better (lower) Life Cycle Cost. A fluoropolymer-based bridge coating system would typically utilize an FEVE-based resin paint as a topcoat, to protect the substrate (or coated material) by increasing the anti-corrosion ability of the substrate and coated material. This has the obvious impact of prolonging the service of the paint system. Furthermore, it contributes to the reduction of CO₂ generation by extending the life of the protected material and delaying or postponing the time between re-coating the bridge structure. Less recoating is equivalent to lowering the CO₂ generated in paint system product manufacture and application.

4. Water Towers

Water towers are high above the ground and therefore have an increased safety risk to coat and recoat. They require scaffolds to obtain a clean finish. In addition to the cost of the coatings package, application costs are significant as well. In fact, the cost of paint is typically less than 20% of the total coating process costs. The major costs of application largely consist of scaffolding and labor costs. The long-life cycle of the FBCs (extended over several decades) has not been shown with polyurethane and other coatings. This decades long life cycle can be realized with an FBCs system due to the durability provided by the fluoropolymer-based resin. Here again, the life-cycle cost is reduced due to the reduction in the number of recoatings required over the life of the water tower.

5. Solar Panels

Fluoropolymers are often used as back sheets (films) in photovoltaic solar panel construction. Materials used in this end-use need UV resistance and stability, corrosion resistance, flexibility, light in weight and have extended durability in full exposure to a variety of environmental conditions and intense sunlight and heat. Other materials used in back sheet applications are polyamides, polyethylene terephthalate, glass and polyesters.

Supplementary description of FEVE and PVDF Fluoropolymer Properties and Applications (Korzeniowski et al., 2022 and noted links)

FEVE

(Main references: see primarily <https://www.agcchem.com> and <https://www.lumiflonusa.com>)

FEVE fluoropolymer resins are polymers consisting of alternating fluoroethylene and alkyl vinyl ether segments. They were developed in 1982 as the first solvent-soluble fluoropolymers in the world. The fluoroethylene segment is largely responsible for the coatings' improved weatherability, durability and chemical resistance. Similarly, the vinyl ether segments provide for clarity, gloss, hardness, flexibility as well as a cross linking site for solubility if needed. The general features of the FEVE fluoropolymer include solubility in general organic solvents as well as being a non-crystalline resin with high transparency. The structure provides for the ability to introduce amorphous functional groups into the vinyl ether segments and as noted the alternating copolymerization structure gives high weather and chemical resistance. FEVE resins are used to make ultra-weatherable coatings for architectural, aerospace, automotive, bridge and industrial maintenance markets. These resins can be used to make both clear and pigmented coatings. They can be formulated with a wide range of gloss (from high gloss to flat finishes) and colors. The FEVE polymer is a platform chemistry that is supplied in various forms, including solvent-based liquid for easy application, water-based resins for low VOC (Volatile Organic Compound) and low odor coatings and a flake for sustainable powder coatings. FEVE powder coating materials provide essentially zero VOC and HAPS (Hazardous Air Pollutants) free coatings.

FEVE coatings protect steel, aluminum and other metals as well as concrete from degradation by UV light, wind and rain and corrosion. Because of their ultra-weatherability, FEVE based coatings offer substantial life cycle cost savings over conventional coatings. They can be used in the field for re-coating of structures or in the shop to manufacture pre-coated panels. FEVE resin chemistry allows for use in coatings that cure at ambient or low temperatures. This is important for use with heat-sensitive substrates like vinyl and fiberglass. Solvent- and water-based FEVE resins may be used to create highly weatherable coatings for vinyl and fiberglass building materials that allow for a cure process that meets the specific needs of these sensitive substrates.

High performance FEVE coatings can extend the lifetime of bridges and water tanks and reduce the frequency of maintenance, by helping to prevent coating degradation at the hands of UV radiation, salt and water. These coatings contain anti-corrosive properties that help maintain the coating's structural integrity for decades. Costs associated with bridge downtime, including increased traffic congestion, are significantly reduced over the life of the coating.

FEVE resins have outperformed even the best acrylic urethane coatings on steel, aluminum, magnesium and plastics like ABS, polyurethane, FRP, PVC, polyethylene, polypropylene and polycarbonate enabling transportation manufacturers to create and maintain the appearance for years. FEVE-based topcoats have been shown to yield over five times the lifespan of acrylic urethane coatings typically used in the transportation industry. FEVE resins can also be blended with traditional resins like acrylics to significantly increase their performance. For example, FEVE-based coatings can reduce maintenance costs in the aerospace market by as much as 50 % over the life of the plane, in addition to substantially reducing the loss of revenue during scheduled repainting. Aircraft coated with FEVE resin typically require no repainting for at least eight years, maintaining outstanding appearance and a durable surface that allows for easy cleaning. In contrast, acrylic urethanes typically begin to fade and chalk after only three years and require repainting after five.

FEVE Alternatives Assessment

The two main alternatives for an FEVE-based coating are polyurethanes and polysiloxanes. Urethanes have a long performance history and are still widely used as durable coatings. In general, polyurethanes will usually start to chalk and change color within 5-10 years. Due to degradation, the coating thickness of urethanes starts to decrease and after 15-25 years will no longer function as a barrier against corrosion. Polysiloxanes come in two types, epoxy and acrylic.

Siloxanes have a couple of advantages. First, they do not require an isocyanate crosslinker; they crosslink via a moisture cure mechanism. Second, they can be used as a two-coat system consisting of a zinc rich primer and a higher film build of siloxane (usually around 6-8 mils). This saves time especially in fabrication shops.

Neither coating system discussed above has been shown to weather as well as FEVE. A typical FEVE coat system will retain color and gloss for 25+ years and can prevent corrosion for up to 60 years, depending on the environment. Outdoor testing done in Japan over a 16-year period showed that a 25 μm FEVE-based coating retained 21 μm of thickness after 16 years. A 75 μm (3 mil) topcoat, typical thickness in a coating project, has a theoretical life of >100 years. In that same test, a 25 μm polyurethane coating was gone after 12 years. There are 30-year test results from bridges in Japan where gloss retention of the FEVE-based coating was 97% with a very small color change. There are test results that show that FEVE-based coatings retain their protective properties for a longer period than either of the other coatings. This makes sense in that the main purposes of the topcoat are to preserve its initial appearance for as long as possible and to act as a barrier film to corrosion initiators like chloride, water and oxygen.

The characteristics and advantages of various FEVE resin forms are summarized in Table 7.

Table 7. The Resin Form of FEVE and Features and Applications

Type of FEVE Resin	Features and Applications
Solvent Base	Use of general organic solvents. Used for general construction. Suitable for new installations
High Build	Can be painted thicker. Low VOC content
Exempt Solvent	Use volatile organic compound (VOC) exempt solvents as determined by EPA. Used for repainting airplanes
Mild Solvents	Mild solvent has smaller number of MIR VOC, (MIR VOC: maximum incremental reactivity VOC. They are classified by their ozone generation ability). With a mild odor, this system can be used for repainting in the city and repainting bridges
Water Base	Emulsions and Dispersions; The amount of VOCs is not more than 5%. Frequently used for repainting on-site coating. Reduced VOCs even in factory coatings
Powder	Essentially zero VOCs. Frequently used for Aluminum panels and building components. Factory painting only. Cannot be painted on site. Grade with the lowest environmental impact.

The benefits of utilizing a FEVE resin in a FBC are:

1. The excellent durability of FEVE lasts for several decades and protects the underlying paint film and substrate, thus reducing the number of surface re-coatings and protection of the underlying paint film and substrate over a long period of time.
2. High affinity for various solvents, hardener, paint additives and antifouling agents allows users to apply the product to a wide range of coating equipment and to achieve a wide variety in coating performance.
3. The high affinity for a wide range of pigments and the ability to select very vivid colors make it possible to achieve a high level of color design including clear metallic color and natural stone.
4. The ability to have colorful designs makes these systems also suitable for stone-like walls, higher design wall, amenities, landmarks and even vehicles.
5. FEVE is amorphous, which makes the coating film very smooth and provides a high gloss and mirror-like surface for itself. On the other hand, its high pigment affinity allows the gloss to be freely adjusted from 0-80 gloss units by using matting agents.

6. An isocyanate curing agent and resulting cross-linking can function at ambient to medium temperature. A block isocyanate curing agent will dry at higher temperatures in a short period of time. After drying, the product has not been shown to dissolve in solvents and exhibits excellent solvent resistance.
7. Long span bridges and large buildings that can only be air dried with crosslinking can be coated outdoors at ambient temperature.
8. FEVE coating reduces the difficult repainting for large, massive structures including existing buildings and structures with deteriorated coatings which can be repainted onsite. The old coating can be given a new life and be given decades of longevity.
9. Using an essentially zero VOC content coating does make a rapid contribution to VOC reduction versus competitive materials. Powder grades which do require baking are factory applied.
10. FEVE requires relatively low temperatures even when curing.

In addition to the increased oxygen permeability, improved weatherability, CO₂ generation reduction and lower overall Life Cycle Costs benefits that were previously noted, there are a number of other advantages and benefits fluoropolymers provide. These additional important benefits and features are as follows:

- Improved mechanical properties, lower corrosion rates, little to no molecular weight changes on exterior use,
- Lower top film consumption, isocyanate crosslinking retention, significantly improved durability,
- Significantly improved chalking performance as well as less fading, much better gloss and color retention
- Improved VOC reduction over the life of the structure

From the available technical data, FBC systems significantly outperform the competitive alternative systems such as polyurethanes, alkyds and chlorinated rubber coatings

PVDF and PVDF Copolymer

(Main reference : <https://www.extremematerials-arkema.com/en/product-families/kynar-pvdf-family/download-performance-characteristics-data-brochure/>)

Polyvinylidene fluoride (PVDF) is a tough engineering thermoplastic that offers a balance of performance properties. It has the characteristic stability of fluoropolymers that help to resist harsh thermal, chemical and ultraviolet environments. PVDF, in addition to being readily melt-processed by standard methods, can be dissolved in polar solvents, such as organic esters and ketones, for coating applications. PVDF can be produced by homopolymerization or copolymerization, providing a full range of products with different molecular architecture along with different ranges of properties. Some of the important properties of PVDF homopolymers and copolymers are a function of the crystalline content

and type of crystalline structure, both of which are affected by the processing methods and conditions.

Features

- Outstanding resistance to sunlight/UV exposure
- Tremendous chemical resistance to a wide range of aggressive chemicals
- Radiation resistance
- Excellent burn characteristics / flame and smoke properties (low flame spread and low quantity of smoke generated)
- Easy processing on industry-standard equipment and easy post-processing, such as fabrication
- Extremely high purity for the most demanding applications
- Extremely high electrochemical stability
- Excellent abrasion resistance
- High temperature rating: RTI 150 °C

Applications

- **Chemical Processing:** Due to its high temperature resistance, low permeability and high mechanical strength, PVDF is used as a contact surface for the production, storage and transfer of corrosive fluids (chemically resistant to halogens and acids). PVDF resin is used in mechanical components, fabricated vessels, tanks, pumps, valves, filters, heat exchangers, tower packing, piping systems and many other applications.
- **Wire and Cable:** PVDF has excellent fire, abrasion, chemical and impact resistance. Depending on the test method, it can have up to a 150°C rating and can be irradiated for even higher ratings.
- **Electricity and Electronics:** Its fire resistance, abrasion resistance, low-smoke emission, chemical and mechanical properties make PVDF resin suitable for protective sheathing, plenum and communications wiring insulation and binder resin for battery manufacture.
- **High Purity:** As semi-conductor and pharmaceutical production require increasingly pure materials, high purity PVDF resin grades meet industry needs (low extractables values). PVDF resin regulatory compliances include food and water use certifications (in FDA 177.2510 and/or 177.2600 compliance, NSF Standard 51 – Food Equipment Materials, NSF Standard 61 – Drinking Water System Components) as well as compliance for use in industries such as healthcare (USP Class VI approval).
- **Transportation:** PVDF resin is used in both public and private transport vehicles as a barrier liner for automotive fuel line and gas station fuel pipes, in decorative films, as a binder in HEV/EV batteries, as molded and thermoformed body components (weathering, anti-grime/graffiti) and as tank trailer linings for corrosion protection. PVDF resin has strength, flame resistance, durability and versatility that make it a preferred material in automotive wiring harnesses, general coatings and plastic optical fibers.

- **Focus on Battery:** PVDF polymers are used in the battery industry as binders for cathodes and anodes in lithium-ion batteries and as battery separators in lithium-ion polymer batteries. PVDF is helping to design thinner and smaller lithium-ion batteries.
- **Architecture:** The excellent outdoor aging and weathering properties of PVDF resin led to its use in long-lasting paints for coating metal sheet for the past 50 years. PVDF resins can also be used to protect thermoplastics through coextrusion or film lamination techniques to obtain anti-grime and anti-graffiti surfaces with excellent weathering properties.
- **Photovoltaic:** PVDF Film is used in the protection of back sheet and for front sheet glazing. Those films provide exceptional solar transmittance and also have excellent dirt shedding and fire resistance properties.
- **Membrane:** PVDF resin is a respected membrane material for applications ranging from bioprocess separations to water purification because it is extremely chemically resistant and well suited to aggressive chemical environments. PVDF tolerates ozone and chlorine (an oxidant increasingly used for water purification) very well. Grades with United States Food and Drug Administration and/or NSF International compliance are compatible with food and/or beverage contact applications. It is used to manufacture flat sheet, hollow fiber and TIPS (thermally induced phase separation) process membranes and/or enclosed shapes that cannot be lined or coated in a conventional manner.
- **Fabrics:** Woven and non-woven fabrics can be produced using specific PVDF grades. These fabrics offer excellent chemical resistance, stability to sunlight and flame retardant properties.

General physical and mechanical properties

PVDF homopolymers and copolymer resin grades give the option to combine rigid and flexible materials when processing. As a material of construction for pumps and pipe, PVDF exhibits excellent resistance to abrasion. PVDF can also be manufactured in thin, flexible and transparent films, filament and tubing. Sunlight has little to no effect on PVDF resins.

- **Strength and toughness:** PVDF fluoropolymers are inherently strong and tough as reflected by their tensile properties and impact strength. An ambient temperature tensile strength at yield of 35-55 MPa (5,000-8,000 psi) and an unnotched impact strength of no break offered by select resins emphasize this. These characteristics are retained over a wide range of temperatures
- **Flexural creep:** Compared to many thermoplastics and fluoropolymers tensile yield of 15-55 MPa (2,200-8,000 psi), PVDF polymers have excellent resistance to tensile creep and fatigue also at elevated temperatures. Likewise, the short-term flexural creep resistance of PVDF homopolymer resins reflects superior load bearing performance.
- **Tensile creep:** Compared to many thermoplastics and fluoropolymers tensile yield of 15-55 MPa (2,200-8,000 psi), PVDF polymers have excellent resistance to tensile creep and fatigue also at elevated temperatures. PVDF resins are able to

maintain a low tensile creep when subjected to constant stress even at high temperatures.

- **Flexural creep:** PVDF is highly rigid and resistant to creep under mechanical stress and load. Likewise, the short-term flexural creep resistance of PVDF homopolymer resins reflects superior load bearing performance.
- **Thermal properties:** PVDF resins exhibit high thermal stability. Prolonged exposure of some PVDF grades at 250 °C (482 °F) in air does not lead to weight loss. No oxidative or thermal degradation has been detected during continuous exposure at 150 °C (302 °F) for a period of ten years. In testing, select resins have been given an RTI of 150 °C. PVDF resins thermally decompose at temperatures greater than 375 °C (707 °F). However, the melt processing range of unfilled PVDF homopolymer resins is very broad – from slightly above the melting point of 155 - 170 °C (311-338 °F) up to 300 °C (572 °F).
- **Electrical properties:** PVDF combines high dielectric strength and excellent mechanical properties over a broad temperature range. This has led PVDF resin to be used for thin-wall primary insulation and as a jacket for industrial control wiring. With proper shielding, PVDF resin can be used as jacketing for high frequency plenum-rated data cables because of its excellent flame and smoke performance.
- **Stability to weather and UV effects:** Many years of outdoor exposure in direct sunlight have little effect on the physical properties of PVDF. Some increases in tensile strength and reduction in elongation do occur over time.
- **Ozone resistance:** Ozone is a powerful oxidizing agent characterized by a high degree of chemical instability. PVDF offers excellent chemical resistance to ozone exposure.

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Appendix A. Glossary

AAMA	American Architectural Manufacturers Association; http://www.aamanet.org
ACC	American Chemistry Council
A/C	Air Conditioning
ACM	Aluminum Composite Material
ARC	Xenon ARC testing uses a highly specialized type of gas discharge lamp, an electric light that produces light by passing electricity through ionized xenon gas at high pressure. It produces a bright white light to simulate sunlight.
ASTM	ASTM International; https://www.astm.org/
AWWA	American Water Works Association; https://www.awwa.org/
CAS Number	Chemical Abstracts Service Number
CEPE	European Council of the Paint, Printing Ink and Artists' Colors Industry; https://www.cepe.org/
CR	Chlorinated Rubber
ECHA	European Chemicals Agency; https://echa.europa.eu/
ECTFE	Ethylene-chlorotrifluoroethylene copolymer
EIF	Entry into Force
EIFS	Exterior Insulation Finishing System
EOL	End of Life
ETFE	Ethylene-tetrafluoroethylene copolymer
EVA	Ethylene vinyl acetate or PEVE: poly (ethylene-vinyl acetate)
FBC	Fluoropolymer Based Coating
FEVE	Fluoroethylene-vinyl ether copolymer
Fluorinated Polymer	The broad generic term to encompass all polymers for which one or more of the monomer units contains the element fluorine, in the backbone and/or in side chains.
Fluorochemical	General, nonspecific name that describes a universe of organic and inorganic substances that contain at least 1 fluorine atom, with vastly different physical, chemical and biological properties. Synonyms include "fluorinated substance" and "fluorinated chemicals."
Fluoroelastomer	An elastic rubber-like polymer to which fluorine is bound. Fluoroelastomers are highly durable and resistant to heat, oils, solvents, fuels and ozone.
Fluoroplastic	A distinct subset of polymers and plastics where some or all of the hydrogen atoms of the hydrocarbon backbone have been replaced with fluorine atoms.
Fluoropolymer	Distinct subset of polymers, namely, those made by (co)polymerization of olefinic monomers, at least one of which contains fluorine bound to one or both of the olefinic carbon atoms, to form a carbon-only polymer

	backbone with fluorine atoms directly attached to it, e.g., polytetrafluoroethylene.
Fluorosurfactant	A substance used to lower aqueous surface tension in which the hydrophobic portion contains F bound to C, often as a perfluoroalkyl moiety, often referred to as “fluorinated surfactants”, “fluorosurfactants,” “fluorinated tensides,” or “fluorotensides”
FPG	Fluoropolymers Product Group, a group within Plastics Europe, the association of Plastics manufacturers; https://fluoropolymers.plasticseurope.org/index.php/about-us
GPC	Gel Permeation Chromatography
Homopolymer	A polymer made with only one monomer
HVAC	Heating Ventilation Air Conditioning
IR	Infrared
I&C	Infrastructure & Construction
ISO	International Organisation for Standardization; https://www.iso.org/about-us.html
JPMA	Japan Paint Manufacturers Association; https://www.toryo.or.jp/eng/
LC	Life Cycle
LCC	Life Cycle Cost
LEED	Leadership in Energy and Environmental Design; https://www.usgbc.org/leed
LOI	Limiting oxygen index
MIR	Maximum Incremental Reactivity
OECD	Organisation for Economic Co-operation and Development; https://www.oecd.org/
PET	Polyethylene terephthalate
PFAS	A very diverse group, per- and poly-fluoroalkyl substances (PFAS), including polymers (fluoropolymers, perfluoropolyethers, side chain fluorinated polymers) and non-polymers. Perfluoroalkyl substances are those for which all hydrogens on all carbon atoms not associated with functional groups have been replaced by fluorine, and polyfluoroalkyl substances are those for which all hydrogens on at least one, but not all, carbon atoms have been replaced by fluorine.
PFP	U.S.-based Performance Fluoropolymer Partnership; https://www.americanchemistry.com/industry-groups/performance-fluoropolymer-partnership-pfp/
PFPE	A perfluoropolyether is a polymer in whose backbone -CF ₂ -, -CF ₂ CF ₂ - and possibly -CF(CF ₃)CF ₂ - units are separated by oxygen atoms.
Polymer of Low Concern (PLC)	A polymer that does not present a notable concern for human health or the environment.
PU	Polyurethane
PVC	Polyvinyl Chloride
PVDF	Polyvinylidene fluoride

REACH	Chemical Control regulation in the European Union (Registration, Evaluation, Authorisation and Restriction of Chemicals); https://environment.ec.europa.eu/topics/chemicals/reach-regulation_en
RI	Refractive Index
SCFP	Side-chain Fluorinated Polymer
SEM	Scanning Electron Microscope, or Micrograph
SMP	Silicone Modified Polyester
SWM	Sunshine Weatherometer, or Weatherometer
TSR	Total Solar Reflectance
USEPA	US Environmental Protection Agency
UV	Ultra Violet Light
VOC	Volatile Organic Compounds

Appendix B. Infrastructure & Coatings Testing and Reference Methods

For each of the I&C end-use applications in this submission there are a set of exacting performance testing and reference methods. This appendix contains a list of some of the critical test methods and what they measure. For the primary end-uses in this submission, designers, architects and builders have specific performance standards they must meet to achieve the desired long lasting coatings performance and surface protection.

Test Method	Test Method Title	Test Method Description
AAMA 621	Voluntary specifications for high performance organic coatings on coil coated architectural hot dipped galvanized (HDG) and zinc-aluminum coated steel substrates	AAMA 621 provides specifications and methods for evaluating coil coatings on hot dipped galvanized and zinc-aluminum coated steel substances for adhesion, impact resistance, chemical resistance and weatherability.
AAMA 2604	Voluntary Specification, Performance Requirements and Test Procedures for Superior Performing Organic Coatings on Aluminum Extrusions and Panels	AAMA 2604 measures film integrity, exterior weatherability and general appearance over years of exposure. It includes humidity resistance (300 hours), salt spray resistance, Florida exposure (5 years), color retention, chalk resistance and gloss retention.
AAMA 2605	Voluntary Specification, Performance Requirements and Test Procedures for Superior Performing Organic Coatings on Aluminum Extrusions and Panels	AAMA 2605 measures film integrity, exterior weatherability and general appearance over years of exposure. It includes humidity resistance (4,000 hours), salt spray resistance, Florida exposure (10 years), color retention, chalk resistance and gloss retention.
ANSI/CRRC S100	Standard Test Methods for Determining Radiative Properties of Materials	From the publicly available online standard: ¹ “This standard provides a practice and method for testing and reporting the <i>radiative properties</i> of roofing products before and after a specified test exposure. Roofing specimens are exposed to specific tests and to the exterior environment throughout a specified time period. The tests provide a relative measure of the roofing product response to the test conditions. The standard does not purport to be representative of all conditions that roofing products experience in the

¹ https://coolroofs.org/documents/ANSI-CRRC-S100-2021_Final.pdf

		field. Variations of the test conditions or specimen construction also affect the specimen response.”
ASTM B117	Standard Practice for Operating Salt Spray (Fog) Apparatus	From the public ASTM B117 website:² “This practice provides a controlled corrosive environment which has been utilized to produce relative corrosion resistance information for specimens of metals and coated metals exposed in a given test chamber.” “This practice covers the apparatus, procedure, and conditions required to create and maintain the salt spray (fog) test environment.”
ASTM B244	Standard Test Method for Measurement of Thickness of Anodic Coatings on Aluminum and of Other Nonconductive Coatings on Nonmagnetic Basis Metals with Eddy-Current Instruments	From the public ASTM B244 website:³ “This test method covers the use of eddy-current instruments for the nondestructive measurement of the thickness of a nonconductive coating on a nonmagnetic basis metal. It is intended to supplement manufacturers’ instructions for the operation of the instruments and is not intended to replace them.” “This test method is particularly useful for measuring the thickness of an anodic coating on aluminum alloys. Chemical conversion coatings are too thin to be measured by this test method.”
ASTM D522	Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings	From the public ASTM D522/D552M website:⁴ “Coatings attached to substrates are elongated when the substrates are dimensionally unstable, or are bent during the manufacture of articles or when the articles are abused in service. These test methods have been useful in rating attached coatings for their ability to resist cracking when elongated. They have been useful in evaluating the flexibility of coatings on flexible substrates.”

² <https://www.astm.org/standards/b117>

³ <https://www.astm.org/b0244-09r21.html>

⁴ https://www.astm.org/d0522_d0522m-17r21.html

ASTM D523	Standard Test Method for Specular Gloss	From the public ASTM D523 website:⁵ “Measured gloss ratings by this test method are obtained by comparing the specular reflectance from the specimen to that from a black glass standard. Since specular reflectance depends also on the surface refractive index of the specimen, the measured gloss ratings change as the surface refractive index changes. In obtaining the visual gloss ratings, however, it is customary to compare the specular reflectances of two specimens having similar surface refractive indices.”
ASTM D662	Standard Test Method for Evaluating Degree of Erosion of Exterior Paints	From the public ASTM D662 website:⁶ “Erosion failure of paint films can occur in use. This test method provides a means of evaluating the degree of failure by comparing to pictorial standards.”
ASTM D968	Standard Test Method for Abrasion Resistance of Organic Coatings by Falling Abrasive	From the public ASTM D968 website:⁷ “These test methods cover the determination of the resistance of organic coatings to abrasion produced by abrasive falling onto coatings applied to a plane rigid surface, such as a metal or glass panel.”
ASTM D1308	Standard Test Method for Effect of Household Chemicals on Clear and Pigmented Coating Systems	From the public ASTM D1308 website:⁸ “Resistance to various liquids used in the home is an important characteristic of organic finishes. These test methods provide the means by which the relative performance of coating systems may be evaluated. It should be recognized that continuous films are necessary for reliable results.” “This test method covers determination of the effect of household chemicals on clear and pigmented organic finishes, resulting in any objectionable alteration in the surface, such as discoloration, change in gloss, blistering, softening, swelling, loss of adhesion, or special phenomena.”

⁵ <https://www.astm.org/standards/d523>

⁶ <https://www.astm.org/d0662-93r19.html>

⁷ <https://www.astm.org/d0968-22.html>

⁸ <https://www.astm.org/d1308-20.html>

ASTM D1400	Standard Test Method for Nondestructive Measurement of Dry Film Thickness of Nonconductive Coatings Applied to a Nonferrous Metal Base	From the public ASTM D1400 website: ⁹ “This test method covers the nondestructive measurement of the dry film thickness of electrically nonconductive coatings applied over a nonferrous metal base using commercially available eddy current instruments. This test method is intended to supplement manufacturers' instructions for the manual operation of the gages and is not intended to replace them.”
ASTM D1654	Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments	From the public ASTM D1654 website: ¹⁰ “This method provides a means of evaluating and comparing basic corrosion performance of the substrate, pretreatment, or coating system, or combination thereof, after exposure to corrosive environments.” “This test method covers the treatment of previously painted or coated specimens for accelerated and atmospheric exposure tests and their subsequent evaluation in respect to corrosion, blistering associated with corrosion, loss of adhesion at a scribe mark, or other film failure.”
ASTM D2244	Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates	From the public ASTM D2244 website: ¹¹ “This practice covers the calculation, from instrumentally measured color coordinates based on daylight illumination, of color tolerances and small color differences between opaque specimens such as painted panels, plastic plaques, or textile swatches.”

⁹ <https://www.astm.org/d1400-94.html>

¹⁰ <https://www.astm.org/d1654-08r16e01.html>

¹¹ <https://www.astm.org/d2244-23.html>

ASTM D2247	Standard Practice for Testing Water Resistance of Coatings in 100% Relative Humidity	From the public ASTM D2247 website:¹² “Water can cause the degradation of coatings, so knowledge of how a coating resists water is helpful for assessing how it will perform in actual service. Failure in tests at 100 % relative humidity may be caused by a number of factors including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. This practice is therefore useful for evaluating coatings alone or complete coating systems.” “This practice covers the basic principles and operating procedures for testing water resistance of coatings by exposing coated specimens in an atmosphere maintained at 100 % relative humidity so that condensation forms on all surfaces of test specimens.”
ASTM D2248	Standard Practice for Detergent Resistance of Organic Finishes	From the public ASTM D2248 website:¹³ “This practice covers the determination of the resistance to failure, in an accelerated manner, of organic finishes when immersed in a detergent solution.”
ASTM D2794	Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact)	From the public ASTM D2794 website:¹⁴ “Coatings attached to substrates are subjected to damaging impacts during the manufacture of articles and their use in service. In its use over many years, this test method for impact resistance has been found to be useful in predicting the performance of organic coatings for their ability to resist cracking caused by impacts.” “This test method covers a procedure for rapidly deforming by impact a coating film and its substrate and for evaluating the effect of such deformation.”

¹² <https://www.astm.org/d2247-15r20.html>

¹³ <https://www.astm.org/d2248-01ar18.html>

¹⁴ <https://www.astm.org/d2794-93r19.html>

ASTM D3359	Standard Test Methods for Rating Adhesion by Tape Test	From the public ASTM D3359 website: ¹⁵ “This test method is limited to evaluating lower levels of adhesion (see 1.3). The intra- and inter-laboratory precision of this test method is similar to other test methods for coated substrates (for example, Test Method D2370 and Test Method D4060), and is insensitive to all but large differences in adhesion.”
ASTM D3363	Standard Test Method for Film Hardness by Pencil Test	From the public ASTM 3363 website: ¹⁶ “Pencil hardness measurements have been used by the coatings industry for many years to determine the hardness of clear and pigmented organic coating films. This test method has also been used to determine the cure of these coatings, especially when using forced dried heat.”
ASTM D4145	Standard Test Method for Coating Flexibility of Prepainted Steel	From the public ASTM D4145 website: ¹⁷ “This test method describes a procedure for determining the flexibility and adhesion of organic coatings (paints) on metallic substrates that are deformed by bending when the sheet is fabricated into building panels or other products. The metal substrate must be capable of passing this test without fracturing and with no excessive grain development.”
ASTM D4214	Standard Test Methods for Evaluating the Degree of Chalking of Exterior Paint Films	From the public ASTM 4214 website: ¹⁸ “The procedures provide a broad range of techniques and photographic references to evaluate chalking of exterior paints.” “These test methods cover the evaluation of the degree of chalking on white or tinted exterior paint films. These test methods describe the procedures recommended for transferring the chalk to a fabric or fingertip, which is then compared to photographic reference standards, or in the case of adhesive tapes, compared to a reflectance table or photographic reference standards, to determine the degree of chalking.”

¹⁵ <https://www.astm.org/standards/d3359>

¹⁶ <https://www.astm.org/d3363-22.html>

¹⁷ <https://www.astm.org/d4145-10r22.html>

¹⁸ <https://www.astm.org/d4214-07r15.html>

ASTM D4585	Standard Practice for Testing Water Resistance of Coatings Using Controlled Condensation	From the public ASTM D4585 website:¹⁹ “Water can cause degradation of coatings, so knowledge of how a coating resists water is helpful in predicting its service life. Failure in a condensation test may be caused by a number of factors including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. The test is therefore useful for evaluating coatings alone or complete coating systems.” “This practice covers basic principles and operating procedures for testing water resistance of coatings using controlled condensation. Condensation is produced by exposing one surface of a coated specimen to a heated, saturated mixture of air and water vapor, while the reverse side of the specimen is exposed to the cooling effect of room temperature air.”
ASTM D7897	Standard Practice for Laboratory Soiling and Weathering of Roofing Materials to Simulate Effects of Natural Exposure on Solar Reflectance and Thermal Emittance	From the public ASTM D7897 website:²⁰ “The solar reflectance of a building envelope surface affects surface temperature and near-surface ambient air temperature. Surfaces with low solar reflectance absorb a high fraction of the incoming solar energy. Sunlight absorbed by a roof or by other building envelope surfaces can be conducted into the building, increasing cooling load and decreasing heating load in a conditioned building, or raising indoor temperature in an unconditioned building. It can also warm the outside air by convection. Determination of solar reflectance can help designers and consumers choose appropriate materials for their buildings and communities.” “Practice D7897 applies to simulation of the effects of field exposure on the solar reflectance and thermal emittance of roof surface materials including but not limited to field-applied coatings, factory-applied coatings, single-ply membranes, modified bitumen products, shingles, tiles, and metal products.”

¹⁹ https://www.astm.org/d4585_d4585m-18.html

²⁰ <https://www.astm.org/d7897-18.html>

ASTM E84	Standard Test Method for Surface Burning Characteristics of Building Materials	From the public ASTM E84 website:²¹ “This test method is intended to provide only comparative measurements of surface flame spread and smoke density measurements with that of select grade red oak and fiber-cement board surfaces under the specific fire exposure conditions described herein.” “This fire-test-response standard for the comparative surface burning behavior of building materials is applicable to exposed surfaces such as walls and ceilings. The test is conducted with the specimen in the ceiling position with the surface to be evaluated exposed face down to the ignition source.”
ASTM E1918	Standard Test Method for Measuring Solar Reflectance of Horizontal and Low-Sloped Surfaces in the Field	From the public ASTM E1918 website:²² “Solar reflectance is an important factor affecting the temperature of a sunlit surface and that of the near-surface ambient air temperature. The test method described herein measures the solar reflectance of surfaces in natural sunlight.” “This test method covers the measurement of solar reflectance of various horizontal and low-sloped surfaces and materials in the field, using an albedometer or pyranometer. The test method is intended for use when the sun angle to the normal from a surface is less than 45°.”

²¹ <https://www.astm.org/standards/e84>

²² <https://www.astm.org/e1918-21.html>

ASTM E1980	Standard Practice for Calculating Solar Reflectance Index of Horizontal and Low-Sloped Opaque Surfaces	From the public ASTM E1980 website:²³ “Solar reflectance and thermal emittance are important factors affecting surface and near-surface ambient air temperature. Surfaces with low solar reflectance, absorb a high fraction of the incoming solar energy. A fraction of this absorbed energy is conducted into ground and buildings, a fraction is convected to air (leading to higher air temperatures), and a fraction is radiated to the sky. For equivalent conditions, the lower the emissivity of a surface the higher its steady-state temperature. Surfaces with low emissivity cannot effectively radiate to the sky and, therefore, get hot. Determination of solar reflectance and thermal emittance, and subsequent calculation of the relative temperature of the surfaces with respect to black and white reference temperature (defined as Solar Reflectance Index, SRI), may help designers and consumers to choose the proper materials to make their buildings and communities energy efficient. The method described here gives the SRI of surfaces based on measured solar reflectances and thermal emissivities of the surfaces.”
ASTM G7	Standard Practice for Natural Weathering of Materials	From the public ASTM G7 website:²⁴ The relative durability of materials in natural exposures can be very different depending on the location of the exposure because of differences in ultraviolet (UV) radiation, relative humidity, time of wetness, temperature, wet-dry cycling, freeze-thaw cycling, pollutants, and other factors. Therefore, it cannot be assumed that results from one exposure in a single location will be useful for determining relative durability in a different location. Exposures in several locations with different climates which represent a broad range of anticipated service conditions are recommended.
AWWA D102-6	AWWA Standard for Coating Steel Water-Storage Tanks	From the public AWWA D102-6 website:²⁵ This standard describes coating systems for coating and recoating the inside and outside surfaces of steel tanks used for potable water storage in water supply service.

²³ <https://www.astm.org/standards/e1980>

²⁴ https://www.astm.org/g0007_g0007m-21.html

²⁵ <https://engage.awwa.org/PersonifyEbusiness/Bookstore/Product-Details/productId/27171>

VDA 233-102	Cyclic Corrosion Testing of Materials and Components in Automotive Construction	From the public VDA 233-102 website:²⁶ “The purpose of this specification is to provide an accelerated test procedure for the assessment of the corrosion behaviour of components and of the corrosion protection provided by coating systems. The accelerated test covers in particular the delamination/corrosion creep around a defined artificial defect in a coating as well as surface and edge corrosion on special test plates, bonding specimens or components. Compared to tests with a higher humidity availability a decreased ageing rate of adhesive is to be expected. This laboratory-scale cyclic corrosion test is also suitable for assessing perforation corrosion in flanged areas or gaps and of unpainted surfaces.” “This method induces corrosion processes and generates reproducible corrosion patterns which correlate well with the results obtained in natural weathering tests (DIN 55665) and driving operation. In particular, the corrosion patterns for the substrates steel, galvanised steel and aluminium closely reflect real-life phenomena.” “The test method is based on real corrosive climate conditions and delivers differentiated results for a large number of uses in automotive applications.”
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²⁶ <https://webshop.vda.de/VDA/en/vda-233-102-06-2013>



December 2023

The American Chemistry Council's (ACC) Performance Fluoropolymer Partnership (hereafter "PFP") has developed a White Paper that focuses on the Infrastructure & Construction (I&C) end-use segments noted below. The PFP's members are some of the world's leading manufacturers, processors and users of fluoropolymers, including fluoroplastics, fluoroelastomers and perfluoropolyethers polymers.

The content provided here in this White Paper was submitted to the REACH Annex XV All PFAS Restriction Proposal in 2 parts. The submittal reference numbers are as follows:

August 27, 2023: Reference number 3eb5e616-f855-4393-abbc-e1eeb7c25ff4 and

September 24, 2023: Reference number 4cc4c0df-35b8-4354-a66c-37401d364694

These comments pertain to the use of fluoropolymers (fluoroplastics) in Infrastructure and Construction (I&C) applications. This is a commercial/industrial application/use segment with little to no direct consumer use. The fluoropolymers highlighted in this submission are listed in **Table 1**.

In this White Paper, we provide compelling case studies and technical data on the use of fluoropolymers in five (5) end-use applications that are often subject to continuous weather extremes based on the climate and/or their physical locations. Those uses are:

1. Building Facades and Protection - Metal Building Panels and Parts;
2. Roofing and Roofing Structures;
3. Bridge and Walkway Structures;
4. Water Towers; and
5. Solar Panels.

Please contact me if you or your colleagues have any questions.

Jay West
Executive Director
Performance Fluoropolymer Partnership

Table 1. Fluoropolymers highlighted in this White Paper

Polymer	PVDF	PVDF-HFP Copolymer	ECTFE	ETFE	FEVE
Name	polyvinylidene fluoride	vinylidene-fluoride, hexafluoro-propene copolymer	ethylene, chlorotrifluoro ethylene copolymer	ethylene, tetrafluoro-ethylene copolymer	fluoroethylene-vinyl ether copolymer
CAS Number	CAS 24937-79-9	CAS 9011-17-0	CAS 25101-45-5	CAS 25038-71-5	CBI
Structure	$-(\text{CF}_2-\text{CH}_2)_n-$	$-(\text{CF}_2-\text{CH}_2)_n-[\text{CF}(\text{CF}_3)-\text{CF}_2]_m-$	$\left[\begin{array}{cccc} \text{F} & \text{Cl} & \text{H} & \text{H} \\ & & & \\ -\text{C} & - & \text{C} & - & \text{C} & - & \text{C}- \\ & & & \\ \text{F} & \text{F} & \text{H} & \text{H} \end{array} \right]_n$	$-(\text{CH}_2-\text{CH}_2-\text{CF}_2-\text{CF}_2)_n-$	contains fluoroethylene and vinyl ether segments

For a Glossary of Terms, see Appendix A.

For Testing and Reference Methods in the I&C End-Uses, see Appendix B. For each of the I&C end-use applications in this submission there are a set of exacting performance testing and reference methods. Appendix B contains a list of the critical test methods and what they measure. For the primary end-uses in this submission, designers, architects and builders have specific performance standards they must meet to achieve the desired long lasting coatings performance and surface protection.

Background on Fluoropolymers (Henry et al., 2018; Korzeniowski et al., 2022)

“Fluoropolymers are high molecular weight polymers with fluorine atoms directly attached to their carbon-only backbone” (Ebnesajjad 2017). The carbon-fluorine (C-F) bond is the strongest bond between carbon and another atom and imparts unique, outstanding and beneficial properties and extraordinary functional performance to fluoropolymers. (Banks et al. 1994, Scheirs 2007, Ameduri and Sawada 2017a, 2017b, Ameduri 2020, FPG 2021) These properties (fluoropolymers enable) include chemical, biological and thermal stability, heat and chemical resistance, unique dielectric properties and durability. Additional fluoropolymer properties include improved fire resistance, weather resistance, non-wetting and non-stick. Fluoropolymers are regarded as irreplaceable in many applications because their unique combination of specific properties, which are critical to help ensure optimal performance in many applications and cannot be achieved by alternative materials (FPG 2021, 2017; PFP 2020; Henry et al. 2018).

There is considerable media and public confusion and misunderstanding regarding PFAS, as the many different chemicals and groups are often not clearly differentiated under the broad term PFAS. PFAS, a large, diverse group of substances with vastly different properties, is too broad to enable effective, science-based assessment and regulation of chemical compounds as an entire group. This point has been raised in recent publications which suggest alternative approaches to effectively group PFAS for regulatory assessment (BDI 2021, Buck et al. 2021, Orgalim 2021, RSC 2021, Wallington et al. 2021, Amcham 2020a; Miller et al. 2020). PFAS must be assessed based on their chemical, physical, thermal and biological property differences and uses (Amcham 2020a, BDI 2021, Buck et al. 2021, RSC 2021, Wallington et al. 2021). As regulatory frameworks such as the subject EU REACH regulation continue to evolve, more work is needed to clearly distinguish among PFAS types, based on their properties to assure that regulations are appropriate in scope, proportional and based on science.

Fluoropolymers have material properties which help define their functionality. The unique properties of fluoropolymers include improved durability, mechanical strength, inertness, thermal stability and resistance to chemical, biological and physical degradation. Some can be classed as Polymers of Low Concern (PLC) to human health and the environment according to OECD criteria as they are chemically stable, biologically stable/inert, negligibly soluble in water, non-bioavailable, non-bioaccumulative; and non-toxic. (Henry et al. 2018, Buck et al. 2011, Korzeniowski et al 2022).

The PLC criteria were developed over time within regulatory frameworks around the world as an outcome of chemical hazard assessment processes which identified physical chemical properties of polymers that determine polymer bioavailability and thereby inform a polymer’s potential for hazard. For example, many of the physicochemical properties, such as molecular weight, limit the ability of a polymer to cross the cell membrane and therefore limit its bioavailability (Kostal 2016, USEPA 2012, Lipinski et al. 2001).

The results from the two PLC publications show that each of the 18 commercially manufactured fluoropolymers in these studies satisfy the widely accepted assessment criteria to be considered polymers of low concern and merit such designation. The study results add further evidence to show that fluoropolymers are demonstrably different and should not be grouped with other PFAS for hazard assessment or regulatory purposes.

For the purposes of this submission supporting the I&C end-use segments noted above, we will focus on uses of fluoropolymers. These are the fluorinated polymers on the left-hand side of **Figure 1** highlighted in light blue.

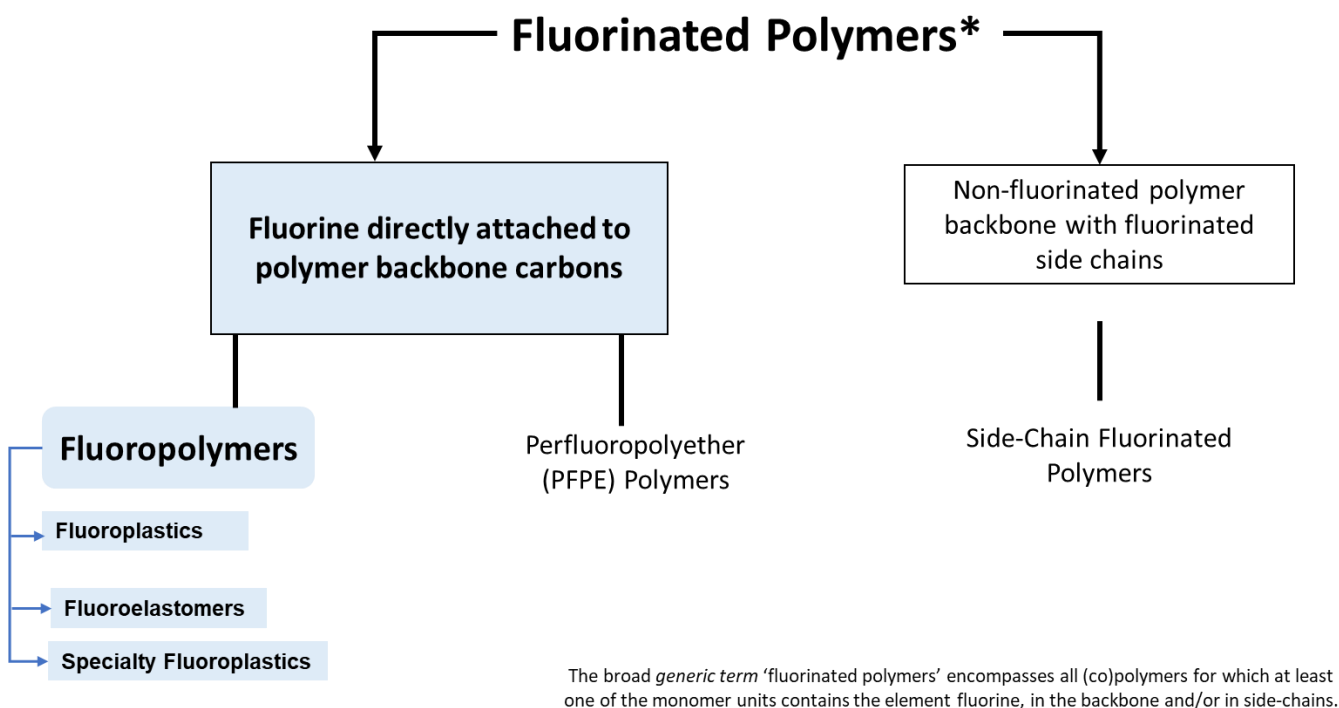


Figure 1. Fluorinated Polymers: Fluoropolymers, Perfluoropolyethers and Side-chain Fluorinated Polymers (Korzeniowski et al, 2022)

Table 2 below describes some of the core properties of the fluoropolymers that are covered in this set of comments. Some of the key critical properties noted here are increased mechanical strength, significant wear resistance, low coefficient of friction, barrier properties and improved resistance to chemicals and weatherability, among others. (Korzeniowski et al, 2022)

Table 2. Fluoropolymer Properties and Functionality.

Table zzz: Fluoropolymer Properties and Functionality Updated 19Apr

Properties		Durable				Inert - Stable					Functional						
Functionality		Mechanical strength	Wear resistance	Flexibility	Low coefficient of friction	Resistance to chemicals	Weatherability	Cryogenic properties (lower than -50°C)	High operating temperature range	High limiting oxygen index	Electrical insulator - high data transmission rate	Piezo-electrical properties	Barrier properties	Ultra High Purity grades for clean applications	Optical clarity	Low refractive index - used for optical effects	Polymer processing additive (PPA)*
Fluoroplastics	PVDF Homopolymer	•	•		•	•	•		•	•		•	•	•	•	•	•
	PVDF Co-polymer	•	•	•	•	•	•		•	•	•	•	•			•	•
	ECTFE Co-polymer	•	•		•	•	•	•	•	•	•		•				
	ECTFE Ter-polymer		•		•	•	•		•	•			•				
	ETFE	•	•		•	•	•		•	•	•		•				
	FEVE	•	•	•	•	•	•		•	•			•		•		

Polymer Processing Additives (PPA)*: also called Polymer Processing Aid, Extrusion Process Aids or Polymer Processing and Recycling Aids

Fluoropolymer Benefits, Features and Performance Properties Expected in I&C Coating End-Uses

The exceptional properties that fluoropolymers provide and/or enable in the I&C coating applications will be described more fully in the detailed end-use application descriptions that follow in this report. To help set the stage for these descriptions, we highlight below the critical parameters that determine how well a Fluoropolymer-Based Coating (FBC) and/or film functions and performs under various environmental conditions.

Flexibility is the ability of the material and its coating to bend without breaking and return to its original shape or position without damage to the exterior coating.

Wear resistance performance measures the ability of the coated surface to resist the aggressiveness of wearing medium.

Impact Resistance and Hardness is defined as the prepainted or coated metal surface's ability to withstand various impacts under the appropriate test conditions. There are various film hardness tests including the pencil test (ASTM D3363). Relative rankings for both impact resistance and hardness are often used when comparing organic coating films.

Color Retention is the ability of the prepainted or coated metal substrate to maintain its color and appearance over extended periods of time under exterior weather conditions and/or appropriate test methods simulating outdoor exposure.

Gloss Retention is a core exterior durability property that measures the retention of film gloss under UV exposure conditions.

Film Erosion is the degree to which paint films erode under harsh and/or weathering conditions. Film erosion of exterior paints and coatings is evaluated by comparison with photographic standards or reasonable facsimile. It can also be measured as a surface loss in $\mu\text{m}/\text{year}$.

Chalking Resistance is the evaluation of the degree of chalking on white or tinted exterior paint films.

Weather Resistance – Abrasion Resistance - is the combined ability of a material or structure to withstand, resist or endure harsh atmospheric weather conditions, such as extremely hot or cold temperatures, UV light, humidity, salt air or similar corrosive conditions.

Harsh Chemical Resistance is the ability of a substance to withstand, resist, or endure a chemical challenge for a specific period of time.

Corrosion Resistance is the ability of a previously painted or coated specimen to withstand accelerated and atmospheric exposure tests and subsequent evaluation with respect to corrosion, blistering as well as loss of adhesion.

Barrier Properties refers to the property of material when a specified permeable object transmits from one side to the other (from high density side into low density side).

Fire Retardancy/Smoke Suppression refers to how the painted metal materials and/or panels are evaluated, on a relative basis, for surface flame spread and smoke density measurements with that of a select grade of red oak and fiber-cement board surfaces. The property of limiting oxygen index (LOI) is the measure of the minimum concentration of oxygen in a mixture of oxygen and nitrogen that is needed to support the flaming combustion of a material. Limiting oxygen index (LOI) is the parameter most frequently used to characterize the improvements in fire retardancy.

Low Refractive Index for Optical Effects concerns the refractive index (RI), the ratio of the speed of light in a vacuum to the speed of light through a material. The lower the refractive index, the less the material bends the light, decreasing the focusing power, the reflective effect and the light dispersion. The material of an optical lens must possess a lower value of refractive index. The clarity or transmittance of a material usually increases with decreasing crystallinity, refractive index, compressibility and intermolecular interaction. Many of the optical properties of a material are related to the refractive index.

Reduced Dirt Collection or Dirt Pick-up Resistance is the ability of a coating to resist adherence of dirt over a defined period of time and avoid film darkening and an uneven appearance.

1. Building Facades and Protection - Metal Building Panels and Parts

Relevant Fluoropolymer Products Used: PVDF and FEVE

The information below is applicable to this end use as well as the metal and cool roofing end-uses.

General Introduction

Fluoropolymer-based coatings (FBCs) offer superior performance, service life, sustainability, appearance and value for applications on a wide variety of metal substrates used in commercial and monumental building projects.

These fluoropolymer-based systems include polyvinylidene fluoride (PVDF) and fluoroethylene vinyl ether (FEVE) resin-based formulations. These two fluoropolymers are the film-forming binder resins in factory-applied industrial and construction coatings used in settings where extreme durability and lifespan of several decades or more are needed to provide substrate protection. FBCs extend the lifespan of the underlying materials and are a critical specification for certain products and end markets.

FBCs are available in both coil and extrusion applications. Each type has specific uses for metal building products.

- Coil coatings are applied to large rolls or “coils” of steel and aluminum by a continuous, automated process that can run up to 700 feet per minute. The coil is unwound, cleaned, pretreated, primed, painted and thermally cured before being recoiled for shipment. This is also known as a pre-paint process.
- Extrusion coatings are spray-applied to aluminum, preformed extruded substrates in a vertical or horizontal line. The extruded product is cleaned and pretreated, then the coating is spray applied and thermally cured to set the system. This also is known as a post-paint process.

FBCs can be applied to a variety of components used in projects ranging from pre-engineered metal buildings to municipal arenas and skyscrapers (**Table 3**).

Table 3. Fluoropolymer Application Uses and Fluoropolymer Building Project Types

Fluoropolymer Application Uses	Fluoropolymer Building Project Types
• Canopies • Column covers • Curtain wall • Decorative accents • Doors and entrances • Façade systems • Fascia • Louvers • Perimeter trim • Rain and wind screens • Roofing • Skylights • Soffits • Storefronts • Sunshades • Wall panels • Windows	• Airports • Apartments and condominiums • Auto dealerships • Banks and financial service providers • Corporate campuses and office buildings • Courthouses and government centers • Hospitals and clinics • Hotels and resorts • Libraries • Museums and galleries • Performing arts centers and theaters • Recreation and community centers • Research laboratories • Restaurants • Schools and universities • Shopping and retail centers • Stadiums and arenas • Transportation stations and transit-oriented developments • Worship and spiritual spaces

Important properties that FBCs enable for construction include, but are not limited to the following:

- Adhesion, flexibility, formability, abrasion resistance, hardness and impact resistance;
- Resistance to chemicals, flame spread/surface burning; and
- Durability as demonstrated by UV-resistance, film integrity, low film erosion rate, humidity resistance and corrosion resistance.

We are unaware of another coating technology that enables the performance parameters of durability and product longevity that are the defining characteristic of FBCs.

Outdoor exposure testing provides data showing FBCs have an erosion rate approaching 50 percent less than other coating technology options used in I&C settings. This difference explains why FBCs have a life expectancy of 50 years or more in many settings compared to 20 years or less for some alternate technologies. This reinforces why FBCs are so unique and useful in the development of durable and essential building products.

Failure of the coating system will lead to the need to recoat the metal substrate or degradation of the metal substrate can occur, which may require its eventual replacement. The difference in coating performance is profound as FBCs can retain their protective properties for more than 50 years. Given the fact that exterior surfaces on infrastructure such as skyscrapers and monumental buildings cannot be easily repainted or replaced, coating performance and its subsequent substrate protection is key to overall sustainability. Driving towards less durable technologies would result in regrettable substitutions requiring field-refinishing and building component replacement leading to increases in waste and carbon emissions.

Even for buildings where repainting or replacement of metal panels is not as difficult as for skyscrapers or other monumental structures, reduced service life can present disruptions in the use of buildings housing areas such as education, medical, government and communications. In addition, field-refinishing brings with it potential release of VOCs to the atmosphere and the possibility of chemical releases to the environment.

PVDF-based Infrastructure and Construction Coatings

Prepainted metal is a high-quality product manufactured under strict quality control in the coil coating process. **Figure 2** illustrates the typical composition of a coated metal.

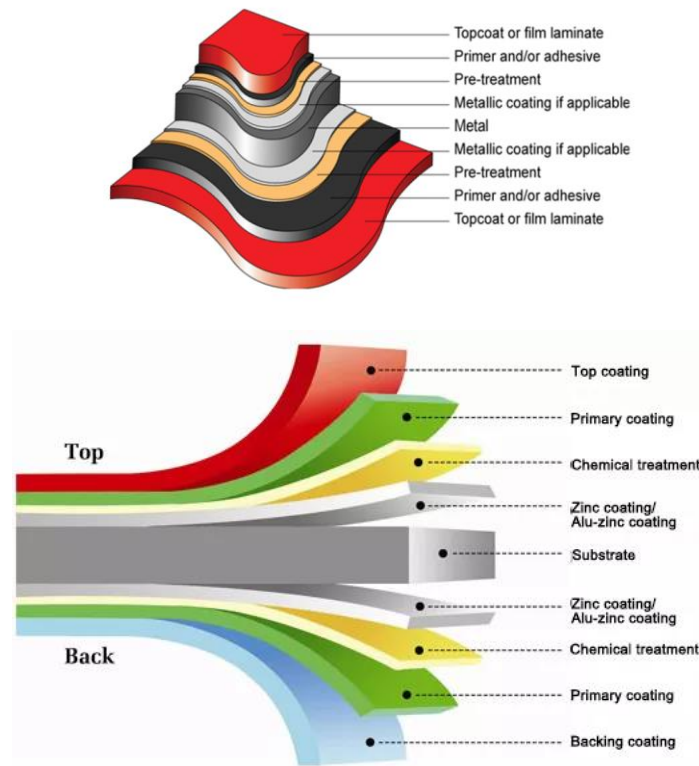
The thickness of coatings is usually quoted with a combination of top-coat and primer. In the majority of cases, the primer is a thin layer, of the order of 4 μm , the majority of the coating being the topcoat. For multi-coat systems, such as 3- or 4-coat PVDF-based coating, the total thickness including primer and 2 or 3 top-coats is usually quoted, the thickness of each layer being required for its individual function in the total system.

Liquid paints are made up of four main constituents:

- Pigments
- Binders
- Solvents
- Additives

The solvent is used as a delivery mechanism, allowing the paint to flow-out and give a smooth wet film before drying and curing. Solvents do not remain in the final, cured product. The function of the finished product is a combination of the binder, pigments and additives, but the industry standard is to refer to coatings based on the type of binder used.

Figure 2. Examples of the composition of a typical prepainted metal product.



Figures with permission from Arkema and www.yumisteel.com.

The binder is a polymeric material which gives structure to the paint. The main types of polymers used for coil coating paints are:

- Polyester
- Polyurethane
- Polyvinylidene fluoride (PVDF) and fluoroethylene vinyl ether (FEVE)
- PVC (plastisol)
- SMP (Silicone Modified Polyester)

PVDF forms a highly stable resin which is not cured in the paint in the same way as polyesters. Instead, it is fused into the paint film as a thermoplastic coating. Unlike other common coating polymers, the PVDF resins have been shown not to be susceptible to attack by UV radiation, leading to a coating that is very stable for long periods in sunlight.

FBCs tend to have coatings in the thickness range of 25 μm to 28 μm , although multi-layer systems can have higher thicknesses up to 55 μm . Unlike polyurethanes, high-build PVDF-based coatings are made up of up to 4 layers rather than the usual 2.

As mentioned above, PVDF-based film coatings have been shown not to be susceptible to attack by UV light, so the resin is highly resistant to degradation upon exposure to sunlight, unlike virtually all other polymers. This property provides a very high resistance to fading and chalking as well as very good long-term maintenance of gloss and color.

Apart from being highly resistant to UV light, the FBCs utilizing PVDF resin are also highly resistant to many chemicals and can have excellent stain resistance. Due to these superior qualities, FBCs also tend to carry a premium price compared to most other coating systems.

For this specific end-use, there has been a licensing program in place for over 50 years in order to help ensure that all specific PVDF-based coatings perform exactly at the expected level by architects and end users. All details are available online (Arkema 2022b).

Case Studies

Arkema Kynar 500® FSF® **PVDF Building Façade Case Studies:**

<https://kynar500.arkema.com/en/media/case-studies/>

Façade – Wall Panels Case Studies:

SEI Investments (PA, USA). Aluminum panel wall system meeting AAMA 2605 standards. PVDF Resin-based coating. 70% Kynar 500®FSF® system:

<https://kynar500.arkema.com/en/media/case-studies/sei-investments/>

The Valley View building on SEI Investments' North Campus in Oaks, Pennsylvania, features an aluminum panel wall system finished in 70% Kynar 500® FSF® PVDF based coil coatings. Along with these architectural coatings' vivid colors, these innovative finishes are formulated with solar reflective pigments. As with other specific 70% PVDF resin-based, high-performance, architectural coating systems, this particular application meets or exceeds AAMA 2605. It has been tested to meet or exceed the equivalent of 10 years south Florida weathering exposure conditions for color retention and resistance to fading, chalking and erosion.

DeWitt Family Service Center (Northwestern College, Iowa) Wall panel system. Coil Coatings PVDF-based system: <https://kynar500.arkema.com/en/media/case-studies/dewitt-family-science-center/>

Completed in 2019, this eco-friendly and state-of-the-art 61,000 square-foot facility creates a grand entrance to the campus of Northwestern College. It serves health science programs including biology, chemistry and the now on-campus nursing department. The building is brought to life with flat lock panels.

Appaloosa Library (Scottsdale, AZ) Wall cladding. Duranar® VARI-cool coatings:
<https://kynar500.arkema.com/en/media/case-studies/appaloosa-library/>

The one-story Appaloosa Branch Library in Scottsdale, AZ is a departure from libraries of the past that featured dark wood and dim lighting. As you approach the new Library, the building's metal skin-20,000 square feet (1,858 m²) of wall cladding changes colors. When applied and cured on properly prepared substrates, Duranar® VARI-Cool coatings offer brilliant color change along with exceptional color stability, chalk resistance, durability, abrasion resistance, chemical resistance and flexibility. The polychromatic coating utilized on the library is designed to help the structure remain beautiful for decades. The pearlescent pigments used in the coating reflect the sun's infrared [heat] energy, which helps the library stay cool and thereby consume less energy for air conditioning, even in the hot Arizona sun.

Stony Brook University (New York) Aluminum wall clad coil coating metal panels. Kynar 500® PVDF system: <https://kynar500.arkema.com/en/media/case-studies/stony-brook-university-student-c/>

An Aluminum Composite Material (ACM) was ordered in bold colors and installed as exterior cladding on an interconnected series of three buildings. The composite consists of two sheets of 0.020" aluminum thermobonded to a polyethylene core in a standard thickness in a continuous process. The composite material was pre-finished with Arkema's Kynar 500® PVDF resin-based coil coating. A wide spectrum of attractive standard and custom colors is available. Approximately 100,000 square feet of the ACM was installed on the buildings in a wide range of colors.

2. Roofing and Roofing Structures

Typical Products Used: PVDF FBCs

FBCs offer superior performance, service life, sustainability, appearance and value for applications on a wide variety of metal substrates used in commercial, monumental and other building projects. FBC systems often include polyvinylidene fluoride (PVDF) resin-based formulations. As previously discussed, PVDF is a film-forming binder resin in factory-applied industrial and construction coatings that is used in settings where extreme durability and lifespan of several decades or more are needed to provide substrate protection. FBCs extend the lifespan of the underlying end product and are a critical specification for certain end-use markets.

FBCs utilizing PVDF are typically only available in coil applications for the roofing end market. Coil-applied coatings over aluminum and steel substrates are used for metal roofing. Coil coatings are applied to large rolls or "coils" of steel and aluminum by a closed system, an automated process that runs up to 700 feet of coated material per minute.

Metal roofing can be incorporated into nearly any building type. Two typical metal roofing products are corrugated and standing seam. Additionally, metal roofing can be painted and stamped to look like other roofing substrates such as wood, shingles and slate.

Metal roofing has many inherent advantages compared to other traditional types of roofing, including:

- Better resistance to wind, hail and fire.
- Better energy efficiency, especially when incorporated with solar reflective pigment systems.
- Less weight than traditional types of roofing.
- Longer life spans (in some cases 50 years or greater) when utilizing FBCs.
- Higher circularity due to the common practices and infrastructure available for the recycling of steel and aluminum.

Important enabling properties of FBCs for metal roofing include, but are not limited to the following:

- Adhesion, flexibility, formability, abrasion resistance, hardness and impact resistance
- Resistance to chemicals, flame spread/surface burning
- Solar reflectance
- Durability as demonstrated by UV-resistance, film integrity, low film erosion rate, humidity resistance and corrosion resistance

As noted above, these fluoropolymer systems have been shown to provide numerous important benefits for both roofing and building facades. (Ref: <https://kynaraquatec.arkema.com/en/products/lower-lifetime-ownership-costs/>)

It is critical to understand that these many favorable attributes combine to provide a lower lifetime ownership cost:

- Lower energy usage from higher solar reflectivity and lower roof temperatures
 - lower carbon footprint
 - reduced dirt pick-up
 - significant mold and mildew resistance
- World-class UV resistance and long-life color retention
- Lower peak energy demand charge

- Longer lifespan of roof coating and longer lifespan of roof substrate
- Lower maintenance costs and less downtime
- Increased efficiency and longer lifespan of HVAC equipment
- Lower VOC emissions
- Support ability to seek tax credits, rebates and building codes
- Help enable Green Building credits applicability to buildings
- Versatile and can be applied to a wide variety of roofing types

Lower Energy Usage from Higher Solar Reflectivity and Lower Roof Temperatures

Higher Reflectivity (TSR value) throughout the roof's life results in lower cooling costs.

A properly formulated FBC can significantly reduce the surface temperature by reflecting the sun's rays. For roofs, it has been shown to reduce the roof's surface temperature by as much as 50°F (28°C) (USDOE) and interior temperatures by 6-9°F (3-5°C) (RCMA), which translates into reducing cooling costs by as much as 30% (CRRC).

Lower Carbon Footprint

Reduced air conditioning means less energy used, less carbon dioxide emitted and more comfortable building conditions. Lower energy bills mean less fossil fuels needed to generate electricity and so a lower carbon footprint. Add in less frequent roof cleanings and recoatings, and the carbon footprint of the project shrinks even further.

Furthermore, FBCs designed for roofing applications have shown the ability to maintain a 3-year Total Solar Reflectance (TSR) above 0.80 (Arkema 2022), well above industry standards for white roofs of 0.55 (as measured by the Cool Roof Rating Council, CRRC). This means a roof utilizing an FBC can reflect over 80% of the sun's rays. By comparison, a Modified Bitumen or Asphalt Shingle has a TSR of only 0.05 - 0.25 (CMR, 2015) (**Figure 3**). FBCs can reduce the "Heat Island Effect" of cities, where the difference between outside air temperatures in a city and its surrounding rural areas can be 5 - 9°C higher (9 -16°F) (Cool Roofs).

Figure 3. Sun's Radiation versus Solar Reflectance vs Thermal Emittance

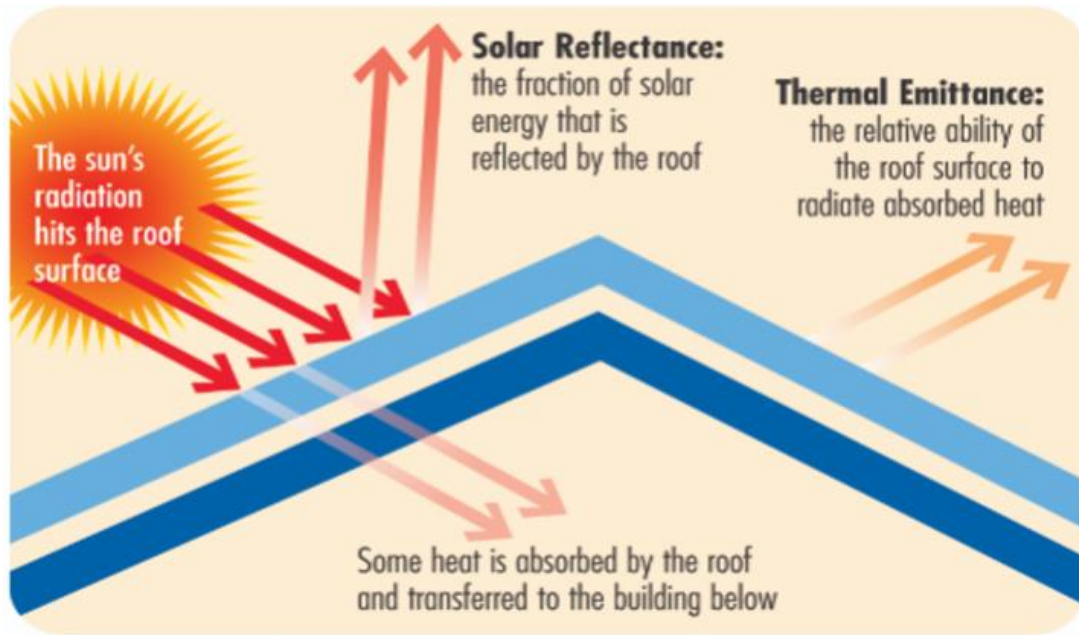


Figure with permission of Arkema.

Reduced Dirt Pick-up

An FBC topcoat's low surface energy promotes dirt shedding. The surface of a formulated FBC reduces dirt pick-up, keeping the building and other structural projects brighter and fresher looking. The pictures below show the results when a 1" square area of carbon black is applied to the paint surface and then is washed off. One can clearly see in **Figure 4** that the surface of the FBC is much easier to clean than the surface of the acrylic based coating.

Figure 4. Dirt Pick Up Study with Acrylic-Based Resin Coating vs Kynar Aquatec® Based System

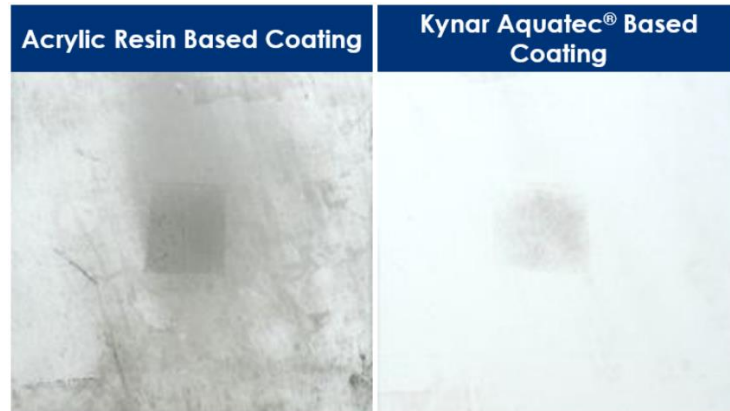


Figure with permission of Arkema

Mold and Mildew Resistance

An FBC topcoat has increased mold and mildew resistance. FBCs help to prevent mold and mildew growth. In the example below in **Figure 5**, the FBC stayed clean vs. the acrylic based coating after 19 months weathering in South Florida. No biocide was added to either coating.

Figure 5. Mold-resistance Study of Acrylic-based coating vs Kynar Aquatec® based coating

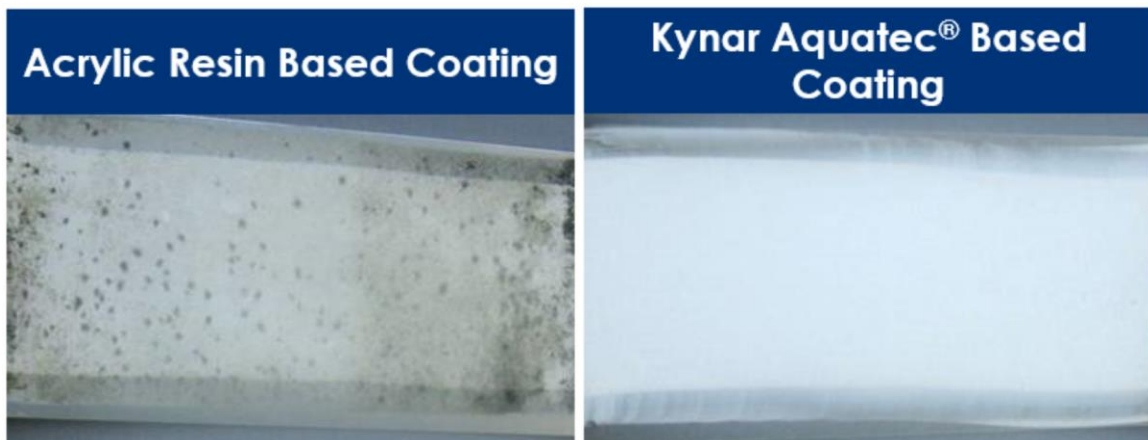


Figure With permission of Arkema.

World-class UV Resistance and Long-Life Color Retention

The FBC provides for long-lasting color retention. FBCs have been used on notable buildings since 1965. Using the same PVDF FBC technology, the FBCs have exhibited the same color fast performance. This picture (**Figure 6**) shows the color fastness after over 20 years of weathering in South Florida.

Figure 6. Twenty years of South Florida Exposure for Various Kynar Color Panels

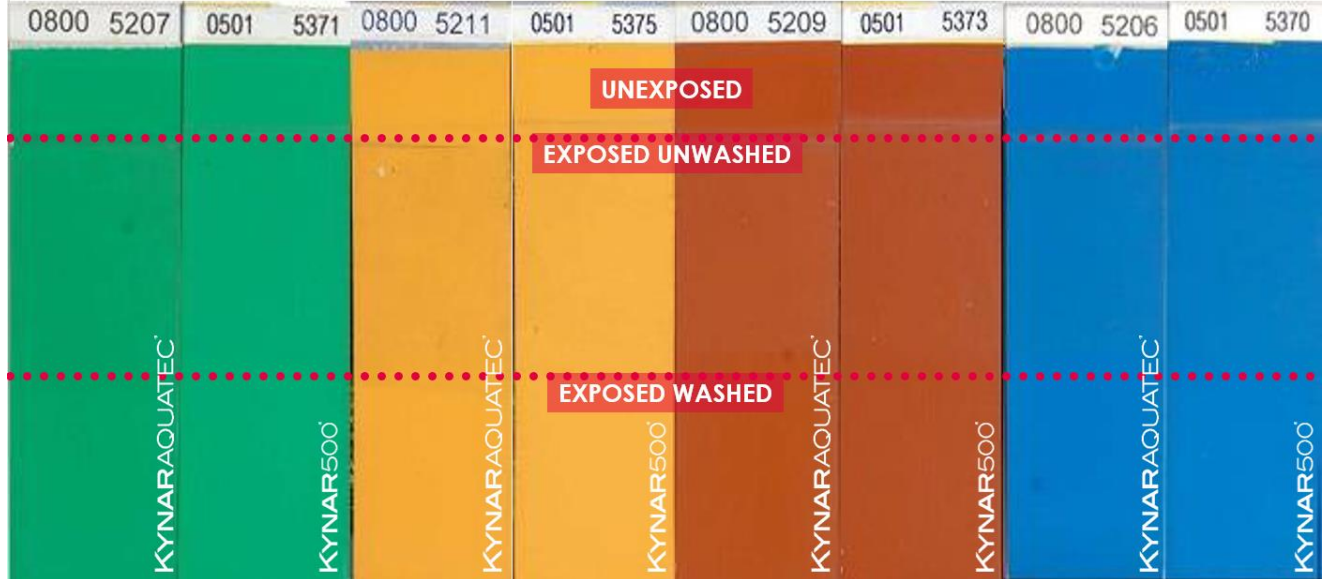


Figure with permission of Arkema.

Lower Peak Energy Demand Charges

Commercial Buildings are often charged peak demand fees by local utilities. Peak demand fees are a significant cost for commercial buildings, often greater than the electricity usage fees themselves (**Figure 7**). A 20-30% reduction in peak demand fees is common for Cool White Roofs (IRRC, 2016).

Figure 7. Kynar Aquatec® Cool Roof Energy Savings Calculator



Figure with permission of Arkema.

Longer Lifespan of Roof Coating and Longer Lifespan of Roof Substrate

Kynar Aquatec® resin-based roof coatings commonly last at least 20 years, much longer than the typical lifespan of an acrylic coating. The ability for the FBCs PVDF-based backbone to withstand the sun's UV ray is well demonstrated. This results in a longer-lasting roof coating. A lifespan of at least 20 years is expected for Kynar Aquatec®-based roof and façade coatings are quite common, well outpacing the lifespan of acrylic coatings which is low as 7 years. Additionally, the cooler surface temperature (by as much as 50°F/28°C) results in less degradation of the roofing substrate, extending the lifespan of the substrate.

Increased Efficiency and Longer Lifespan of HVAC Equipment

A cooler roof means less air conditioning (A/C) use and also means your existing equipment is more effective, extending the lifespan of your A/C unit. Alternatively, a smaller, less-expensive A/C unit could be adequate.

The cooler surface temperature (by as much as 50°F/28°C) of a Kynar Aquatec® resin-based roof coating results in several benefits: (1) less use and less wear and tear on the HVAC equipment, translating into longer service life for the equipment; (2) higher efficiency of rooftop units (due to lower inlet temperatures to rooftop air units) (Haverstic, 2016); and (3) for new construction, a small HVAC unit could be specified reducing the upfront HVAC investment.

Lower VOC Emissions

Kynar Aquatec® coatings are formulated to be low VOC. In addition, the FBCs long lifespan means less recoating (and less VOC's emitted during the recoating process) versus the other alternatives. Each time there is a recoating, volatile organic compounds (VOCs) are emitted into the atmosphere. Therefore, the less frequent coatings mean less VOCs over a defined period of time, or the lifetime of the structure. In fact, a study by Lawrence Berkeley National Laboratory showed a 30-40% reduction in VOC emissions. (CMR 2015)

No other coating technology enables the performance parameters of durability and product longevity that are the defining characteristic of FBC. Outdoor exposure testing provides data showing FBCs have an erosion rate nearly 50 percent lower than other coating technology options used in construction. This difference explains why FBCs can have a life expectancy of up to 50 years in many settings compared to less than 20 years for some alternate technologies in the same end uses. This also reinforces why FBC are critical in the development of durable and essential building products.

Failure of the coating system will likely lead to the need to repaint a metal roof or degradation of the metal substrate, which may require eventual replacement of the metal roof. The difference in coating performance is profound as FBC can last more than 50 years. Given the fact that exterior surfaces on metal roofing cannot be easily repainted or

replaced, coating performance and its subsequent substrate protection is key to meeting important sustainability objectives. Driving towards less durable technologies would result in regrettable substitutions requiring field-refinishing and building component repair and replacement, which in turn will lead to increased waste and a larger carbon footprint.

Reduced service life of metal roofing can present disruptions in the use of buildings housing areas such as education, medical, government and communication. In addition, field-refinishing brings with it potential release of VOCs to the atmosphere and exposure risks to people, animal life and the environment.

Case Studies (i.e., heat reflecting and temperature reductions).

FBCs PVDF Building Case Studies: <https://kynar500.arkema.com/en/media/case-studies/>

Florida Roofing and Sheet Metal Contractors Association (FRSA; Orlando, FL): Roof and Gutters: <https://kynar500.arkema.com/en/media/case-studies/frsa-case-study/>

This case study employed a water-based FBC PVDF resin that does not need to be baked at temperatures over 375°F, making it ideal for air-dry, field-applied coatings. The premium, weather-resistant coating can be easily applied to a variety of substrates, including metals, plastics, concrete, fiber cement, stucco, Exterior Insulation Finishing System (EIFS) and previously painted surfaces.

The use of this PVDF FBC resin and complex inorganic pigments gives the final coating system the ability to resist film erosion, chalking and fading caused by harsh UV exposure. For more information see the case study details:

https://kynar500.arkema.com/files/live/sites/hpp_kynaraquatec/files/downloads/literature-case-studies/Case-Study-FRSA-Durable-Exterior-Coating-Gets-New-HQ-Building-Ready-for-the-Long-Haul.pdf

Vinita Health Center (Tribal health center in Oklahoma): Metal Roofing. LEED Silver certified. FBC PVDF resin: <https://kynar500.arkema.com/en/media/case-studies/vinita-health-center/>

Cherokee Nation Health System, the largest tribally owned health care system in the United States, made plans to expand the 4,000 square-foot Vinita Health Center into a 92,000 square-foot building, making it 23 times larger than the original and the second largest center in the health system. With the overall inspiration taken from the community's past, historic materials like wood and stone were used as the primary construction materials. To help increase the durability and expand the lifespan of the center, a metal roof was installed on the structure. Furthermore, the use of a metal roof was selected to match surrounding community buildings, as standing seam roofs are commonly used on many other Cherokee Nation buildings. A standing seam roof, which required 43,500 square feet of Snap Clad panels finished in an FBC coating was installed.

Brandon Dunes Golf Resort (Brandon, Oregon): Metal Roof. Kynar 500®FSF® PVDF resin-based system: <https://kynar500.arkema.com/en/media/case-studies/bandon-dunes-golf-resort/>

FBCs based on PVDF resin were chosen to protect roofs of the clubhouse, snack bar and lodge against the rigors of the coastal weather.

Charles de Gaulle Airport (Paris, France). Cool Flat Roof:
<https://kynaraquatec.arkema.com/en/media/case-studies/charles-de-gaulle-airport/>
(Figure 8)

The airport has taken a step forward and chose to test the concept of saving energy linked to air conditioning thanks to passive cooling via cool roofing. A white paint that reflects the sun light waves during sunny periods was applied on the West Pier of Terminal 2G. Over 1,160 square meters were covered with the Cool Roof paint from the Cool Roof France Company. The application required 10 days and two people for the preparation of the roof/ coating application. The coating system included two layers of base coat formulated with an acrylic based paint and a topcoat based on an FBC latex.

The West (with cool roof) and East Pier (without cool roof) of Roissy airport were monitored by a consultant to estimate the efficiency of the cool roof paint system in lowering the temperature at the surface of the roof. The temperature at the surface of the roof, the temperature of the ceiling above and the ambient temperature were monitored from June 1 to September 30. A weather station also measured outside temperature (°C) and solar radiation (W/m²). During this period, the two Piers were air-conditioned and used in similar conditions with regard to passengers, traffic, etc.

Figure 8. Comparison of Cool Roof Surface Treatments at CDG Airport

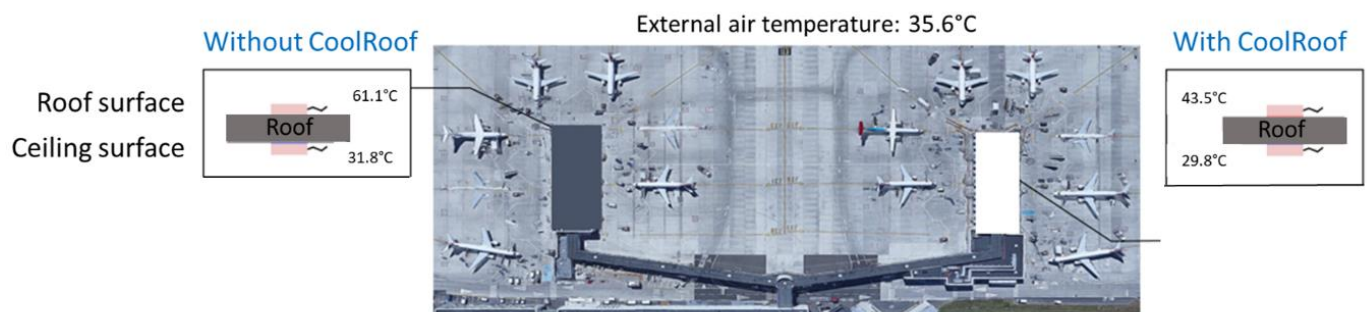


Figure with permission of Arkema.

The recorded data clearly displays the facts: the temperature of the passive cooled roof sharply lowered by 24.2°C and the energy consumption linked to air conditioning to reach desired settings inside building has seen a drop of 21% (6374 kWh, 5.5 kWh/m²). In addition, employees working all day long inside the Pier have reported a great improvement in thermal comfort during this period (as well as following years). A dark roof

absorbs most of the energy received by the sun, heating the roof structure and transferring most of heat flow to the underlying building or to the surrounding air: air conditioners that suck hot air and dump it outside can further exacerbate the cooling requirement of a building. The cool roof technology not only reflects as much of the sun's energy as possible, but also affects surrounding temperatures and offset carbon emissions.

Changwon Tunnel (S. Korea). Ceiling Coating:

https://kynaraquatec.arkema.com/files/live/sites/hpp_kynaraquatec/files/downloads/literature-case-studies/changwon-tunnel-case-study-2020.pdf See **Figure 9**

The light-reflecting characteristics of a ceiling finish enhance the overall efficiency and effectiveness of tunnel interior lighting systems. The presence of moisture and engine exhaust products in the tunnel - especially emissions from diesel power trucks - creates an atmosphere that can darken unfinished surfaces, detracting from their light-reflecting qualities and the aesthetic impression it leaves upon users. The evaluation and selection process for tunnel finish materials must therefore consider reflectivity, adaptability, cleanability, durability and public safety considerations. To improve illumination, visibility, cleanliness and safety within the Changwon Tunnel, the team responsible for maintaining the structure decided to paint the unfinished ceiling, which was dulling as a result of dirt and other airborne pollutants. Because the coating was to be applied inside the tunnel, the use of a low-VOC water-based coating was a key requirement. Other important coating performance characteristics desired were long-term durability; ability to resist dirt pick-up, biological growth accumulation and other weathering factors; and retention of reflective value and color.

Figure 9. Four-lane Changwon Tunnel in South Korea

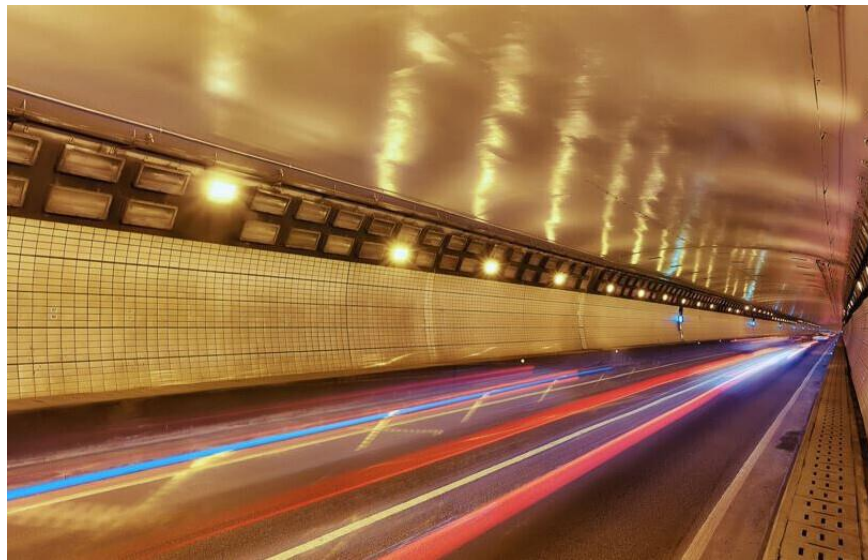


Figure with permission from Arkema.

3. Bridge Structures

Typical Products Used: FEVE

While the information in this section largely focuses on bridges, the general properties descriptions also apply to building facades and, in some cases, roofing.

Bridge structures clearly need durable coating performance to protect the painted metal substrate below and maintain the bridge's structural integrity. Any coating system must last a long time given how difficult, disruptive and expensive the recoat process is. Bridges are subject to highly adverse environmental conditions including high intensity sunlight, fog, rain, saltwater (coastal areas) spray and constant automobile exhaust among other stressor factors. The high weathering performance of FEVE allows the paint system to prolong the bridge's service life and protecting the substrate (or coated material), which subsequently decrease the number of re-painting cycles of the bridge infrastructure or building. This eventually contributes to a better (lower) Life Cycle Cost.

With its noted performance of water resistance and low oxygen permeability, a fluoropolymer-based coating systems that typically uses an FBC utilizing FEVE as a topcoat could protect the substrate (or coated material) by increasing the anti-corrosion ability of the substrate and coated material. This has the impact of prolonging the service of the paint system. Furthermore, it contributes to the reduction of CO₂ generation by extending the life of the protected material and delaying or postponing the time between re-coating the bridge structure. Less recoating is equivalent to lowering the CO₂ generated in paint system product manufacture and installation.

Oxygen Permeability Coefficient after accelerated weathering with a Sunshine Weather Meter (or weatherometer). See **Table 4**.

Oxygen contributes significantly to the ability of a substance to corrode. FEVE has demonstrated significant shielding effect under 5000 hours accelerated weathering test. Its permeability coefficient is unchanged after the 5000 hours test while the comparative alternative polyurethane film structure was deteriorated and broken after 2000 test hours.

Table 4. Permeability Coefficient for O₂ in FEVE and Polyurethane Coatings

Gas	SWM Exposure time (hrs)	Permeability Coefficient (cc • cm/cm • cm sec cm Hg)	
		FEVE	Polyurethane
O ₂	0	4.2×10^{-11}	2.6×10^{-10}
	5000	4.5×10^{-11}	Broken at 2000hrs

Data with permission of AGC.

Mechanical Properties

The FEVE coating film has almost the same mechanical modulus (E), complex modulus and attenuation rate even for 3,000 hours after sunshine weatherometer (SWM) irradiation. **Figure 10** shows retention of the ability to protect the underlying coating film and substrate over a long period of time. This means that the FEVE coating protects the base coating function as well as the substrate itself (i.e., bridge metal structure).

Figure 10. Mechanical Properties Graphs of FEVE Coating Film. In the legend, “SMW” stands for “sunshine weather meter.”

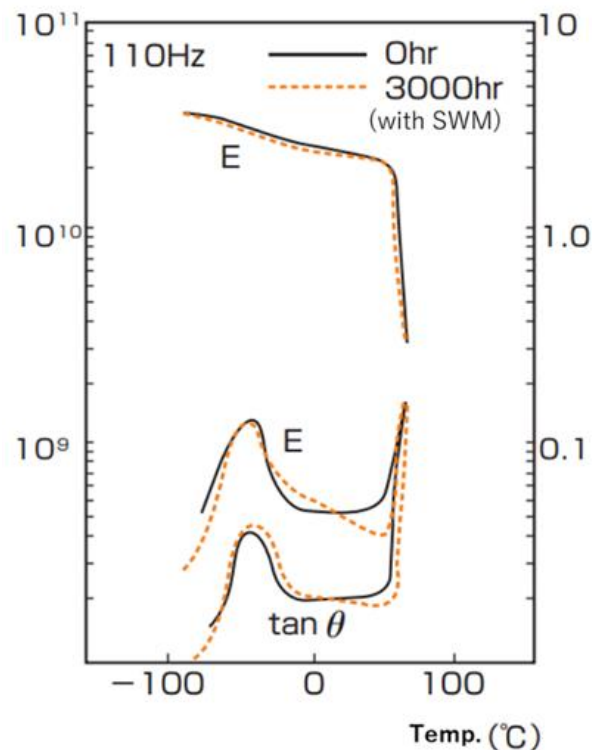


Figure with permission of AGC.

Comparison of weatherability and corrosion protection effects for four topcoat systems. FEVE was evaluated versus topcoats of polyurethane, chlorinated rubber and an alkyd system with a steel panel as the primary substrate. Each system also had a primer coating, an undercoat and an intermediate coat below the subject topcoats. These steel panels were evaluated initially by SEM (a scanning electron microscope) and then again after 2000 hours of accelerated exposure. While the alkyd surface structure was completely destroyed after the 2000 hours exposure and the polyurethane and chlorinated rubber systems also exhibited visible surface damage, the FEVE system was largely unchanged (**Figure 11**).

Figure 11. Comparison of weatherability and corrosion protection effects for topcoat systems. Picture of scanning electron micrograph for each of 4 systems along with data table for before and after exposure.

System	Topcoat	Fluoro-polymer	Polyurethane	Chlorinated Rubber	Alkyd
Substrate	steel panel				
Primer	zinc-rich primer				Wash primer
Undercoat	Epoxy resin	Epoxy resin	Epoxy resin	Chlorinated rubber	Anti corrosive Undercoating
Intermediate Coat	Epoxy resin	Epoxy resin	Epoxy resin	Chlorinated rubber	Alkyd
Top coat	Fluoro-polymer	Polyurethane	Chlorinated rubber	Alkyd	
Total Film thickness(μm)		255	255	245	170

Observation with SEM
(Scanning Electron Microscopes)

Initial surface

After Exposure surface
with SWM after 2000hrs

Results:

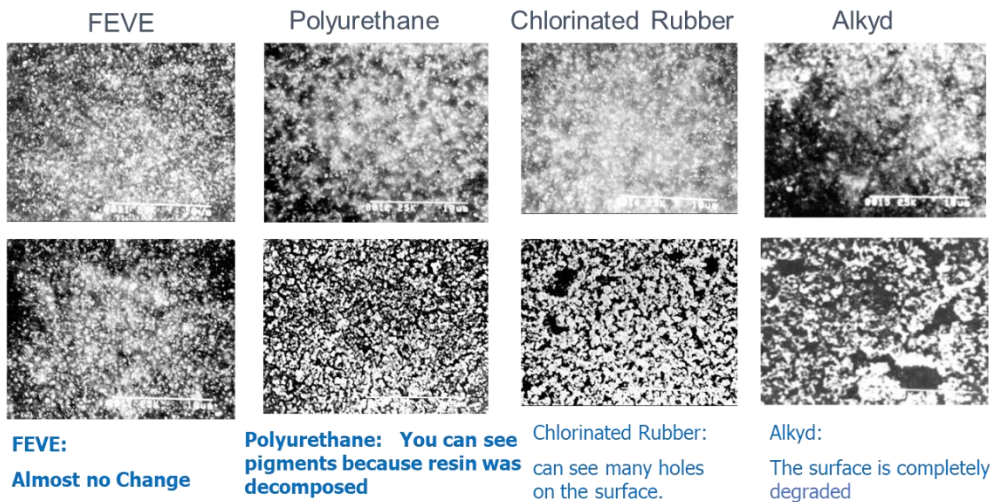


Figure with permission of AGC.

Molecular Weight Change for FEVE – Lumiflon® System vs Polyurethane. A study was conducted by the Honshu-Shikoku Bridge Authority (**Figure 12**) of the actual bridge and the test sample panel samples. **Figure 13** shows a Gel Permeation Chromatography (GPC) chart that can measure molecular weight. Molecular weight had been changed to about 1/6 for polyurethane within 3 years of offshore bridge exposure. On the other hand, FEVE has no change in the charts and little change in molecular weight. The polyurethane coating system has a broken polymer backbone. The FEVE system is intact.

Figure 12. Honshu-Shikoku Bridge Authority Coatings Study

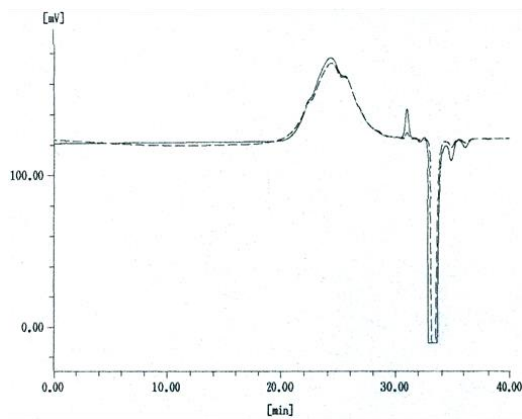


Figure with permission of AGC.

Figure 13. Molecular Weight Change Upon 3 Years Exposure in Two Bridge Coating Systems

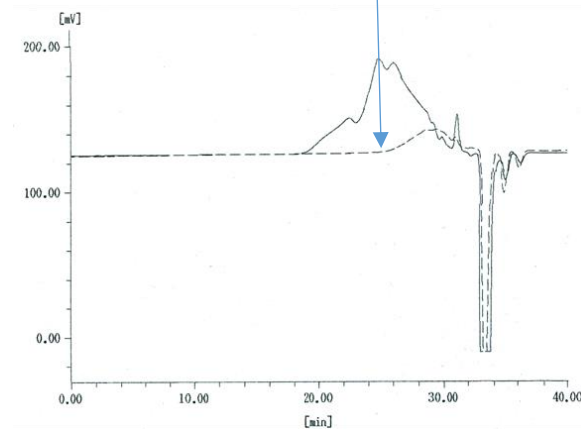
solid line - initial coated year
dotted line - 3 years after exposure

FEVE Lumiflon ® System



PU System

SHIFT



Resin	LUMIFLON		Polyurethane	
Period	initial	3 years	initial	3 years
Molecular Weight	9,000	8,400	3,600	600

Data and graphs with permission of AGC

Film consumptions of FEVE vs Polyurethane including 20 years of data for 4 topcoat systems: Alkyd; Chlorinated Rubber; Polyurethane; FEVE.

This test was done as a Hiroshima rooftop exposure about 1 km (0.6 miles) from the Japanese coast. All the systems except the FEVE system exhibited chalking. It was noted that the film coating for both the polyurethane and chlorinated rubber were severely eroded. The coating thickness of the FEVE and polyurethane systems were then measured to determine yearly film exposure loss after a 15-year exposure period. The evaluation showed a 2 μm loss/year for the polyurethane and a 0 – 0.1 μm loss/year for the FEVE system (**Figures 14 and 15**).

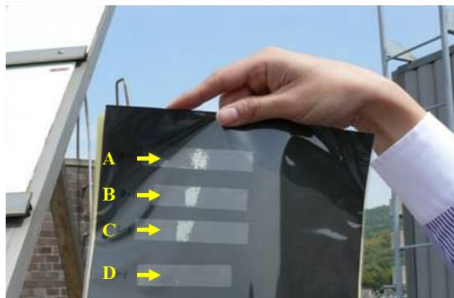
Figure 14. Film Erosion Study: 20-Year Rooftop Exposure of 4 Coating Systems.

When looking at the reflection of sunlight, everything except FEVE was chalking, and the coating film of polyurethane and chlorinated rubber was severely eroded.



20 Years Exposure

- A: Alkyd system
- B: Chlorinated Rubber system
- C: Polyurethane system
- D: FEVE system



Film Consumptions by Year
Polyurethane: 2 μm /year
FEVE: 0-0.1 μm /year

Figure and data with permission of AGC.

The ability of the anticorrosion effects depends on the coating's ability to prevent the diffusion of water and oxygen moving through the coating. Maintaining film thickness is fundamental to controlling the diffusion of corrosion substances. The fact that the topcoat of FEVE maintains its thickness for a long period of time is linked to the fact that the thickness of the middle and bottom coats is maintained, and the anti-corrosion function is maintained. On the other hand, epoxy resin, which is the under layer of polyurethane resin, loses film thickness each year due to sunlight. After the topcoat of polyurethane resin wears off, the overall coating film thickness decreases rapidly, resulting in a rapid loss of anticorrosion effects.

Figure 15. Film Erosion Study FEVE vs Polyurethane: 15-Years Rooftop Exposure

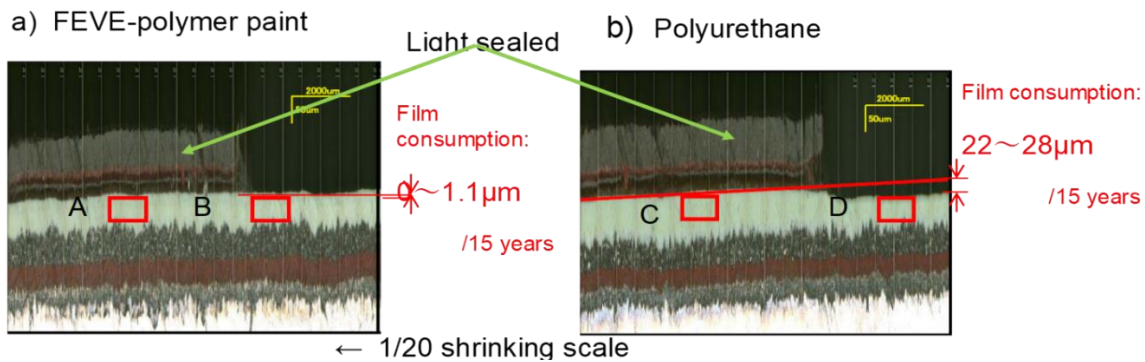


Figure and data with permission of AGC.

Polyurethane decreases by 22-28 μm in 15 years and about 1.5-1.9 μm per year. FEVE had a depletion rate of 0-1.1 μm at 15 years and less than 0.1 μm at 1 year. It can be seen that FEVE has much better weather resistance than polyurethane.

Isocyanate crosslinking retention of FEVE vs Polyurethane over a 15-year sunlight test exposure

Crosslinking in a film coating is often critical to the longevity and integrity of the film. The residual level of isocyanate cross-linking can be measured by Infrared (IR) spectroscopy. **Figure 16** shows the FEVE and polyurethane coatings in contrasting pictures, one of a light-sealed area and one in a light-irradiated area. It is quite clear that the isocyanate cross-linking in the polyurethane system was retained poorly, while the FEVE system provided good retention and will likely protect the substrate for several decades.

Figure 16. 15-Year Sunlight Exposure of FEVE polymer and polyurethane systems

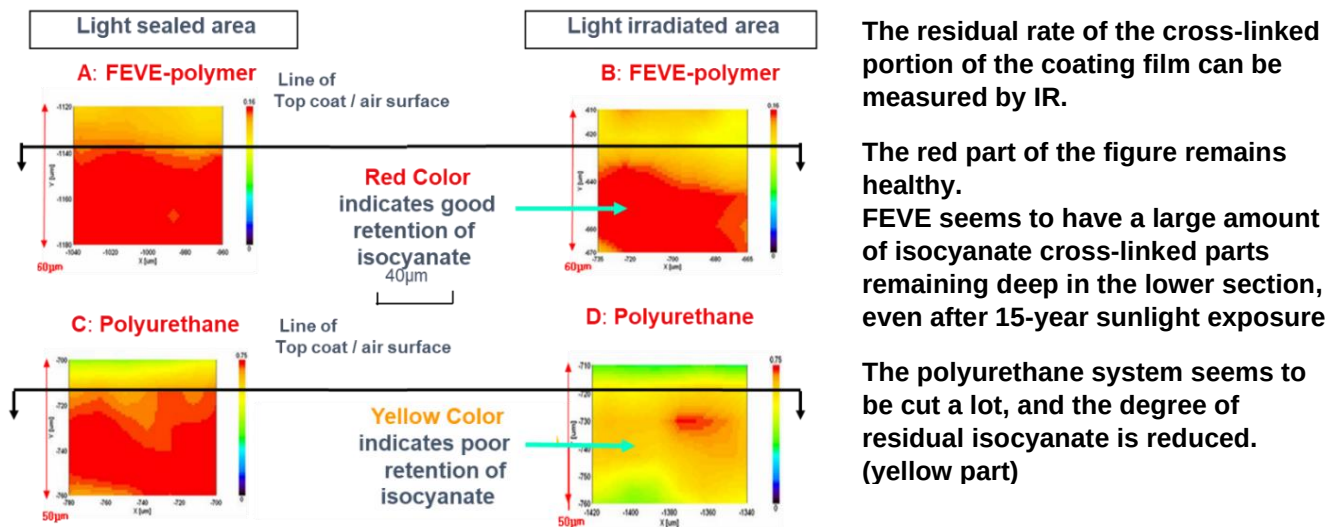


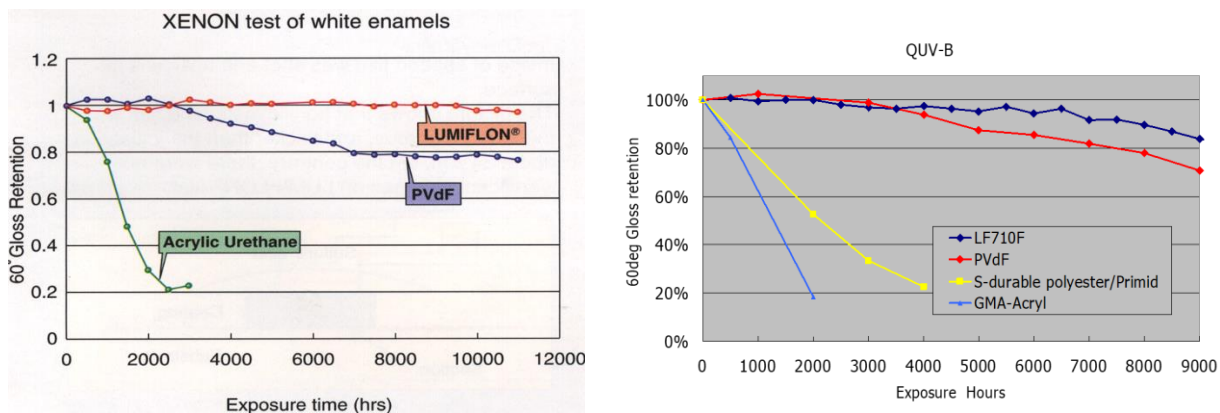
Figure with permission of AGC.

FEVE High Durability with Accelerated Weathering Tests – Gloss Retention

A standard method for evaluating exterior durability to sunlight exposure is by accelerated weathering tests. Two test types are via Xenon ARC and QUV-B. As shown in **Figure 17**, both the Lumiflon® FEVE and PVDF coatings on white enamel retained their gloss at >10,000 hours while the acrylic urethane lost about 80% of its gloss at 2,000 hours of exposure.

Similarly, both the Lumiflon® system and the PVDF coating retained their gloss even after 8,000 exposure hours in the QUV-B test. Both the Polyester and Acrylic systems suffered severe gloss retention loss at 2,000 exposure hours.

Figure 17. Fluoropolymer High Durability with Accelerated Weathering Tests



Figures with test data with permission of AGC.

FEVE low-dirt pick up systems (applicable to facades and bridges and other similar end-uses)

FEVE is compatible with many types of additives. In combination with inorganic low dirt-pick up agent such as silicate, it is possible to create hydrophilic low-staining surfaces. Façade stains are caused by dust deposited on the top, which is carried down the wall by rain and adheres to the wall. If the dirt is organic, such as black carbon, it is adsorbed by the paint film on its way down because it has a higher affinity for the same organic material than for water. Dust deposited at an angle at the top forms a strong stain on the wall with each rainfall. On the other hand, the silicate that bleeds from the silicate-added paint film onto the surface is hydrolyzed on the surface, and the silanol groups formed by hydrolysis are hydrophilic enough to adsorb water, so the surface is hydrophilic. Therefore, water forms a thin film between the paint films and dirt, and the dirt is washed away, preventing it from adhering to the paint film. Dust on the wall is washed away as water gets between the paint film. This means rain helps clean the coating system. Resin manufacturers have developed this system and shared it with paint manufacturers, making it possible to produce a much better low-dirt pick up paint film, or stain-free façade (**Figure 18**). The fact

that the surface stays cleaner may well mean improved roof aesthetics, improved solar reflectivity and heat resistance as well as less need for recoating, maintenance and cleaning.

Figure 18. Dirt Pick Up and Wash Off with Fluoropolymer-based systems

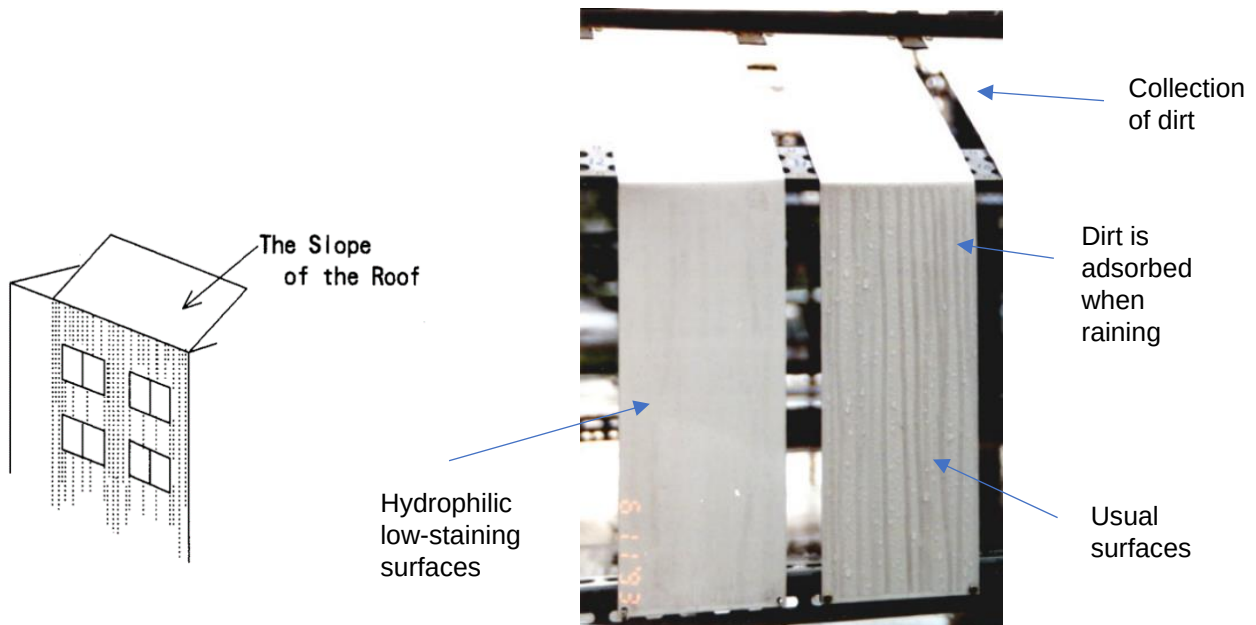


Figure with permission of AGC.

Estimation of Degradation Processes of Polyurethane System

To help visualize what occurs to a multicoat film system, a comparative FEVE versus polyurethane schematic was developed (**Figure 19**). This schematic covers a 60-year coating period for the two subject film systems. This report has provided significant information to show the longevity of the FEVE systems to indicate their useful life is in the 30–60-year range, if not longer. This schematic gives the 4-layer over substrate (steel) system – zinc rich primer, under coat, middle coat and topcoat. From the information that has been provided, it is clear that the FEVE top-coat system largely is intact throughout the study period. On the other hand, the polyurethane system exhibits marked degradation after 8-12 years and potentially catastrophic losses in the 30–60-year period of exposure.

Figure 19. Pictorial Schematic of degradation over time of FEVE vs Polyurethane

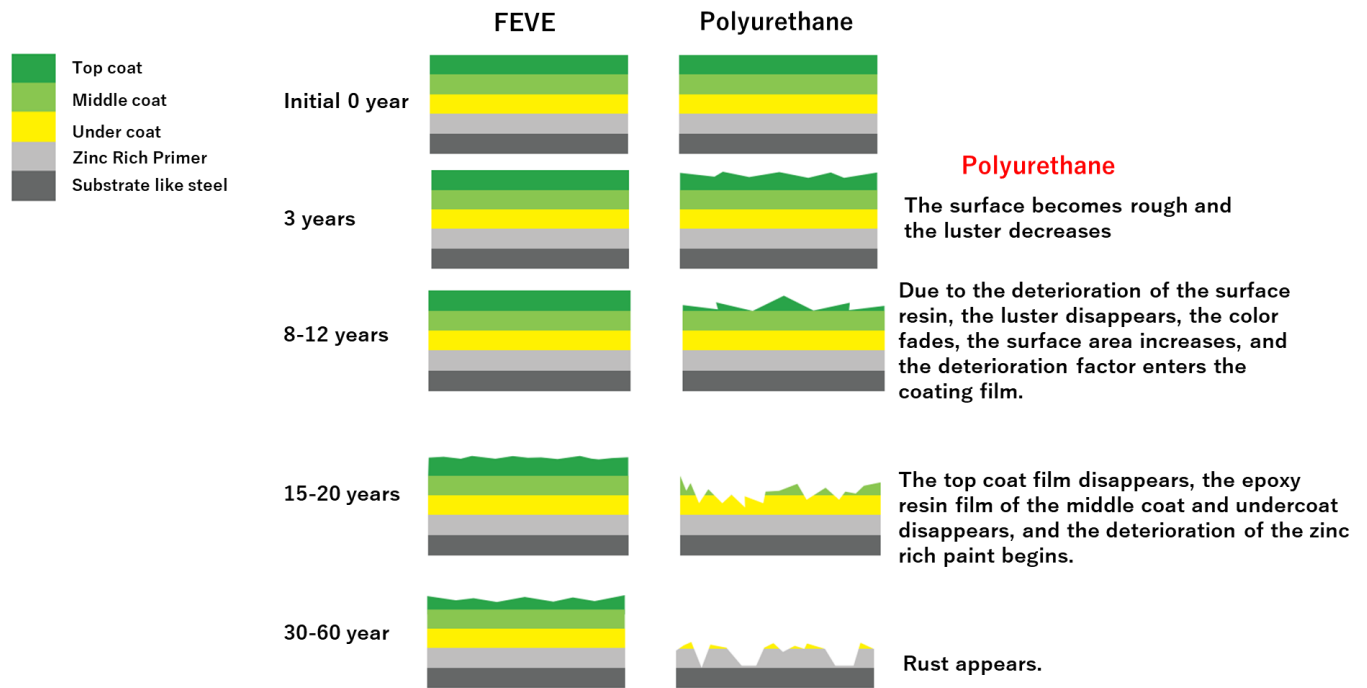


Figure with permission of AGC.

Chalking, Fading and Corrosion on Bridge Structures

Suigo Bridge Painting - 18 years of exposure for FEVE, Chlorinated Rubber and Alkyd Resin side-by-side painting comparisons.

The comparative pictures in **Figure 20** provide clear indications of the durability and long term FEVE film coating performance in terms of color fading, corrosion and chalking. A similar performance pattern can be seen when looking at the photos in **Figure 21** of the Daiichi-Mukaiyama Bridge (Mountainous area, Hiroshima). After 30 years of exposure, no chalking was evident. Gloss retention was excellent. The bolts, edges and abdominal plates were all in very good shape.

Figure 20. Suigo Bridge Paint Study



FEVE/Chlorinated Rubber rubber resin/Alkyd resin
Divided Painting

Chlorinated Rubber/FEVE



Fading

Chlorinated Rubber/FEVE



Fading



**Chlorinated
Rubber:
Chalking**

Chlorinated Rubber/Alkyd



Corrosive

Alkyd



Chalking

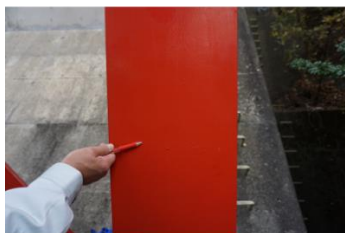
Alkyd



Corrosive

Figure with permission of AGC.

Figure 21. Daiichi-Mukaiyama Bridge (Mountainous area, Hiroshima): FEVE vs Alkyd Topcoats. FEVE topcoat after 30 years of exposure vs. alkyd topcoat after 16 years of exposure.



No chalking.
Gloss retention:
Good.
Bolts, edges,
and abdominal
plates:
Good

Alkyd section
16 years later,
peeling, rust,
With chalking

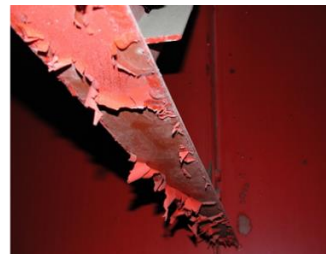
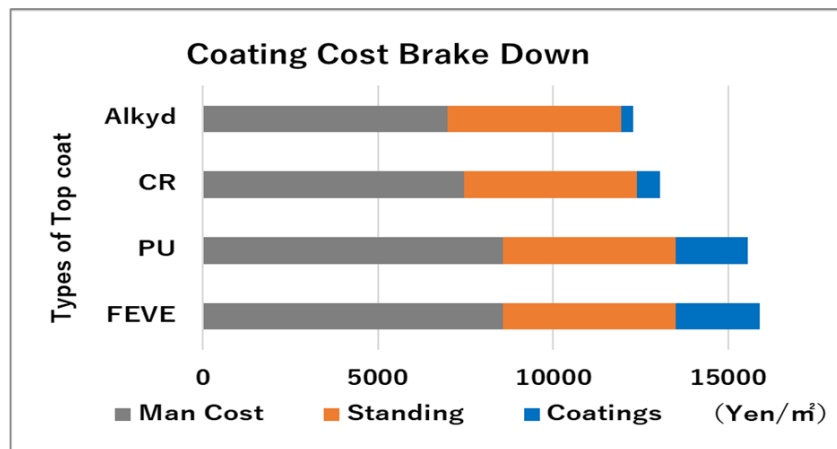


Figure with permission of AGC.

FEVE Service Life Estimated at >50 Years

Life Cycle Cost and Life Cycle Cost Reduction in Bridge Coatings using FEVE versus competitive materials such as polyurethane, chlorinated rubber and alkyd resin in **Figure 22**. It is important in creating a full picture to describe what it costs to paint a bridge structure. The estimated costs for the 4 subject topcoat systems are shown in the Cost Break Down Figure. In all 4 cases, the labor and scaffolding costs overwhelm the actual topcoat costs. The actual resin cost is only 3-15% of the total coating costs. And it is noteworthy that the FEVE system has only about a 6% price premium vs. the polyurethane system.

Figure 22. Coating Cost Breakdown for 4 Topcoat Systems. Life cycle total cost mainly consists of labor and scaffolding costs. The better the durability and the longer the repainting period interval, the lower the total cost.



Main cost (80% up) of painting cost are mainly Man - Labor and Standings (Scaffolders).

Resin cost is only 3-15% of total.

Only 6% difference between PU(Polyurethane) and FEVE system of total painting initial cost including man and scaffolder.

Figure and data with permission of AGC.

If a system is more durable and the recoat frequency is significantly lower (or extended), then the long-term ultimate maintenance costs can be significantly lower using the FBC system. Therefore, over time the costs can be lower, and the Life Cycle Costs (LCC) are greatly reduced with the FBCs.

In the Tokiwa bridge example shown in **Figure 23**, the study looked at an FBC FEVE-based coating system vs. a chlorinated rubber coating system over a > 30-year life span of the bridge coatings. The chlorinated rubber system needed repair every eight (8) years whereby the FBC FEVE-based system was intact even at >30 years. The pictures

show the visible performance of the FEVE system even after 30 years of exposure. The overall LCC savings can be significant even though the initial total coating costs were about 47% higher. Please take note that over the >30-year exposure horizon, the FBC system costs about 37% of the alternative chlorinated rubber system.

Figure 23. Tokiwa Bridge FEVE vs Chlorinated Rubber 30-Year Exposure Test

Tokiwa Bridge 30years

3y



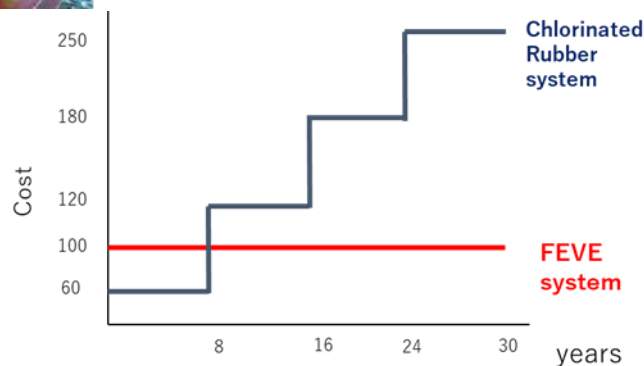
16y



30years



Item	Unit	FEVE System	Chlorinated Rubber	Ratio F/C
Top Coat	¥/m ²	502	101	500%
Pain total	¥/m ²	1,724	278	620%
Man Cost	¥/m ²	3,696	2,796	132%
Standing	¥/m ²	3,957	3,297	120%
Total	¥/m ²	9,377	6,371	147%
Durable Life	years	> 30	8	> 375%
Interval	time	Only initial	4 estimated	-
Total Cost	¥/m ²	9,377	25,484	> 37%



Actual Life Cycle Cost Reduction with FEVE

Figure with permission of AGC.

For clarity, the items in the table below include the standing cost which is the scaffolding. The Man cost is the labor. The Paint costs are the primer, under and intermediate layer costs. And the topcoat is either the FBC or the chlorinated rubber system. A relative comparison of the total cost ratio of 4 topcoat systems as well as the projected 100-year costs are shown in **Figure 24**.

Figure 24. Comparison of The Total Cost Ratio in 4 Topcoat Systems and the 100-Year Costs

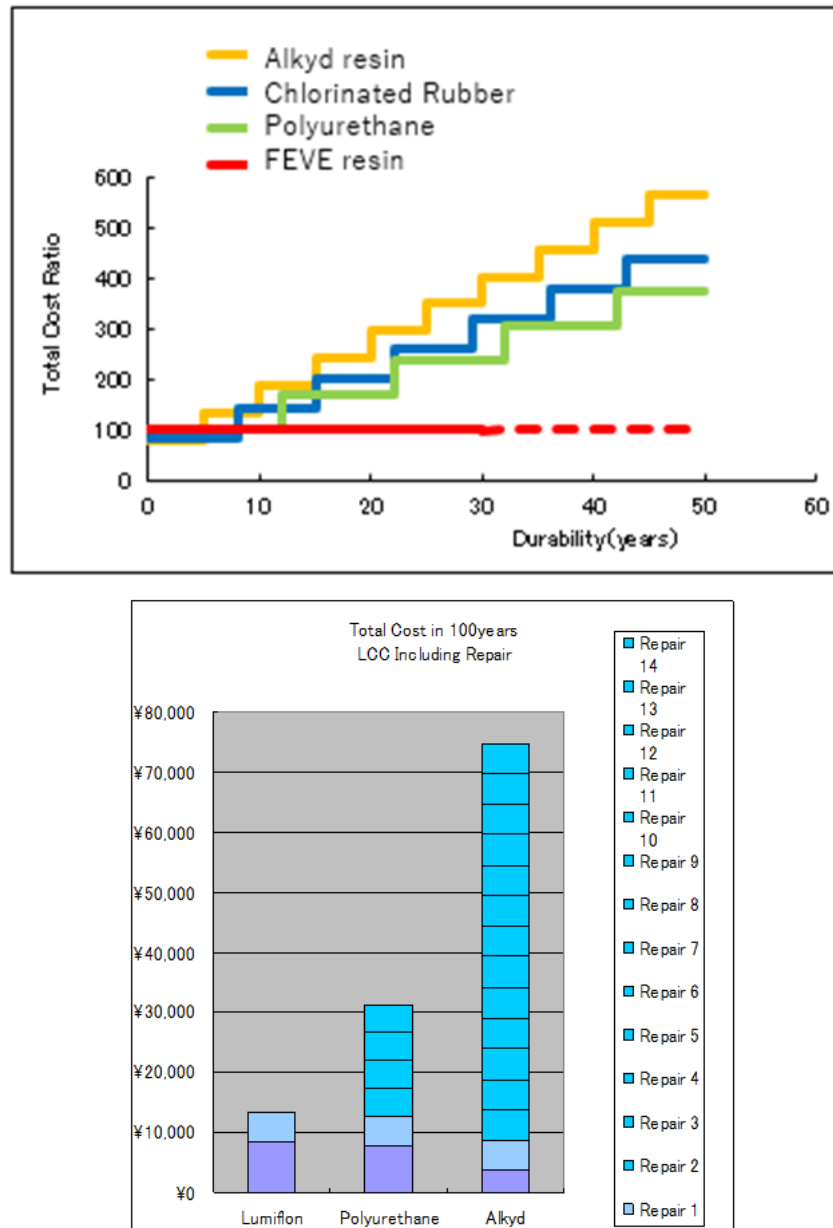


Figure with permission of AGC.

Expected Lifetime by Japan Paint Manufacturers Association (JPMA)

Table 5. Expected Topcoat Lifetime of an FEVE and a PU System

Authority	FEVE Top system	Polyurethane Top system
JPMA	60 years	18 years

Table with permission from AGC.

JPMA calculated the lifetime as the repainting time when the film thickness of the topcoat is reduced by 80% and rust has not appeared on the coating (**Table 5**; JPMA, 2002).

FBCs have a much longer durability when compared to more standards systems/chemistries, leading to a much lower impact on the environment (in kg CO₂). The extended durability and reduced need for both recoating and repairs can lead to a much lower overall LCC. By using an FBC as a topcoat, the overall cost over the lifetime of the system can be much lower, leading to more than 50% cost decrease (ECCA, 2023).

Life cycle and global impact assessment: Independent studies have been conducted by the European Council of the Paint, Printing Ink and Artist's Colours Industry (CEPE) leading to the following conclusions in building cladding panels (**Figure 25**).

Figure 25. Comparison of kg CO₂-equivalents Emissions Estimates for Various Cladding Panels

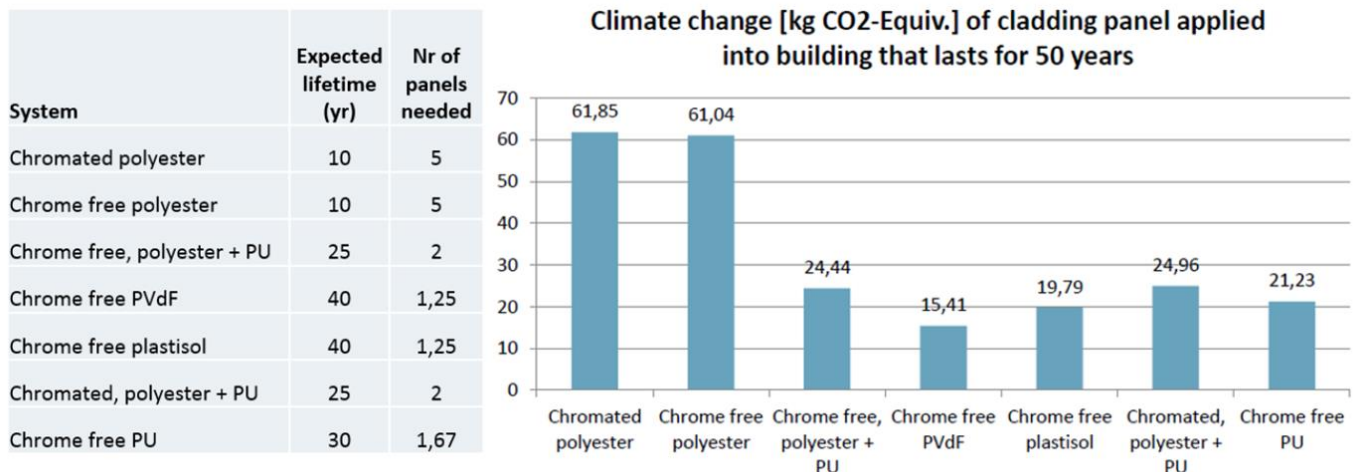
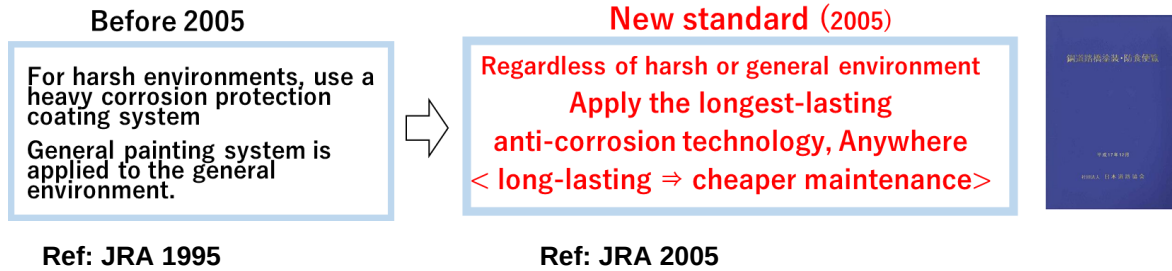


Figure with permission of CEPE.

Specification and Standards Discussions

Japan. Beginning in 2005, the only permitted topcoat system for bridges in Japan are the FBCs utilizing an FEVE-backbone. The other alternative systems, including polyurethane, chlorinated rubber and alkyd resins cannot be used as they have been withdrawn from the standards. The objective of the new regulation was life cycle cost reduction as well as sustainability. In summary:



ISO 12944-5

This ISO standard includes binders for the coating base that contain free hydroxyl groups (e.g., polyester, acrylic, epoxy, polyether, fluororesin (FBC)) which react with suitable isocyanate curing resin. In addition, there is a description of FEVE coatings noted as a special type of polyurethane based on fluoropolymers. **Table 6** lists some of the other global standards that include fluoropolymer systems like FEVE.

Table 6. Application, Specifications and Regulation in the World

No	Nation	Name (Organization /remarks)
ISO12944-5	Global	Paint and varnish – Corrosion protection of steel structures by protective paint systems
HG-T3792-2011	China	Standard for Cross-linked Fluoropolymer Coatings (Paint Industry Association)
HG-T4104-2009		Standard for Waterborne Fluoropolymer Paint (Paint Industry Association)
TBT 1527-2011		Protection Coating Standard for Railway Steel Bridges (Ministry of Railways)
TBT 3228-2010		Protective Coating Standard for Concrete on Railroads (Ministry of Railways)
JT T722-2008		Technical Standard for Steel Corrosion Protection for Public Road Bridges (Ministry of Highway)
13201-639、99-7.7	Korea	Anti-corrosion Coating Standard for Highway Bridges, Other 2 organization
TCVN11416	Vietnam	Fluoro resin paint for steel structure
	Myanmar	QUALITY CONTROL MANUAL FOR STEEL BRIDGE
Spec2911/2PU	Aus. N.Z.	Coating Organizations (including government)
D102-06	US	Water Tank (American Water Works)
BMS10-72		Boeing Standards
Mil-L5606,L7808		U.S. Air Force Standards
AAMA2605-05		AAMA (American Aluminum Manufacturers Association)
SSPC		
Qualicoat	EU	Class 3

Table with permission of AGC.

Numerous long-span bridges were built based using these standards. The following pictures provide real-world examples (pictures with permission of AGC).

- **Akashi Strait Bridge:** At the time of construction, it was the longest suspension bridge in the world. It is now the second longest bridge in the world.
- **Tokyo Gate Bridge:** This bridge was installed at the entrance and exit of Tokyo Bay.
- **Ping Tang Bridge:** After the FBC coated bridge standard was established, this bridge was built as a combined railroad and road bridge.

Akashi Strait Bridge (1998)



Tokyo Gate Bridge (2012)



Ping Tang Bridge (China)



VOC Reduction

Figure 26 shows the VOC emissions of solvent-based resin paints over time. The calculations are for the topcoat only. The calculations were made according to the JPMA (Japan Paint Manufacturers Association) service life for Alkyd, polyurethane and FBCs utilizing FEVE, which were calculated to be 7, 18 and 60 years, respectively. The longer service life of FBCs reduces the number of re-coats and significantly reduces the amount of VOC emissions. Since the middle and bottom coats are also protected by FEVE and have a long service life and do not need to be recoated, the overall coating system, including the middle and bottom coats, can achieve even greater reductions in VOC emissions than shown in the Figure.

Figure 26. VOC Emissions Over >100 Years Service Life for 3 Topcoat Systems

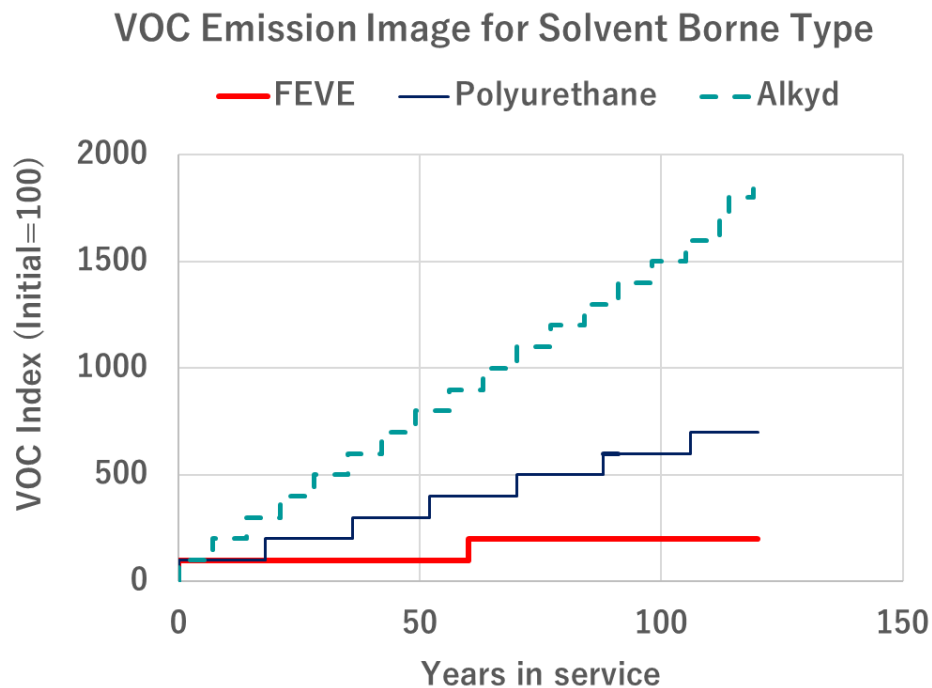


Figure with permission of AGC.

One also needs to consider the VOC reductions in powder FBCs utilizing FEVE Powder Coatings. The VOC emissions for the powder FBCs are essentially zero for the several decades of service life for the façade-wall panels or roofing panels. **Figure 27** compares the VOC index for the FEVE-Powder Coating to both a polyester-water based system and a polyester-solvent based system. The VOC reduction is significant with the powder FBCs utilizing FEVE Powder Coatings.

Figure 27. VOC Emissions Index for 3 Coating Systems over 50 Years

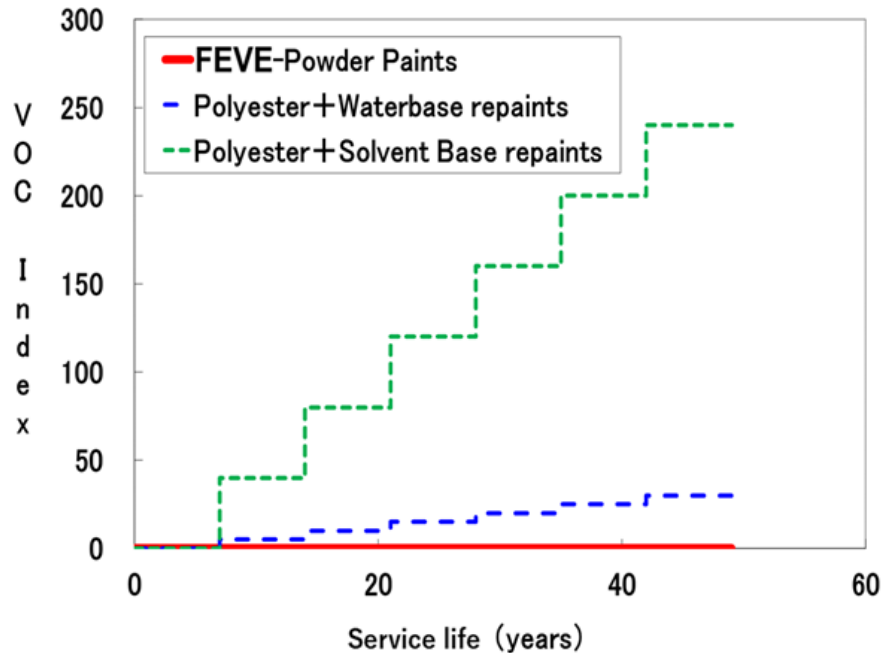


Figure with permission of AGC.

Powder FBCs utilizing FEVE ultra durability reduces VOC emissions over decades.

CO2 Reduction in the field for Façade and Building Panel Life Cycle

The CO2 emissions of paint systems using panels painted with the powder FBCs utilizing FEVE save CO2 - significantly more than polyester paint system in architectural fields over a 100-year structure evaluation.

The powder FBCs utilizing FEVE have a significantly lower life-cycle CO2 emissions than the polyester powder paint system by 47%. For emissions during the initial coating phase, the FEVE powder paint system emits more CO2 than the polyester powder paint system. However, overall emissions are lower due to its higher durability and lower number of repaints over the 100-year life of the building. Note that the repainting system is usually done twice with epoxy/polyurethane. At the time of these calculations there was no inventory of epoxy resin, so polyurethane was substituted. However, it is estimated that there is no significant difference between the two recoat systems (**Figure 28**).

Figure 28. CO₂ Reduction Over 100-Year Life of Building Façade-Panel

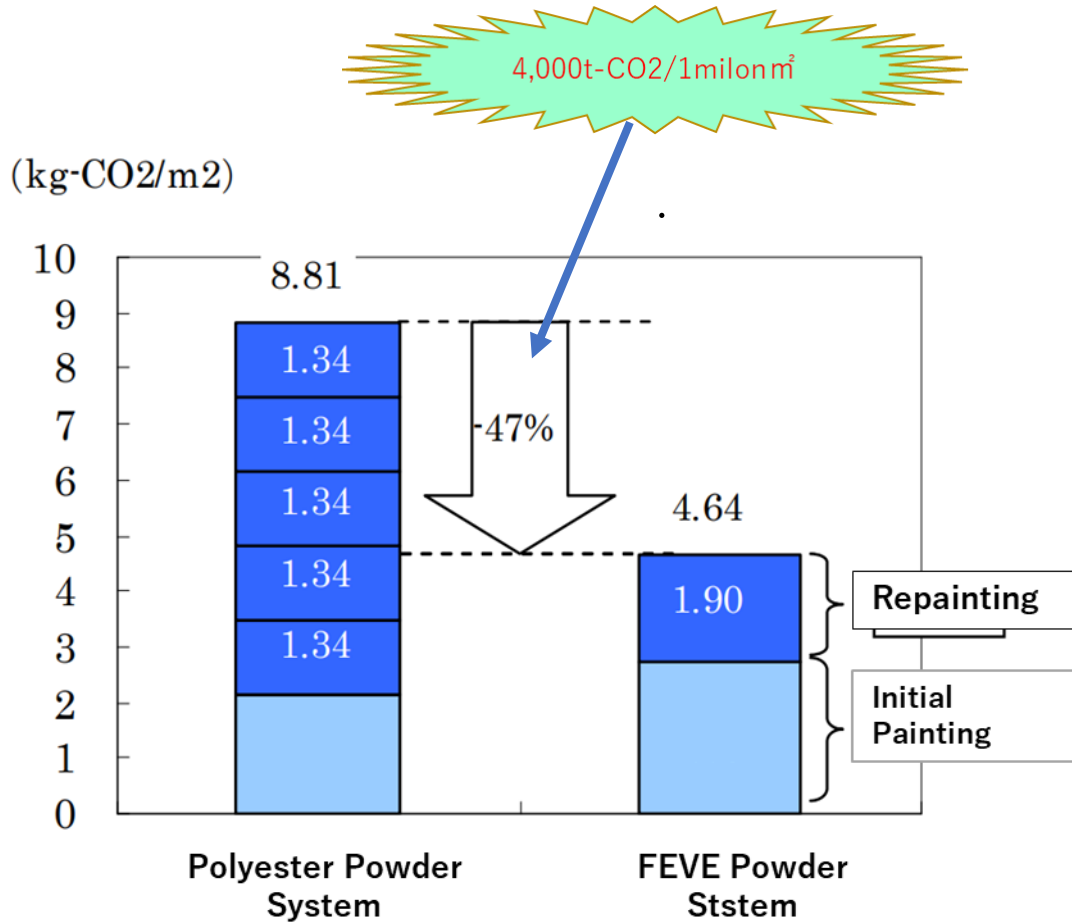


Figure with permission of AGC.

CO₂ Reduction in the field for bridges LC (Life cycle)

The FEVE protective coating system saves approximately 38% more CO₂ than a polyurethane protective system in 100-year life evaluation of bridges (**Figure 29**). As is the case above with facades and panels, the initial CO₂ emissions during the first coating were higher than the polyurethane system. Predictably, overall emissions are expected to be lower due to the FEVE system higher durability and lower number of repaints over the 100-year evaluation life of the bridge.

Figure 29. CO₂ Reduction Over 100-Year Life of a Bridge

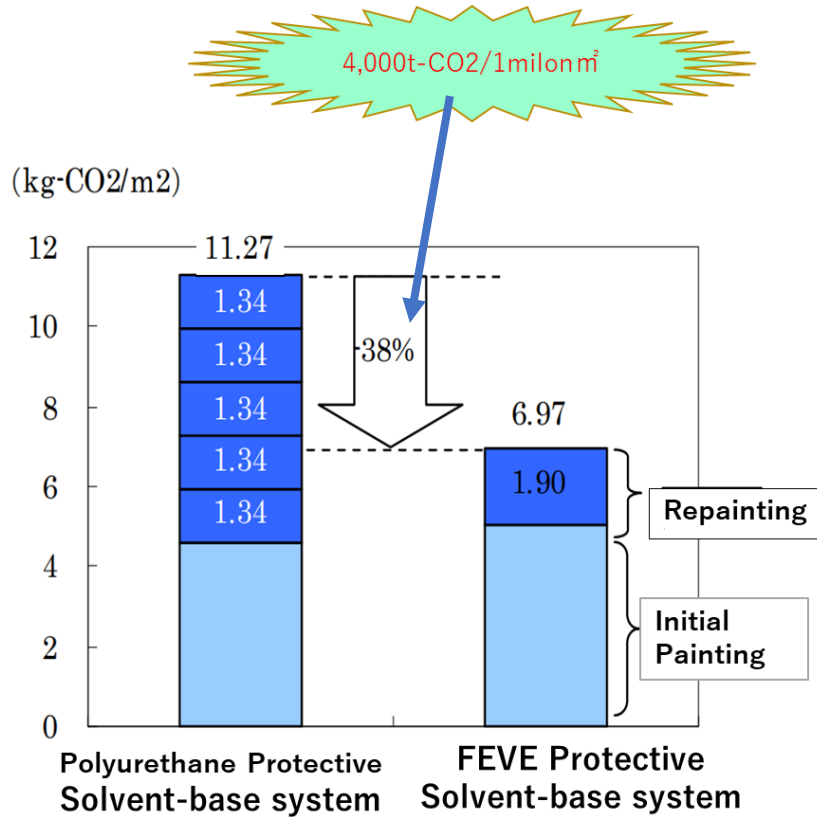


Figure with permission of AGC.

Green Building Certification

An important recent certification for CO₂ reduction and VOC reduction is green building certification. The certification is an important point of appeal for ESG (environmental, social, governance) investment. FEVE powder- and water-based grades earn green points with the paint maker's declaration. In New York City, the 10 Hudson Yards building achieved LEED Platinum, while 30 Hudson Yards achieved LEED Gold.

Photo of 10 and 30 Hudson Yards, NY, NY



Permission obtained from Carlos David/Shutterstock.com.

Examples of LEED-certified buildings:

[LEED Platinum Office Building Revitalized Downtown Pittsburgh with High Performance Energy Efficient Façade – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[Architects Design First LEED Platinum Government Building in Maryland – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[Architects Design Award Winning Multi-Family Housing Complex with Stunning Exterior Designs – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[NBBJ Designs Facebook Spring District In Washington With Sustainable Design – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[Architecture – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

[Award Winning Hudson Yards Lobby Features Mixture of Tactile Materials – Lumiflon FEVE Resins \(lumiflonusa.com\)](#)

Figure 30 (photos with permission of AGC) shows three different types of low-to-no VOC concrete skyscraper coatings, including:

- a. FBC utilizing FEVE which can be applied at ambient temperature and on-site solvent coating;
- b. FBC utilizing FEVE which is water-based, where there is less concern about VOCs and solvent odors; and
- c. Concrete panels which can be coated with FBCs utilizing FEVE in the factory at temperatures below 100°C and installed on site.

Figure 30. Three Types of Concrete Building Coating Systems Illustrated by Office Buildings in Tokyo

a. Painted on site



b. Water-based repainting on site coating



c. Low temperature coating panel in factory



Water Towers

Products Used: FEVE

FBCs utilizing FEVE have become more common for water tank coatings (in the US). These FBCs utilizing FEVE do have a price premium for the initial cost of application. As discussed below, there are considerable coating and applications cost savings over the life of the FBC utilizing FEVE-coated water tank. Therefore, coating costs are lower over the lifetime of the tank. There is also a reduced environmental burden in terms of lower solvent emissions as well as surface preparation and blast media for removing the old coating and materials disposal.

One of the most important advantages of an FBCs utilizing FEVE is that it can be cured at ambient temperature. Therefore, it is possible to apply the coating outdoors and/or on site. This would include not only newly constructed water tanks, but also existing water tanks with deteriorated coatings that can be refurbished on site and given a longer service life.

This FEVE fluoropolymer-based system can be used to coat the exterior of the water tank at the same time the tank interior is repainted with an epoxy or related system, thus reducing overall down time. The interior coatings are not subject to the exterior harsh environment of the tank itself therefore an epoxy-type system is appropriate. The interior and exterior coating life can be closely matched so they are repainted at the same time and cut down time by up to 50%. For towns and water districts with limited budgets or future budget uncertainties, lowering infrastructure costs is helpful and often necessary.

Another advantage that an FBC utilizing FEVE product has is that it can produce very beautiful and vivid colors on the exterior of the water tank. Using an FBC protects this investment. See the water tank images at <https://lumiflonusa.com>

These familiar designs could be used as a community amenity or landmark. It is possible for them to become one of the region's representative infrastructures. An FBC utilizing FEVE has a longer life expectancy with the expectation of not fading for decades. This has not been shown with conventional polyurethane resins that fade in a few years.

Water tanks are high above the ground and therefore have an increased safety risk to paint and repaint, and they require scaffolds for a clean finish. Painting work other than paint is usually expensive. As was noted in the bridges section, the cost of paint is less than 20% of the total coating process costs. The major costs largely consist of scaffolding and labor costs. The long-life cycle of the fluoropolymer-based paint system (extended over several decades) has not been shown with polyurethane coatings. The several decades life cycle can be realized with FEVE fluoropolymer-based resin system. The Life-Cycle Cost is reduced due to the reduction in the number of recoatings required over the life of the water tank. With fewer repainting cycles there is less tank downtime.

FEVE thus serves as a stable technology for the long-term maintenance and management of water tanks as an important infrastructure that supplies the life-giving water that is essential to human life. The FEVE Coating system has been incorporated into the water tank painting standards (AWWA, 2007).

Solar Panels

Products Used: ETFE; PVDF; Zeffle®; FEVE; PVF

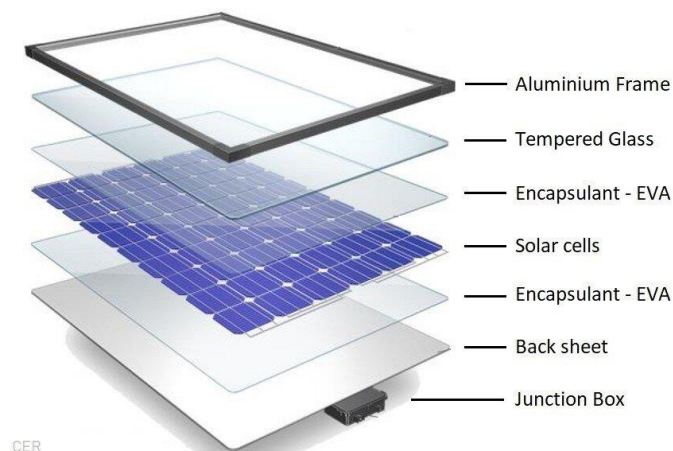
Fluoropolymers are often used as back sheets (films) in photovoltaic solar panel construction (**Figure 31**). Materials used in this end-use should have significant UV resistance and stability, corrosion resistance and flexibility. Fluoropolymers are light in weight and have extended durability in full exposure to a variety of environmental conditions, including intense sunlight and heat. Other materials used in back sheet applications are polyamides, polyethylene terephthalate (PET), glass and polyesters. A number of studies have been conducted to evaluate these materials and viable alternatives. (DuPont PV Study, 2020; OECD, 2022; GSPI, 2021)

Numerous uses of fluoropolymers are documented in solar panel manufacture and use. Fluoropolymer coatings or films may be incorporated into the glass top layer of panels, the encapsulant film that surrounds the solar cells and the back sheet. Fluoropolymers reportedly increase durability, transparency, UV-resistance, heat-resistance, mechanical strength, dirt-repellency and energy production, and they are lightweight. Halar® (ETFE), Tefzel® (ETFE) and Lumiflon® (FEVE), as well as polyvinyl fluoride (PVF) and PVDF, are among the fluoropolymers used for solar panels. (GSPI, 2021; AGC, 2021)

Back sheets are used on solar panels to help protect the solar cell from weather, humidity, loads, and impact damage. It has also been noted that they also help provide electrical isolation for safety purposes. The proper choice of the back sheet can increase the panel life and reduce the cost of electricity generated from the panel over the solar panel cell's life. Requirements for the back sheet include opacity and high reflectivity.

Back sheets as shown in **Figure 31** are typically laminates often consisting of PVF, PET and poly (ethylene-vinyl acetate) (EVA or PEVA) films. For example, PET films are used in applications where increased UV stability is desirable. These applications include back sheets on solar panels as well as architectural and automotive protective films. It should be noted that PET will degrade over time reducing its ability to protect the desired substrate. PVF and Lumiflon® FEVE have been used as a weather resistant topcoat layer that helps protect the PET and EVA from degradation, especially from UV light.

Figure 31. The 6 main components used in the construction of a solar panel



From: <https://www.cleanenergyreviews.info/blog/solar-panel-components-construction>

To demonstrate the benefits of the fluoropolymer coating on the non-fluorinated film layer, two examples are provided below for illustrative purposes. The first is a xenon arc accelerated weathering test. In this test, the FEVE polymer-coated PET film was subjected to 3,000 hours in a weatherometer, a device used to evaluate UV aging. The results were compared to the uncoated PET film and the Color change (ΔE) was measured. Results are shown below in **Figure 32**. After 3,000 hours, the PET film coated with the FEVE-based topcoat shows no change in color, while the uncoated film has a visible decline in appearance.

Figure 32. Xenon Arc Weatherometer Test Results of FEVE-coated and Uncoated PET Film

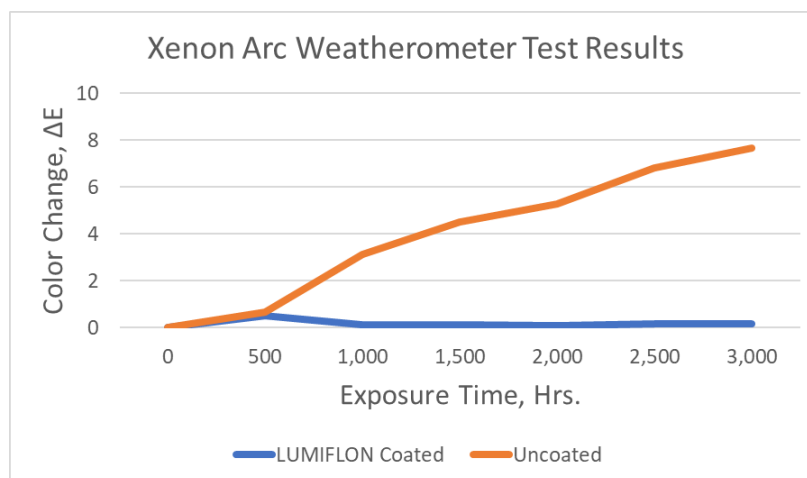


Figure with permission of AGC.

In the second test to evaluate UV stability of the Lumiflon® FEVE-based fluorourethane coating compared to that of PVF-based coating, panels were placed in the Xenon Arc Weatherometer for 5,000 hours. When color change of polymers is measured, B* is an indicator of yellowing. B* was monitored over the duration of the test; results are shown in **Figure 33** below.

Figure 33. Xenon Arc Weatherometer Test of PVF and FEVE Laminate Films

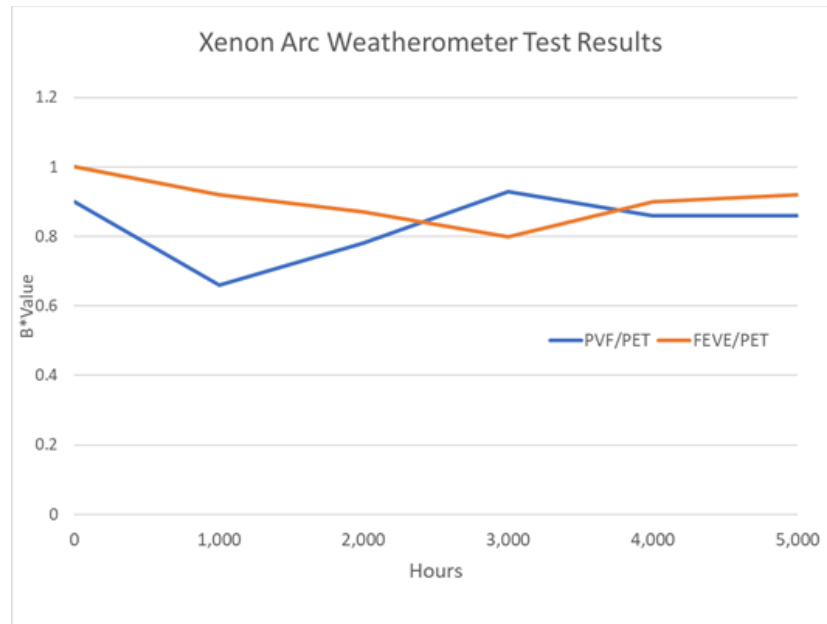


Figure with permission of AGC.

Both the FEVE-based fluorourethane coating and the PVF-based topcoat film performed extremely well in this test by preventing yellowing of the PET film over the 5,000-hour duration of the test (Madico, Inc., 2013).

Conclusions

Fluoropolymers are high molecular weight polymers with fluorine atoms directly attached to their carbon-only backbone. The carbon-fluorine (C-F) bond is the strongest bond between carbon and another atom and imparts unique, outstanding and beneficial properties along with extraordinary functional performance. These properties include chemical, biological and thermal stability, heat and chemical resistance, unique dielectric properties and durability. Additional fluoropolymer properties include increased fire resistance, weather resistance, non-wetting and adhesion resistance.

Many fluoropolymers, including the fluoropolymers used in the I&C end-uses, have been shown to meet the "polymers of low concern" (PLC) criteria, and as such, do not present a notable concern for human health or the environment (Henry et al. 2018, Korzeniowski et al. 2022). As discussed in those references, fluoropolymers are negligibly soluble in water, non-mobile, non-bioavailable, non-bioaccumulative and non-toxic.

Fluoropolymers are regarded as irreplaceable in many applications because their unique combination of specific properties, which are critical to ensure optimal performance in many applications and cannot be achieved or guaranteed by alternative materials. In the particular I&C end-uses covered in this document, there are a number of specific properties that enable the unparalleled performance fluoropolymers provide versus a number of major alternatives such as polyurethanes, chlorinated rubbers, alkyds and polyesters.

The exceptional properties that fluoropolymers provide and/or enable in the I&C coating applications are:

Flexibility;	Abrasion Resistance
Wear resistance;	Harsh Chemical Resistance
Impact Resistance and Hardness	Corrosion Resistance
Color Retention	Barrier Properties
Gloss Retention	Fire Retardancy and Smoke Suppression
Film Erosion	Low Refractive Index for Optical Effects
Chalking Resistance	
Weather Resistance	Reduced Dirt Collection

The unique combination of these properties in the subject I&C end-uses provide several significant benefits that include:

- VOC reduction due to extended service life and longer (less frequent) recoat time intervals;
- CO₂ reduction due to improved functioning of building HVAC systems as a result of lower peak and regular energy demands;
- Lower energy demands lead to lower carbon footprint;
- Life Cycle Costs (LCC) that are significantly reduced due to the extended service life of the end product, requiring less recoating, better color and gloss retention as well as little to no surface chalking;
- Dirt pickup is reduced and the surface in question is easier to maintain and is less susceptible to environmental damage;

- Mold and Mildew resistance is improved with FBCs; and
- And finally, help in qualification for Green Building Certification.

We are unaware of another coating technology that meets the performance parameters of durability and product longevity that also provides the cited benefits that are the defining characteristic of FBCs.

The five (5) I&C end-use applications described in this submission are:

1. Building Facades and Protection – Metal Building Panels and Parts

Fluoropolymer-based coatings (FBCs) offer superior performance, service life, sustainability, appearance and value for various applications which are used on a wide variety of metal substrates for commercial, monumental and other building projects. These fluoropolymer-based systems include polyvinylidene fluoride (PVDF) and fluoroethylene vinyl ether (FEVE) resin-based formulations. These two fluoropolymers are the film-forming binder resins in factory-applied industrial and construction coatings used in settings where extreme durability and lifespan of several decades or more are needed to provide substrate protection. FBCs extend the lifespan of the underlying materials and are a critical specification for certain products in the building and construction markets.

FBCs are available in both coil (roll-applied) and extrusion (spray-applied) applications. Each type has specific uses for various construction and architectural metal building products. Coil coatings are applied to large rolls or “coils” of steel and aluminum by a continuous, automated process that typically occurs in a controlled factory environment. Extrusion coatings are spray-applied to aluminum preformed extruded substrates, in a vertical or horizontal line also in a highly automated factory environment. FBCs can be applied to a variety of metal components used in projects ranging from pre-engineered metal buildings to municipal arenas, skyscrapers and many others.

2. Roofing and Roofing Structures

Roofing that incorporates a fluoropolymer-based topcoat system has significant advantages versus conventional roofing. These fluoropolymer-based systems have been shown to provide numerous important benefits for both roofing and building facades. Many favorable attributes combine to provide a lower lifetime ownership cost including lower energy usage from higher solar reflectivity and lower roof temperatures. This leads to lower carbon footprint, reduced dirt pick-up and improved mold and mildew resistance. Other important benefits from using these fluoropolymer-based systems include:

- World-class UV resistance and long-life color retention;
- Lower peak energy demand charge;
- Longer lifespan of roof coating and longer lifespan of roof substrate;
- Lower maintenance costs and less downtime;
- Increased efficiency and longer lifespan of HVAC equipment; and
- Lower VOC emissions.

3. Bridge and Walkway Structures

Bridge structures need durable coating performance to protect the painted metal substrate and maintain the bridge’s structural integrity. Any coating system must demonstrate through rigorous testing to be reliable and last a long time given safety considerations and how difficult, disruptive and expensive the recoat process is. Bridges

are subject to highly adverse environmental conditions including, but not limited to, high intensity sunlight, fog, rain, saltwater spray (in coastal areas) and constant automobile exhaust. The high weathering performance of the subject fluoropolymer-based resin allows the paint system to prolong the bridge's service life and protect the substrate (or coated material), which subsequently decrease the number of re-painting cycles of the bridge infrastructure or building. This eventually contributes to a better (lower) Life Cycle Cost. A fluoropolymer-based bridge coating system would typically utilize an FEVE-based resin paint as a topcoat, to protect the substrate (or coated material) by increasing the anti-corrosion ability of the substrate and coated material. This has the obvious impact of prolonging the service of the paint system. Furthermore, it contributes to the reduction of CO₂ generation by extending the life of the protected material and delaying or postponing the time between re-coating the bridge structure. Less recoating is equivalent to lowering the CO₂ generated in paint system product manufacture and application.

4. Water Towers

Water towers are high above the ground and therefore have an increased safety risk to coat and recoat. They require scaffolds to obtain a clean finish. In addition to the cost of the coatings package, application costs are significant as well. In fact, the cost of paint is typically less than 20% of the total coating process costs. The major costs of application largely consist of scaffolding and labor costs. The long-life cycle of the FBCs (extended over several decades) has not been shown with polyurethane and other coatings. This decades long life cycle can be realized with an FBCs system due to the durability provided by the fluoropolymer-based resin. Here again, the life-cycle cost is reduced due to the reduction in the number of recoatings required over the life of the water tower.

5. Solar Panels

Fluoropolymers are often used as back sheets (films) in photovoltaic solar panel construction. Materials used in this end-use need UV resistance and stability, corrosion resistance, flexibility, light in weight and have extended durability in full exposure to a variety of environmental conditions and intense sunlight and heat. Other materials used in back sheet applications are polyamides, polyethylene terephthalate, glass and polyesters.

Supplementary description of FEVE and PVDF Fluoropolymer Properties and Applications (Korzeniowski et al., 2022 and noted links)

FEVE

(Main references: see primarily <https://www.agcchem.com> and <https://www.lumiflonusa.com>)

FEVE fluoropolymer resins are polymers consisting of alternating fluoroethylene and alkyl vinyl ether segments. They were developed in 1982 as the first solvent-soluble fluoropolymers in the world. The fluoroethylene segment is largely responsible for the coatings' improved weatherability, durability and chemical resistance. Similarly, the vinyl ether segments provide for clarity, gloss, hardness, flexibility as well as a cross linking site for solubility if needed. The general features of the FEVE fluoropolymer include solubility in general organic solvents as well as being a non-crystalline resin with high transparency. The structure provides for the ability to introduce amorphous functional groups into the vinyl ether segments and as noted the alternating copolymerization structure gives high weather and chemical resistance. FEVE resins are used to make ultra-weatherable coatings for architectural, aerospace, automotive, bridge and industrial maintenance markets. These resins can be used to make both clear and pigmented coatings. They can be formulated with a wide range of gloss (from high gloss to flat finishes) and colors. The FEVE polymer is a platform chemistry that is supplied in various forms, including solvent-based liquid for easy application, water-based resins for low VOC (Volatile Organic Compound) and low odor coatings and a flake for sustainable powder coatings. FEVE powder coating materials provide essentially zero VOC and HAPS (Hazardous Air Pollutants) free coatings.

FEVE coatings protect steel, aluminum and other metals as well as concrete from degradation by UV light, wind and rain and corrosion. Because of their ultra-weatherability, FEVE based coatings offer substantial life cycle cost savings over conventional coatings. They can be used in the field for re-coating of structures or in the shop to manufacture pre-coated panels. FEVE resin chemistry allows for use in coatings that cure at ambient or low temperatures. This is important for use with heat-sensitive substrates like vinyl and fiberglass. Solvent- and water-based FEVE resins may be used to create highly weatherable coatings for vinyl and fiberglass building materials that allow for a cure process that meets the specific needs of these sensitive substrates.

High performance FEVE coatings can extend the lifetime of bridges and water tanks and reduce the frequency of maintenance, by helping to prevent coating degradation at the hands of UV radiation, salt and water. These coatings contain anti-corrosive properties that help maintain the coating's structural integrity for decades. Costs associated with bridge downtime, including increased traffic congestion, are significantly reduced over the life of the coating.

FEVE resins have outperformed even the best acrylic urethane coatings on steel, aluminum, magnesium and plastics like ABS, polyurethane, FRP, PVC, polyethylene, polypropylene and polycarbonate enabling transportation manufacturers to create and maintain the appearance for years. FEVE-based topcoats have been shown to yield over five times the lifespan of acrylic urethane coatings typically used in the transportation industry. FEVE resins can also be blended with traditional resins like acrylics to significantly increase their performance. For example, FEVE-based coatings can reduce maintenance costs in the aerospace market by as much as 50 % over the life of the plane, in addition to substantially reducing the loss of revenue during scheduled repainting. Aircraft coated with FEVE resin typically require no repainting for at least eight years, maintaining outstanding appearance and a durable surface that allows for easy cleaning. In contrast, acrylic urethanes typically begin to fade and chalk after only three years and require repainting after five.

FEVE Alternatives Assessment

The two main alternatives for an FEVE-based coating are polyurethanes and polysiloxanes. Urethanes have a long performance history and are still widely used as durable coatings. In general, polyurethanes will usually start to chalk and change color within 5-10 years. Due to degradation, the coating thickness of urethanes starts to decrease and after 15-25 years will no longer function as a barrier against corrosion. Polysiloxanes come in two types, epoxy and acrylic.

Siloxanes have a couple of advantages. First, they do not require an isocyanate crosslinker; they crosslink via a moisture cure mechanism. Second, they can be used as a two-coat system consisting of a zinc rich primer and a higher film build of siloxane (usually around 6-8 mils). This saves time especially in fabrication shops.

Neither coating system discussed above has been shown to weather as well as FEVE. A typical FEVE coat system will retain color and gloss for 25+ years and can prevent corrosion for up to 60 years, depending on the environment. Outdoor testing done in Japan over a 16-year period showed that a 25 μm FEVE-based coating retained 21 μm of thickness after 16 years. A 75 μm (3 mil) topcoat, typical thickness in a coating project, has a theoretical life of >100 years. In that same test, a 25 μm polyurethane coating was gone after 12 years. There are 30-year test results from bridges in Japan where gloss retention of the FEVE-based coating was 97% with a very small color change. There are test results that show that FEVE-based coatings retain their protective properties for a longer period than either of the other coatings. This makes sense in that the main purposes of the topcoat are to preserve its initial appearance for as long as possible and to act as a barrier film to corrosion initiators like chloride, water and oxygen.

The characteristics and advantages of various FEVE resin forms are summarized in Table 7.

Table 7. The Resin Form of FEVE and Features and Applications

Type of FEVE Resin	Features and Applications
Solvent Base	Use of general organic solvents. Used for general construction. Suitable for new installations
High Build	Can be painted thicker. Low VOC content
Exempt Solvent	Use volatile organic compound (VOC) exempt solvents as determined by EPA. Used for repainting airplanes
Mild Solvents	Mild solvent has smaller number of MIR VOC, (MIR VOC: maximum incremental reactivity VOC. They are classified by their ozone generation ability). With a mild odor, this system can be used for repainting in the city and repainting bridges
Water Base	Emulsions and Dispersions; The amount of VOCs is not more than 5%. Frequently used for repainting on-site coating. Reduced VOCs even in factory coatings
Powder	Essentially zero VOCs. Frequently used for Aluminum panels and building components. Factory painting only. Cannot be painted on site. Grade with the lowest environmental impact.

The benefits of utilizing a FEVE resin in a FBC are:

1. The excellent durability of FEVE lasts for several decades and protects the underlying paint film and substrate, thus reducing the number of surface re-coatings and protection of the underlying paint film and substrate over a long period of time.
2. High affinity for various solvents, hardener, paint additives and antifouling agents allows users to apply the product to a wide range of coating equipment and to achieve a wide variety in coating performance.
3. The high affinity for a wide range of pigments and the ability to select very vivid colors make it possible to achieve a high level of color design including clear metallic color and natural stone.
4. The ability to have colorful designs makes these systems also suitable for stone-like walls, higher design wall, amenities, landmarks and even vehicles.
5. FEVE is amorphous, which makes the coating film very smooth and provides a high gloss and mirror-like surface for itself. On the other hand, its high pigment affinity allows the gloss to be freely adjusted from 0-80 gloss units by using matting agents.

6. An isocyanate curing agent and resulting cross-linking can function at ambient to medium temperature. A block isocyanate curing agent will dry at higher temperatures in a short period of time. After drying, the product has not been shown to dissolve in solvents and exhibits excellent solvent resistance.
7. Long span bridges and large buildings that can only be air dried with crosslinking can be coated outdoors at ambient temperature.
8. FEVE coating reduces the difficult repainting for large, massive structures including existing buildings and structures with deteriorated coatings which can be repainted onsite. The old coating can be given a new life and be given decades of longevity.
9. Using an essentially zero VOC content coating does make a rapid contribution to VOC reduction versus competitive materials. Powder grades which do require baking are factory applied.
10. FEVE requires relatively low temperatures even when curing.

In addition to the increased oxygen permeability, improved weatherability, CO₂ generation reduction and lower overall Life Cycle Costs benefits that were previously noted, there are a number of other advantages and benefits fluoropolymers provide. These additional important benefits and features are as follows:

- Improved mechanical properties, lower corrosion rates, little to no molecular weight changes on exterior use,
- Lower top film consumption, isocyanate crosslinking retention, significantly improved durability,
- Significantly improved chalking performance as well as less fading, much better gloss and color retention
- Improved VOC reduction over the life of the structure

From the available technical data, FBC systems significantly outperform the competitive alternative systems such as polyurethanes, alkyds and chlorinated rubber coatings

PVDF and PVDF Copolymer

(Main reference : <https://www.extremematerials-arkema.com/en/product-families/kynar-pvdf-family/download-performance-characteristics-data-brochure/>)

Polyvinylidene fluoride (PVDF) is a tough engineering thermoplastic that offers a balance of performance properties. It has the characteristic stability of fluoropolymers that help to resist harsh thermal, chemical and ultraviolet environments. PVDF, in addition to being readily melt-processed by standard methods, can be dissolved in polar solvents, such as organic esters and ketones, for coating applications. PVDF can be produced by homopolymerization or copolymerization, providing a full range of products with different molecular architecture along with different ranges of properties. Some of the important properties of PVDF homopolymers and copolymers are a function of the crystalline content

and type of crystalline structure, both of which are affected by the processing methods and conditions.

Features

- Outstanding resistance to sunlight/UV exposure
- Tremendous chemical resistance to a wide range of aggressive chemicals
- Radiation resistance
- Excellent burn characteristics / flame and smoke properties (low flame spread and low quantity of smoke generated)
- Easy processing on industry-standard equipment and easy post-processing, such as fabrication
- Extremely high purity for the most demanding applications
- Extremely high electrochemical stability
- Excellent abrasion resistance
- High temperature rating: RTI 150 °C

Applications

- **Chemical Processing:** Due to its high temperature resistance, low permeability and high mechanical strength, PVDF is used as a contact surface for the production, storage and transfer of corrosive fluids (chemically resistant to halogens and acids). PVDF resin is used in mechanical components, fabricated vessels, tanks, pumps, valves, filters, heat exchangers, tower packing, piping systems and many other applications.
- **Wire and Cable:** PVDF has excellent fire, abrasion, chemical and impact resistance. Depending on the test method, it can have up to a 150°C rating and can be irradiated for even higher ratings.
- **Electricity and Electronics:** Its fire resistance, abrasion resistance, low-smoke emission, chemical and mechanical properties make PVDF resin suitable for protective sheathing, plenum and communications wiring insulation and binder resin for battery manufacture.
- **High Purity:** As semi-conductor and pharmaceutical production require increasingly pure materials, high purity PVDF resin grades meet industry needs (low extractables values). PVDF resin regulatory compliances include food and water use certifications (in FDA 177.2510 and/or 177.2600 compliance, NSF Standard 51 – Food Equipment Materials, NSF Standard 61 – Drinking Water System Components) as well as compliance for use in industries such as healthcare (USP Class VI approval).
- **Transportation:** PVDF resin is used in both public and private transport vehicles as a barrier liner for automotive fuel line and gas station fuel pipes, in decorative films, as a binder in HEV/EV batteries, as molded and thermoformed body components (weathering, anti-grime/graffiti) and as tank trailer linings for corrosion protection. PVDF resin has strength, flame resistance, durability and versatility that make it a preferred material in automotive wiring harnesses, general coatings and plastic optical fibers.

- **Focus on Battery:** PVDF polymers are used in the battery industry as binders for cathodes and anodes in lithium-ion batteries and as battery separators in lithium-ion polymer batteries. PVDF is helping to design thinner and smaller lithium-ion batteries.
- **Architecture:** The excellent outdoor aging and weathering properties of PVDF resin led to its use in long-lasting paints for coating metal sheet for the past 50 years. PVDF resins can also be used to protect thermoplastics through coextrusion or film lamination techniques to obtain anti-grime and anti-graffiti surfaces with excellent weathering properties.
- **Photovoltaic:** PVDF Film is used in the protection of back sheet and for front sheet glazing. Those films provide exceptional solar transmittance and also have excellent dirt shedding and fire resistance properties.
- **Membrane:** PVDF resin is a respected membrane material for applications ranging from bioprocess separations to water purification because it is extremely chemically resistant and well suited to aggressive chemical environments. PVDF tolerates ozone and chlorine (an oxidant increasingly used for water purification) very well. Grades with United States Food and Drug Administration and/or NSF International compliance are compatible with food and/or beverage contact applications. It is used to manufacture flat sheet, hollow fiber and TIPS (thermally induced phase separation) process membranes and/or enclosed shapes that cannot be lined or coated in a conventional manner.
- **Fabrics:** Woven and non-woven fabrics can be produced using specific PVDF grades. These fabrics offer excellent chemical resistance, stability to sunlight and flame retardant properties.

General physical and mechanical properties

PVDF homopolymers and copolymer resin grades give the option to combine rigid and flexible materials when processing. As a material of construction for pumps and pipe, PVDF exhibits excellent resistance to abrasion. PVDF can also be manufactured in thin, flexible and transparent films, filament and tubing. Sunlight has little to no effect on PVDF resins.

- **Strength and toughness:** PVDF fluoropolymers are inherently strong and tough as reflected by their tensile properties and impact strength. An ambient temperature tensile strength at yield of 35-55 MPa (5,000-8,000 psi) and an unnotched impact strength of no break offered by select resins emphasize this. These characteristics are retained over a wide range of temperatures
- **Flexural creep:** Compared to many thermoplastics and fluoropolymers tensile yield of 15-55 MPa (2,200-8,000 psi), PVDF polymers have excellent resistance to tensile creep and fatigue also at elevated temperatures. Likewise, the short-term flexural creep resistance of PVDF homopolymer resins reflects superior load bearing performance.
- **Tensile creep:** Compared to many thermoplastics and fluoropolymers tensile yield of 15-55 MPa (2,200-8,000 psi), PVDF polymers have excellent resistance to tensile creep and fatigue also at elevated temperatures. PVDF resins are able to

maintain a low tensile creep when subjected to constant stress even at high temperatures.

- **Flexural creep:** PVDF is highly rigid and resistant to creep under mechanical stress and load. Likewise, the short-term flexural creep resistance of PVDF homopolymer resins reflects superior load bearing performance.
- **Thermal properties:** PVDF resins exhibit high thermal stability. Prolonged exposure of some PVDF grades at 250 °C (482 °F) in air does not lead to weight loss. No oxidative or thermal degradation has been detected during continuous exposure at 150 °C (302 °F) for a period of ten years. In testing, select resins have been given an RTI of 150 °C. PVDF resins thermally decompose at temperatures greater than 375 °C (707 °F). However, the melt processing range of unfilled PVDF homopolymer resins is very broad – from slightly above the melting point of 155 - 170 °C (311-338 °F) up to 300 °C (572 °F).
- **Electrical properties:** PVDF combines high dielectric strength and excellent mechanical properties over a broad temperature range. This has led PVDF resin to be used for thin-wall primary insulation and as a jacket for industrial control wiring. With proper shielding, PVDF resin can be used as jacketing for high frequency plenum-rated data cables because of its excellent flame and smoke performance.
- **Stability to weather and UV effects:** Many years of outdoor exposure in direct sunlight have little effect on the physical properties of PVDF. Some increases in tensile strength and reduction in elongation do occur over time.
- **Ozone resistance:** Ozone is a powerful oxidizing agent characterized by a high degree of chemical instability. PVDF offers excellent chemical resistance to ozone exposure.

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Testing and Reference Methods – See Appendix B

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Appendix A. Glossary

AAMA	American Architectural Manufacturers Association; http://www.aamanet.org
ACC	American Chemistry Council
A/C	Air Conditioning
ACM	Aluminum Composite Material
ARC	Xenon ARC testing uses a highly specialized type of gas discharge lamp, an electric light that produces light by passing electricity through ionized xenon gas at high pressure. It produces a bright white light to simulate sunlight.
ASTM	ASTM International; https://www.astm.org/
AWWA	American Water Works Association; https://www.awwa.org/
CAS Number	Chemical Abstracts Service Number
CEPE	European Council of the Paint, Printing Ink and Artists' Colors Industry; https://www.cepe.org/
CR	Chlorinated Rubber
ECHA	European Chemicals Agency; https://echa.europa.eu/
ECTFE	Ethylene-chlorotrifluoroethylene copolymer
EIF	Entry into Force
EIFS	Exterior Insulation Finishing System
EOL	End of Life
ETFE	Ethylene-tetrafluoroethylene copolymer
EVA	Ethylene vinyl acetate or PEVE: poly (ethylene-vinyl acetate)
FBC	Fluoropolymer Based Coating
FEVE	Fluoroethylene-vinyl ether copolymer
Fluorinated Polymer	The broad generic term to encompass all polymers for which one or more of the monomer units contains the element fluorine, in the backbone and/or in side chains.
Fluorochemical	General, nonspecific name that describes a universe of organic and inorganic substances that contain at least 1 fluorine atom, with vastly different physical, chemical and biological properties. Synonyms include "fluorinated substance" and "fluorinated chemicals."
Fluoroelastomer	An elastic rubber-like polymer to which fluorine is bound. Fluoroelastomers are highly durable and resistant to heat, oils, solvents, fuels and ozone.
Fluoroplastic	A distinct subset of polymers and plastics where some or all of the hydrogen atoms of the hydrocarbon backbone have been replaced with fluorine atoms.
Fluoropolymer	Distinct subset of polymers, namely, those made by (co)polymerization of olefinic monomers, at least one of which contains fluorine bound to one or both of the olefinic carbon atoms, to form a carbon-only polymer

	backbone with fluorine atoms directly attached to it, e.g., polytetrafluoroethylene.
Fluorosurfactant	A substance used to lower aqueous surface tension in which the hydrophobic portion contains F bound to C, often as a perfluoroalkyl moiety, often referred to as “fluorinated surfactants”, “fluorosurfactants,” “fluorinated tensides,” or “fluorotensides”
FPG	Fluoropolymers Product Group, a group within Plastics Europe, the association of Plastics manufacturers; https://fluoropolymers.plasticseurope.org/index.php/about-us
GPC	Gel Permeation Chromatography
Homopolymer	A polymer made with only one monomer
HVAC	Heating Ventilation Air Conditioning
IR	Infrared
I&C	Infrastructure & Construction
ISO	International Organisation for Standardization; https://www.iso.org/about-us.html
JPMA	Japan Paint Manufacturers Association; https://www.toryo.or.jp/eng/
LC	Life Cycle
LCC	Life Cycle Cost
LEED	Leadership in Energy and Environmental Design; https://www.usgbc.org/leed
LOI	Limiting oxygen index
MIR	Maximum Incremental Reactivity
OECD	Organisation for Economic Co-operation and Development; https://www.oecd.org/
PET	Polyethylene terephthalate
PFAS	A very diverse group, per- and poly-fluoroalkyl substances (PFAS), including polymers (fluoropolymers, perfluoropolyethers, side chain fluorinated polymers) and non-polymers. Perfluoroalkyl substances are those for which all hydrogens on all carbon atoms not associated with functional groups have been replaced by fluorine, and polyfluoroalkyl substances are those for which all hydrogens on at least one, but not all, carbon atoms have been replaced by fluorine.
PFP	U.S.-based Performance Fluoropolymer Partnership; https://www.americanchemistry.com/industry-groups/performance-fluoropolymer-partnership-pfp/
PFPE	A perfluoropolyether is a polymer in whose backbone -CF ₂ -, -CF ₂ CF ₂ - and possibly -CF(CF ₃)CF ₂ - units are separated by oxygen atoms.
Polymer of Low Concern (PLC)	A polymer that does not present a notable concern for human health or the environment.
PU	Polyurethane
PVC	Polyvinyl Chloride
PVDF	Polyvinylidene fluoride

REACH	Chemical Control regulation in the European Union (Registration, Evaluation, Authorisation and Restriction of Chemicals); https://environment.ec.europa.eu/topics/chemicals/reach-regulation_en
RI	Refractive Index
SCFP	Side-chain Fluorinated Polymer
SEM	Scanning Electron Microscope, or Micrograph
SMP	Silicone Modified Polyester
SWM	Sunshine Weatherometer, or Weatherometer
TSR	Total Solar Reflectance
USEPA	US Environmental Protection Agency
UV	Ultra Violet Light
VOC	Volatile Organic Compounds

Appendix B. Infrastructure & Coatings Testing and Reference Methods

For each of the I&C end-use applications in this submission there are a set of exacting performance testing and reference methods. This appendix contains a list of some of the critical test methods and what they measure. For the primary end-uses in this submission, designers, architects and builders have specific performance standards they must meet to achieve the desired long lasting coatings performance and surface protection.

Test Method	Test Method Title	Test Method Description
AAMA 621	Voluntary specifications for high performance organic coatings on coil coated architectural hot dipped galvanized (HDG) and zinc-aluminum coated steel substrates	AAMA 621 provides specifications and methods for evaluating coil coatings on hot dipped galvanized and zinc-aluminum coated steel substances for adhesion, impact resistance, chemical resistance and weatherability.
AAMA 2604	Voluntary Specification, Performance Requirements and Test Procedures for Superior Performing Organic Coatings on Aluminum Extrusions and Panels	AAMA 2604 measures film integrity, exterior weatherability and general appearance over years of exposure. It includes humidity resistance (300 hours), salt spray resistance, Florida exposure (5 years), color retention, chalk resistance and gloss retention.
AAMA 2605	Voluntary Specification, Performance Requirements and Test Procedures for Superior Performing Organic Coatings on Aluminum Extrusions and Panels	AAMA 2605 measures film integrity, exterior weatherability and general appearance over years of exposure. It includes humidity resistance (4,000 hours), salt spray resistance, Florida exposure (10 years), color retention, chalk resistance and gloss retention.
ANSI/CRRC S100	Standard Test Methods for Determining Radiative Properties of Materials	From the publicly available online standard: ¹ “This standard provides a practice and method for testing and reporting the <i>radiative properties</i> of roofing products before and after a specified test exposure. Roofing specimens are exposed to specific tests and to the exterior environment throughout a specified time period. The tests provide a relative measure of the roofing product response to the test conditions. The standard does not purport to be representative of all conditions that roofing products experience in the

¹ https://coolroofs.org/documents/ANSI-CRRC-S100-2021_Final.pdf

		field. Variations of the test conditions or specimen construction also affect the specimen response.”
ASTM B117	Standard Practice for Operating Salt Spray (Fog) Apparatus	From the public ASTM B117 website:² “This practice provides a controlled corrosive environment which has been utilized to produce relative corrosion resistance information for specimens of metals and coated metals exposed in a given test chamber.” “This practice covers the apparatus, procedure, and conditions required to create and maintain the salt spray (fog) test environment.”
ASTM B244	Standard Test Method for Measurement of Thickness of Anodic Coatings on Aluminum and of Other Nonconductive Coatings on Nonmagnetic Basis Metals with Eddy-Current Instruments	From the public ASTM B244 website:³ “This test method covers the use of eddy-current instruments for the nondestructive measurement of the thickness of a nonconductive coating on a nonmagnetic basis metal. It is intended to supplement manufacturers’ instructions for the operation of the instruments and is not intended to replace them.” “This test method is particularly useful for measuring the thickness of an anodic coating on aluminum alloys. Chemical conversion coatings are too thin to be measured by this test method.”
ASTM D522	Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings	From the public ASTM D522/D552M website:⁴ “Coatings attached to substrates are elongated when the substrates are dimensionally unstable, or are bent during the manufacture of articles or when the articles are abused in service. These test methods have been useful in rating attached coatings for their ability to resist cracking when elongated. They have been useful in evaluating the flexibility of coatings on flexible substrates.”

² <https://www.astm.org/standards/b117>

³ <https://www.astm.org/b0244-09r21.html>

⁴ https://www.astm.org/d0522_d0522m-17r21.html

ASTM D523	Standard Test Method for Specular Gloss	From the public ASTM D523 website:⁵ “Measured gloss ratings by this test method are obtained by comparing the specular reflectance from the specimen to that from a black glass standard. Since specular reflectance depends also on the surface refractive index of the specimen, the measured gloss ratings change as the surface refractive index changes. In obtaining the visual gloss ratings, however, it is customary to compare the specular reflectances of two specimens having similar surface refractive indices.”
ASTM D662	Standard Test Method for Evaluating Degree of Erosion of Exterior Paints	From the public ASTM D662 website:⁶ “Erosion failure of paint films can occur in use. This test method provides a means of evaluating the degree of failure by comparing to pictorial standards.”
ASTM D968	Standard Test Method for Abrasion Resistance of Organic Coatings by Falling Abrasive	From the public ASTM D968 website:⁷ “These test methods cover the determination of the resistance of organic coatings to abrasion produced by abrasive falling onto coatings applied to a plane rigid surface, such as a metal or glass panel.”
ASTM D1308	Standard Test Method for Effect of Household Chemicals on Clear and Pigmented Coating Systems	From the public ASTM D1308 website:⁸ “Resistance to various liquids used in the home is an important characteristic of organic finishes. These test methods provide the means by which the relative performance of coating systems may be evaluated. It should be recognized that continuous films are necessary for reliable results.” “This test method covers determination of the effect of household chemicals on clear and pigmented organic finishes, resulting in any objectionable alteration in the surface, such as discoloration, change in gloss, blistering, softening, swelling, loss of adhesion, or special phenomena.”

⁵ <https://www.astm.org/standards/d523>

⁶ <https://www.astm.org/d0662-93r19.html>

⁷ <https://www.astm.org/d0968-22.html>

⁸ <https://www.astm.org/d1308-20.html>

ASTM D1400	Standard Test Method for Nondestructive Measurement of Dry Film Thickness of Nonconductive Coatings Applied to a Nonferrous Metal Base	From the public ASTM D1400 website: ⁹ “This test method covers the nondestructive measurement of the dry film thickness of electrically nonconductive coatings applied over a nonferrous metal base using commercially available eddy current instruments. This test method is intended to supplement manufacturers' instructions for the manual operation of the gages and is not intended to replace them.”
ASTM D1654	Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments	From the public ASTM D1654 website: ¹⁰ “This method provides a means of evaluating and comparing basic corrosion performance of the substrate, pretreatment, or coating system, or combination thereof, after exposure to corrosive environments.” “This test method covers the treatment of previously painted or coated specimens for accelerated and atmospheric exposure tests and their subsequent evaluation in respect to corrosion, blistering associated with corrosion, loss of adhesion at a scribe mark, or other film failure.”
ASTM D2244	Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates	From the public ASTM D2244 website: ¹¹ “This practice covers the calculation, from instrumentally measured color coordinates based on daylight illumination, of color tolerances and small color differences between opaque specimens such as painted panels, plastic plaques, or textile swatches.”

⁹ <https://www.astm.org/d1400-94.html>

¹⁰ <https://www.astm.org/d1654-08r16e01.html>

¹¹ <https://www.astm.org/d2244-23.html>

ASTM D2247	Standard Practice for Testing Water Resistance of Coatings in 100% Relative Humidity	From the public ASTM D2247 website:¹² “Water can cause the degradation of coatings, so knowledge of how a coating resists water is helpful for assessing how it will perform in actual service. Failure in tests at 100 % relative humidity may be caused by a number of factors including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. This practice is therefore useful for evaluating coatings alone or complete coating systems.” “This practice covers the basic principles and operating procedures for testing water resistance of coatings by exposing coated specimens in an atmosphere maintained at 100 % relative humidity so that condensation forms on all surfaces of test specimens.”
ASTM D2248	Standard Practice for Detergent Resistance of Organic Finishes	From the public ASTM D2248 website:¹³ “This practice covers the determination of the resistance to failure, in an accelerated manner, of organic finishes when immersed in a detergent solution.”
ASTM D2794	Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact)	From the public ASTM D2794 website:¹⁴ “Coatings attached to substrates are subjected to damaging impacts during the manufacture of articles and their use in service. In its use over many years, this test method for impact resistance has been found to be useful in predicting the performance of organic coatings for their ability to resist cracking caused by impacts.” “This test method covers a procedure for rapidly deforming by impact a coating film and its substrate and for evaluating the effect of such deformation.”

¹² <https://www.astm.org/d2247-15r20.html>

¹³ <https://www.astm.org/d2248-01ar18.html>

¹⁴ <https://www.astm.org/d2794-93r19.html>

ASTM D3359	Standard Test Methods for Rating Adhesion by Tape Test	From the public ASTM D3359 website: ¹⁵ “This test method is limited to evaluating lower levels of adhesion (see 1.3). The intra- and inter-laboratory precision of this test method is similar to other test methods for coated substrates (for example, Test Method D2370 and Test Method D4060), and is insensitive to all but large differences in adhesion.”
ASTM D3363	Standard Test Method for Film Hardness by Pencil Test	From the public ASTM 3363 website: ¹⁶ “Pencil hardness measurements have been used by the coatings industry for many years to determine the hardness of clear and pigmented organic coating films. This test method has also been used to determine the cure of these coatings, especially when using forced dried heat.”
ASTM D4145	Standard Test Method for Coating Flexibility of Prepainted Steel	From the public ASTM D4145 website: ¹⁷ “This test method describes a procedure for determining the flexibility and adhesion of organic coatings (paints) on metallic substrates that are deformed by bending when the sheet is fabricated into building panels or other products. The metal substrate must be capable of passing this test without fracturing and with no excessive grain development.”
ASTM D4214	Standard Test Methods for Evaluating the Degree of Chalking of Exterior Paint Films	From the public ASTM 4214 website: ¹⁸ “The procedures provide a broad range of techniques and photographic references to evaluate chalking of exterior paints.” “These test methods cover the evaluation of the degree of chalking on white or tinted exterior paint films. These test methods describe the procedures recommended for transferring the chalk to a fabric or fingertip, which is then compared to photographic reference standards, or in the case of adhesive tapes, compared to a reflectance table or photographic reference standards, to determine the degree of chalking.”

¹⁵ <https://www.astm.org/standards/d3359>

¹⁶ <https://www.astm.org/d3363-22.html>

¹⁷ <https://www.astm.org/d4145-10r22.html>

¹⁸ <https://www.astm.org/d4214-07r15.html>

ASTM D4585	Standard Practice for Testing Water Resistance of Coatings Using Controlled Condensation	From the public ASTM D4585 website:¹⁹ “Water can cause degradation of coatings, so knowledge of how a coating resists water is helpful in predicting its service life. Failure in a condensation test may be caused by a number of factors including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. The test is therefore useful for evaluating coatings alone or complete coating systems.” “This practice covers basic principles and operating procedures for testing water resistance of coatings using controlled condensation. Condensation is produced by exposing one surface of a coated specimen to a heated, saturated mixture of air and water vapor, while the reverse side of the specimen is exposed to the cooling effect of room temperature air.”
ASTM D7897	Standard Practice for Laboratory Soiling and Weathering of Roofing Materials to Simulate Effects of Natural Exposure on Solar Reflectance and Thermal Emittance	From the public ASTM D7897 website:²⁰ “The solar reflectance of a building envelope surface affects surface temperature and near-surface ambient air temperature. Surfaces with low solar reflectance absorb a high fraction of the incoming solar energy. Sunlight absorbed by a roof or by other building envelope surfaces can be conducted into the building, increasing cooling load and decreasing heating load in a conditioned building, or raising indoor temperature in an unconditioned building. It can also warm the outside air by convection. Determination of solar reflectance can help designers and consumers choose appropriate materials for their buildings and communities.” “Practice D7897 applies to simulation of the effects of field exposure on the solar reflectance and thermal emittance of roof surface materials including but not limited to field-applied coatings, factory-applied coatings, single-ply membranes, modified bitumen products, shingles, tiles, and metal products.”

¹⁹ https://www.astm.org/d4585_d4585m-18.html

²⁰ <https://www.astm.org/d7897-18.html>

ASTM E84	Standard Test Method for Surface Burning Characteristics of Building Materials	From the public ASTM E84 website:²¹ “This test method is intended to provide only comparative measurements of surface flame spread and smoke density measurements with that of select grade red oak and fiber-cement board surfaces under the specific fire exposure conditions described herein.” “This fire-test-response standard for the comparative surface burning behavior of building materials is applicable to exposed surfaces such as walls and ceilings. The test is conducted with the specimen in the ceiling position with the surface to be evaluated exposed face down to the ignition source.”
ASTM E1918	Standard Test Method for Measuring Solar Reflectance of Horizontal and Low-Sloped Surfaces in the Field	From the public ASTM E1918 website:²² “Solar reflectance is an important factor affecting the temperature of a sunlit surface and that of the near-surface ambient air temperature. The test method described herein measures the solar reflectance of surfaces in natural sunlight.” “This test method covers the measurement of solar reflectance of various horizontal and low-sloped surfaces and materials in the field, using an albedometer or pyranometer. The test method is intended for use when the sun angle to the normal from a surface is less than 45°.”

²¹ <https://www.astm.org/standards/e84>

²² <https://www.astm.org/e1918-21.html>

ASTM E1980	Standard Practice for Calculating Solar Reflectance Index of Horizontal and Low-Sloped Opaque Surfaces	From the public ASTM E1980 website:²³ “Solar reflectance and thermal emittance are important factors affecting surface and near-surface ambient air temperature. Surfaces with low solar reflectance, absorb a high fraction of the incoming solar energy. A fraction of this absorbed energy is conducted into ground and buildings, a fraction is convected to air (leading to higher air temperatures), and a fraction is radiated to the sky. For equivalent conditions, the lower the emissivity of a surface the higher its steady-state temperature. Surfaces with low emissivity cannot effectively radiate to the sky and, therefore, get hot. Determination of solar reflectance and thermal emittance, and subsequent calculation of the relative temperature of the surfaces with respect to black and white reference temperature (defined as Solar Reflectance Index, SRI), may help designers and consumers to choose the proper materials to make their buildings and communities energy efficient. The method described here gives the SRI of surfaces based on measured solar reflectances and thermal emissivities of the surfaces.”
ASTM G7	Standard Practice for Natural Weathering of Materials	From the public ASTM G7 website:²⁴ The relative durability of materials in natural exposures can be very different depending on the location of the exposure because of differences in ultraviolet (UV) radiation, relative humidity, time of wetness, temperature, wet-dry cycling, freeze-thaw cycling, pollutants, and other factors. Therefore, it cannot be assumed that results from one exposure in a single location will be useful for determining relative durability in a different location. Exposures in several locations with different climates which represent a broad range of anticipated service conditions are recommended.
AWWA D102-6	AWWA Standard for Coating Steel Water-Storage Tanks	From the public AWWA D102-6 website:²⁵ This standard describes coating systems for coating and recoating the inside and outside surfaces of steel tanks used for potable water storage in water supply service.

²³ <https://www.astm.org/standards/e1980>

²⁴ https://www.astm.org/g0007_g0007m-21.html

²⁵ <https://engage.awwa.org/PersonifyEbusiness/Bookstore/Product-Details/productId/27171>

VDA 233-102	Cyclic Corrosion Testing of Materials and Components in Automotive Construction	From the public VDA 233-102 website:²⁶ “The purpose of this specification is to provide an accelerated test procedure for the assessment of the corrosion behaviour of components and of the corrosion protection provided by coating systems. The accelerated test covers in particular the delamination/corrosion creep around a defined artificial defect in a coating as well as surface and edge corrosion on special test plates, bonding specimens or components. Compared to tests with a higher humidity availability a decreased ageing rate of adhesive is to be expected. This laboratory-scale cyclic corrosion test is also suitable for assessing perforation corrosion in flanged areas or gaps and of unpainted surfaces.” “This method induces corrosion processes and generates reproducible corrosion patterns which correlate well with the results obtained in natural weathering tests (DIN 55665) and driving operation. In particular, the corrosion patterns for the substrates steel, galvanised steel and aluminium closely reflect real-life phenomena.” “The test method is based on real corrosive climate conditions and delivers differentiated results for a large number of uses in automotive applications.”
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²⁶ <https://webshop.vda.de/VDA/en/vda-233-102-06-2013>

Critical Review

A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers

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Abstract

Fluoropolymers are a distinct class of per- and polyfluoroalkyl substances (PFAS), high molecular weight (MW) polymers with fluorine attached to their carbon-only backbone. Fluoropolymers possess a unique combination of properties and unmatched functional performance critical to the products and manufacturing processes they enable and are irreplaceable in many uses. Fluoropolymers have documented safety profiles; are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic. Although fluoropolymers fit the PFAS structural definition, they have very different physical, chemical, environmental, and toxicological properties when compared with other PFAS. This study describes the composition, uses, performance properties, and functionalities of 14 fluoropolymers, including fluoroplastics and fluoroelastomers, and presents data to demonstrate that they satisfy the widely accepted polymer hazard assessment criteria to be considered polymers of low concern (PLC). The PLC criteria include physicochemical properties, such as molecular weight, which determine bioavailability and warn of potential hazard. Fluoropolymers are insoluble (e.g., water, octanol) solids too large to migrate into the cell membrane making them nonbioavailable, and therefore, of low concern from a human and environmental health standpoint. Further, the study results demonstrate that fluoropolymers are a distinct and different group of PFAS and should not be grouped with other PFAS for hazard assessment or regulatory purposes. When combined with an earlier publication by Henry et al., this study demonstrates that commercial fluoropolymers are available from the seven participating companies that meet the criteria to be considered PLC, which represent approximately 96% of the global commercial fluoropolymer market. *Integr Environ Assess Manag* 2022;00:1–29. © 2022 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Applications, Fluoropolymers, Low concern, PFAS, Property Combinations

This article contains online-only Supporting Information.

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INTRODUCTION

“Fluoropolymers are high MW polymers with fluorine atoms directly attached to their carbon-only backbone” (Ebnesajjad, 2017). The carbon–fluorine (C–F) bond is the strongest bond between carbon and another atom and imparts unique, outstanding, and beneficial properties and extraordinary functional performance to fluoropolymers (Ameduri, 2020; Ameduri & Sawada, 2017a, 2017b; Banks et al., 1994; Fluoropolymer Products Group of Plastics Europe [FPG], 2021a; Scheirs, 2007). These properties

include chemical, biological, and thermal stability, heat and chemical resistance, unique dielectric properties, and durability. Additional fluoropolymer properties include fire resistance, weather resistance, nonwetting, and nonstick. Fluoropolymers are regarded as irreplaceable in many applications because their unique combination of specific properties, which are critical to ensure optimal performance in many applications, cannot be achieved or guaranteed by alternative materials (FPG, 2021a, 2017; Henry et al., 2018; Performance Fluoropolymer Partnership of the American Chemistry Council [PFP], 2020).

Per- and polyfluoroalkyl substances (PFAS), a universe of substances with widely diverse properties that have been used in industrial and consumer applications since the 1950s, include fluoropolymers as a distinct class (Buck et al., 2011; Henry et al., 2018). A single, globally harmonized definition for PFAS has not yet been agreed upon. PFAS have been defined differently based on their structure and atomic composition (Buck et al., 2021; Wallington et al., 2021). For example, the USEPA's working PFAS structure definition is "a structure that contains the unit $R-CF_2-CF(R')(R'')$, where R , R' , and R'' do not equal "H" and the carbon-carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included" (USEPA, 2021a). The European Chemicals Agency (ECHA) employed a much broader PFAS structural definition (ECHA, 2020). A recent Organisation for Economic Cooperation and Development (OECD) report, which defined PFAS as fluorinated substances that contain in their structure at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), that is, with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$; OECD, 2021). This report acknowledges that the term "PFAS" is broad, general, and nonspecific, which does not inform whether a compound presents risk or not, but only communicates that the compounds under this term share the same structural trait of having a fully fluorinated methyl or methylene carbon moiety. Further, the report highlights that, among the substances defined as PFAS, there are distinct substances with very different properties: polymers and nonpolymers; solids, liquids and gases; persistent and nonpersistent substances; highly reactive and inert substances; mobile and insoluble (immobile) substances; and (eco) toxic and nontoxic chemicals. In addition, the report recognizes that PFAS have diverse molecular structures (e.g., neutral, anionic, cationic, or zwitterionic; with or without aromatic rings; nonpolymers or polymers; low or high molecular weight (MW), and thus diverse physical, chemical, and biological properties (e.g., involatile or volatile; water soluble or water insoluble; reactive vs. inert; bioaccumulative or nonbioaccumulative) and as such highly recommends that such diversity be properly recognized and communicated in a clear, specific, and descriptive manner when communicating about PFAS.

There is considerable media and public confusion and misunderstanding regarding PFAS, as the many different chemicals and groups are often not clearly differentiated under the broad term PFAS. Per- and polyfluoroalkyl substances, a large, diverse group of substances with vastly different properties, is too broad to allow effective, science-based assessment and regulation of chemical compounds as an entire group. This point has been raised in recent publications that suggest approaches to effectively group PFAS for regulatory assessment (American Chamber of Commerce in Europe [Amcham], 2020a; Buck et al., 2021; Bundesverband der Deutschen Industrie e.V. [BDI], 2021; Fiedler et al., 2020; Miller et al., 2020; Orgalim, 2021; Royal Society of Chemistry [RSC], 2021; Sha et al., 2019; Wallington et al., 2021). A clear understanding of the origin of PFAS found in the environment, the PFAS that are commercially relevant (Buck et al., 2021), and assessment of their properties are needed to be able to determine which classes of PFAS require management action. PFAS must be assessed based on their chemical, physical, thermal, and biological property differences and uses (Amcham, 2020a; BDI, 2021; Buck et al., 2021; RSC, 2021; Wallington et al., 2021). As regulatory frameworks, such as the EU REACH regulation, continue to evolve, more work is needed to distinguish clearly among PFAS based on their properties to assure that regulations are appropriate in scope, proportionate, and are science-based.

Per- and polyfluoroalkyl substances are divided into two primary categories: nonpolymers and polymers (Buck et al., 2011). Polymeric PFAS, generally known as "fluorinated polymers," include fluoropolymers (discussed here), perfluoropolyethers (PFPE), and side-chain fluorinated polymers (SCFP; Buck et al., 2011; Henry et al., 2018 and Supporting Information: Figure 6.1). This article deals strictly with fluoropolymers. Neither PFPE nor SCFP are discussed here.

The nonpolymer category includes perfluoroalkyl substances and polyfluoroalkyl substances. Certain nonpolymer PFAS substances, for example, short- and long-chain per- and polyfluoroalkyl carboxylic acids and sulfonic acids, received regulatory scrutiny recently due to their toxicity, as well as their persistence, potential to bioaccumulate, and/or mobility in the environment. Regulatory processes have been launched worldwide to address these concerns related to specific nonpolymer PFAS. These targeted regulatory measures have evolved increasingly into restrictions on the entire family of PFAS. For example, five Member States of the European Economic Area have initiated a procedure to prepare a joint restriction proposal under the EU REACH Regulation to limit the risks to human health and the environment from the manufacture and use of all substances in the PFAS family based on structure alone (ECHA, 2020). Although fluoropolymers fit the PFAS structural definition, they have vastly different physicochemical, environmental, and toxicological properties than other PFAS in addition to substantial societal benefits and importance (Fluoropolymer Products Group of Plastics Europe [FPG], 2017, 2021a). For

these reasons, fluoropolymers should be considered separately and not aggregated with all other PFAS for regulatory action. Concurrently, the USEPA prepared a PFAS Strategic Roadmap laying out how it plans to evaluate and potentially regulate PFAS (USEPA, 2021a). Recognizing that there are many PFAS very diverse in their physical form, chemical structure and composition, functional characteristics, and toxicity profiles, USEPA “is conducting new research to better understand the similar and different characteristics of specific PFAS and whether and how to address groups and categories of PFAS.”

Fluoropolymers have documented safety profiles, are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, non-bioaccumulative, and nontoxic (Henry et al., 2018). Some fluoropolymers have been demonstrated to meet the “polymers of low concern” (PLC) criteria, and as such do not present notable concern for human health or the environment (Henry et al., 2018). PLC criteria were developed over time within regulatory frameworks around the world as an outcome of chemical hazard assessment processes, which identified physical–chemical properties of polymers that determine polymer bioavailability and thereby report a polymer’s potential hazard. For example, many of the physicochemical properties, such as MW, limit the ability of a polymer to cross the cell membrane and therefore limit its bioavailability (Kostal, 2016; Lipinski et al., 2001; USEPA, 2012). The USEPA built on this knowledge to adopt a polymer exemption rule to exempt low-hazard polymers from certain regulatory notification requirements under the Toxic Substances Control Act’s (TSCA) new chemicals program (United States Federal Register [USFR], 1984). An OECD expert group on polymers reached consensus on these criteria and their respective metrics, documenting the data required for a polymer to qualify as a PLC to human health and the environment (OECD, 1993). Subsequently, an additional OECD work group concurred that PLC have “insignificant environmental health and human health impacts” (OECD, 2009). In addition, the European Commission commissioned a report (BIO by Deloitte, 2015) wherein several member countries agreed on the polymer properties predictive of adverse human health and environmental hazard. The report outlined eligibility criteria for a polymer to be considered a PLC. In 2019, the industry-led European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a “Conceptual Framework for Polymer Risk Assessment” (“CF4Polymers”; ECETOC, 2019). CF4Polymers provides guiding elements to be considered in assessing potential ecological and human health hazards and risks posed by polymer substances. CF4Polymers also considers specific life-cycle stages of polymer products and their associated routes of exposure. The authors of the CF4Polymers framework support the PLC approach as a means to accomplish polymer risk assessments. They specifically support the findings of Henry et al. (2018) and state that they are “...unaware of scientific evidence to justify generally assigning fluoropolymers the same level of

regulatory concern as other PFAS” (ECETOC, 2019). In 2020, the European Commission contracted a study to propose criteria for the identification of polymers requiring registration (PRR) under REACH (Wood, 2020a). The Wood report states that the authors consider that fluoropolymers meet the criteria to be considered PLC, “following the recommendations of Henry et al.” Considerable debate and comment on proposals have been put forward as the process and discussion advances (American Chamber of Commerce in Europe [Amcham], 2020b; FPG, 2021a; Hafer, 2021).

Four major fluoropolymers have previously been demonstrated to meet the criteria as PLC (Henry et al., 2018). This 2018 study raised interest in gathering similar data for additional commercial fluoropolymer products, both in scope and polymer type. In this study, seven global fluoropolymer manufacturers from the USA, Europe, and Asia collaborated to gather and present data for 14 additional fluoropolymers. In addition to information describing chemical composition, uses, performance properties, and functionalities of the 14 fluoropolymers, author company data for each of the PLC criteria are presented and discussed. The results demonstrate that each of the 14 commercially manufactured fluoropolymers in this study satisfy the widely accepted assessment criteria to be considered PLC and merit such designation. The study results add further evidence to demonstrate that fluoropolymers are demonstrably different and should not be grouped with other PFAS for hazard assessment or regulatory purposes.

USES, PERFORMANCE PROPERTIES, AND FUNCTIONALITY OF FLUOROPLASTICS AND FLUOROELASTOMERS IN THIS STUDY

The fluoropolymers described and evaluated in this study are high-performance materials used in commercial and industrial applications. Described herein are the industries and sectors (Table 1) and the performance properties and functionalities (Table 2) of the study fluoropolymers. The unparalleled combination of properties makes fluoropolymers critical materials for a broad range of applications and industrial sectors including automotive, aerospace, energy production and storage, and electronics (Table 1). Fluoropolymers are an important driver of the European Green Deal (FPG, 2021a) and UN Sustainability Development Goals (United Nations [UN], 2021), supporting smart mobility, clean energy, and sustainable industry. They are used in various components of renewable energy installations, such as hydrogen and photovoltaic panels and facilitate advanced energy storage and conversion technologies such as lithium-ion batteries (FPG, 2021a). Fluoropolymers are (i) durable, stable, and mechanically strong in harsh conditions; (ii) chemically inert, meeting the requirements for low levels of contaminants and particulates in manufacturing environments that are critical to the food and beverage, pharmaceutical, medical, and semiconductor industries; and (iii) biocompatible, nonwetting, nonstick, and highly resistant to

TABLE 1 Fluoropolymer end uses and industries

Industries End uses	Transportation		Health care		Chemical		Consumer		Telecommunications		Infra-structure	Renewable energy			
	Automotive	Aerospace	Pharma- ceuticals	Medical devices	Oil and gas	Chemical process industry (CPI)	Production of goods	Protection and packaging	Filtration	Electronics and semicon- ductors	Internet and wireless communica- tions	Textiles Technical textiles	Energy production	Hydrogen production	Energy storage
Fluoroplastics															
PVDF homopolymer	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
PVDF copolymer	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
ECTFE copolymer	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
ECTFE terpolymer			•		•	•									
PCTFE		•	•							•					
FEVE	•	•								•		•			
EFEP	•			•		•				•					
CPT	•									•					
THV	•	•	•	•		•	•	•	•	•		•	•		•
Fluoroelastomers															
FEPM	•	•	•	•	•	•	•			•		•	•		
FKM	•	•	•	•	•	•	•	•		•		•	•	•	•
FFKM		•	•	•	•	•	•			•					
Specialty															
Amorphous		•	•	•		•				•	•			•	•
Ionomer	•			•		•			•	•			•	•	•

Note: See also Chapter 5 in the Supporting Information.

Abbreviations: CPT, chlorotrifluoroethylene-tetrafluoroethylene; ECTFE, ethylene-chlorotrifluoroethylene; EFEP, ethylene-tetrafluoroethylene-hexafluoropropylene; FEPM, trifluoroethylene-propylene copolymer; FEVE, fluoroethylene-vinyl ether; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMVE perfluoroelastomer; PCTFE, polychlorotrifluoroethylene; PVDF, polyvinylidene fluoride; THV, TFE-HFP-VF2.

TABLE 2 Fluoropolymer properties and functionality

See Supporting Information: Chapter 2 for property descriptions	Durable				Inert—Stable			
	Mechanical strength	Wear resistance	Flexibility	Low coefficient of friction	Resistance to chemicals	Weatherability	Cryogenic properties (lower than −50 °C)	High operating temperature range
High limiting oxygen index								
Fluoroplastics								
PVDF Homopolymer	•	•		•	•	•		•
PVDF Copolymer	•	•		•	•	•		•
ECTFE Copolymer	•	•		•	•	•	•	•
ECTFE Terpolymer		•		•	•	•		•
PCTFE	•	•		•	•	•	•	•
FEVE	•	•	•	•	•	•		•
EEEP	•	•		•	•	•	•	•
CPT				•	•	•	•	•
THV			•		•	•		•
Fluoroelastomers								
FEP	•	•	•		•	•		•
FKM	•	•	•		•	•		•
FFKM	•	•	•		•			•
Specialty								
Amorphous			•	•	•			•
Ionomer			•		•			•
See Supporting Information: Chapter 2 for property descriptions	Electrical insulator—high data transmission rate	Ionic conductivity	Piezo-electrical properties	Barrier properties	Nonstick properties	Ultra high purity grades for clean applications	Optical clarity	Low refractive index—used for optical effects
Polymer processing additive (PPA) ^a								
Fluoroplastics								
PVDF Homopolymer			•	•		•		•
PVDF Copolymer			•	•	•			•

(Continued)

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TABLE 2 (Continued)

See Supporting Information: Chapter 2 for property descriptions	Functional							Polymer processing additive (PPA) ^a
	Electrical insulator—high data transmission rate	Ionic conductivity	Piezo-electrical properties	Barrier properties	Nonstick properties	Ultra high purity grades for clean applications	Optical clarity	Low refractive index—used for optical effects
ECTFE Copolymer	•			•				
ECTFE Terpolymer				•				
PCTFE				•	•	•	•	•
FEVE				•			•	
EFEP				•	•		•	•
CPT				•	•	•	•	
THV				•			•	•
Fluoroelastomers								
FEP	•			•				
FKM				•	•			•
FFKM	•			•		•		
Specialty								
Amorphous	•	•		•	•	•	•	•
Ionomer	•	•		•			•	

Note: See Chapter 5 in the Supporting Information.
Abbreviations: CPT, chlorotrifluoroethylene-tetrafluoroethylene; ECTFE, ethylene-chlorotrifluoroethylene; EFEP, ethylene-tetrafluoroethylene-hexafluoropropylene; FEP, trifluoroethylene-propylene copolymer; FEVE, fluoroethylene-vinyl ether; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMVE perfluoroelastomer; PCTFE, polychlorotrifluoroethylene; PVDF, polyvinylidene fluoride; THV, TFE-HFP-VF2.
^aPolymer Processing Additives (PPA); also known as Polymer Processing Aid, Extrusion Process Aids or Polymer Processing and Recycling Aids.

temperature, fire, and weather (Table 2). Fluoropolymers are the preferred choice of material because of their unique combination of properties that are not achievable from other materials or via other functions. As a result, fluoropolymers have become a critical mainstay for our society providing vital, reliable functionality to a broad range of industrial and consumer products.

Three fluoropolymer types are included in this study: fluoroplastics, fluoroelastomers, and specialty fluoroplastics. Here, we describe briefly each included in this study. Additional details about each polymer are provided in the Supporting Information: Chapter 5.

Fluoroplastics

The fluoroplastics included in this study are: polyvinylidene fluoride (PVDF) homopolymer, PVDF copolymer, ethylene-chlorotrifluoroethylene (ECTFE) copolymer, ECTFE terpolymer, polychlorotrifluoroethylene (PCTFE), fluoroethylene-vinyl ether (FEVE), ethylene-tetrafluoroethylene-hexafluoropropylene (EFEP) terpolymer, chlorotrifluoroethylene-tetrafluoroethylene (CPT) terpolymer, and tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride (TFE-HFP-VF2 [THV]) terpolymer as well as the specialty fluoroplastics, amorphous fluoropolymers, and fluorinated ionomers. Typical monomers used in the manufacture of fluoroplastics include tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinylidene fluoride (VDF or VF2), chlorotrifluoroethylene (CTFE), vinyl fluoride (VF), trifluoroethylene (TrFE), and perfluoroalkyl vinyl ethers (PAVEs), which include trifluoromethyl trifluorovinyl ether (PMVE), pentafluoroethyl trifluorovinyl ether (PEVE), and heptafluoropropyl trifluorovinyl ether (PPVE). In some copolymers, monomers that do not contain fluorine attached to the olefinic carbons may be used. These include ethylene, propylene, perfluoroalkyl-substituted ethylenes, and others (Ebnesajjad, 2000, 2003; Grot, 2011).

Fluoroelastomers

The fluoroelastomers included in this study are: trifluoroethylene-propylene copolymer (FEP), HFP-VF2 polymer and HFP-VF2-TFE polymers (FKM), and TFE-PMVE perfluoroelastomer (FFKM). Typical monomers used in the manufacture of fluoroelastomers include VDF, HFP, TFE, CTFE, PAVEs, as well as propylene, 1-hydropentafluoropropene (HPFP), and 2,3,3,3-tetrafluoropropene (HFO-1234yf; FPG, 2021a). Although fluoroelastomers are based on many of the monomers that are also used for the synthesis of fluoroplastics, they are different because of the specific composition, flexibility with subambient glass transition temperatures, as well as their elastomeric properties, resulting from the cross-linking process. Cross-linking, known as curing or vulcanizing, is a hardening process to form chemical bonds between polymer chains that gives polymers their elasticity (Améduri et al., 2001; Drobny, 2016).

PVDF homo- and copolymers

Polyvinylidene fluoride fluoropolymers are specified by end users across the world for their outstanding combination of properties. Because they have high temperature resistance, low permeability, and high mechanical strength, and provide chemical resistance to a wide range of aggressive chemicals, PVDF fluoropolymers are used as a contact surface for the production, storage, and transfer of corrosive fluids (chemically resistant to halogens and acids) in the chemical processing industry, oil and gas transportation, and cables industry (Arkema, 2021a; Gujarat Fluorochemicals Limited, 2018, 2022; Solvay, 2021a). The outstanding resistance to sunlight/UV exposure make PVDF suitable for architectural coatings. The outdoor aging and weathering properties of PVDF resin led to its use in long-lasting paints for coating metal sheet for the past 50 years. PVDF resins can also be used to protect thermoplastics through coextrusion or film lamination techniques to obtain antigraffiti surfaces with exceptional weathering properties. PVDF fluoropolymers also exhibit radiation resistance, desirable burn characteristics, flame, and smoke properties, easy processing on industry-standard equipment, and easy postprocessing steps, such as welding and fabrication. PVDF is used as a binder in lithium-ion batteries as well as PVDF film for solar power panels because of its high thermal and electrochemical stability, its stability under harsh environmental conditions, and its strong adhesion properties are critical to achieving environmental goals.

ECTFE (co- and terpolymers)

Ethylene chlorotrifluoroethylene (ECTFE) is a semicrystalline and melt-processable fluoropolymer obtained by the copolymerization of the two monomers, ethylene and chlorotrifluoroethylene, with an essentially 1:1 alternating structure (Ebnesajjad, 2017). Due to its chemical structure, ECTFE offers a unique combination of properties including chemical resistance, high thermal rating, and very good mechanical properties (Solvay, 2021b). ECTFE terpolymer with added hexafluoroisobutylene monomer displays enhanced stress-cracking performances resulting from chain-structure modifications of the polymer. ECTFE is used widely in anticorrosion applications such as coatings or in self-supporting construction (pipes) and architectural films (Solvay, 2021c). One of the principal advantages of ECTFE fluoropolymer is the ease with which it can be processed. It is a true thermoplastic that can be handled by conventional techniques of extrusion as well as by blow, compression, injection, rotational, and transfer molding. Powder coating methods are also applicable. ECTFE embodies an exemplary trade-off among general properties, offering high chemical and mechanical resistance combined with easy processing of the resin.

PCTFE

Polychlorotrifluoroethylene is a homopolymer of chlorotrifluoroethylene. PCTFE is melt processable and can be

extruded or molded (Satokawa, 1990). PCTFE has outstanding mechanical properties, especially hardness, and chemical resistance compared with PTFE and PFA, although it is slightly inferior to PFA and FEP in heat resistance and chemical resistance (Daikin, 2021a; Satokawa, 1990). PCTFE has been applied widely in the semiconductor industries and aerospace industries (Curbell, 2021; Daikin, 2021a). In addition to distinguished thermal and chemical stability, it has very low moisture absorption and permeation; therefore, PCTFE is used in pharmaceutical packaging (Honeywell, 2021).

FEVE

Fluoroethylene-vinyl ether fluoropolymer resins are manufactured by copolymerization of fluoroethylene monomer and a vinyl ether monomer and consist of alternating fluoroethylene and alkyl vinyl ether segments (AGC Chemicals Company, 2021a; Parker & Blankenship, 2015). They were developed in 1982 as the first solvent-soluble fluoropolymers in the world (Darden & Parker, 2021; Kojima & Yamabe, 1984; Munekata, 1988; Yamabe et al., 1984). The alternating fluorinated segments provide outstanding UV stability, weather resistance, and chemical resistance, while the vinyl ether segments provide solvent compatibility and cross-linking sites (Parker & Blankenship, 2015; Scheirs, 2007). FEVE resins are used to make ultra-weatherable coatings for architectural, aerospace, automotive, bridge, and industrial maintenance markets (Hoshino & Morizawa, 2017).

EFEP

Ethylene-tetrafluoroethylene-hexafluoropropylene is a terpolymer of ethylene, tetrafluoroethylene, and hexafluoropropylene. It was designed to have many of the properties of ETFE. It has a lower processing temperature, which allows it to be coextruded with conventional thermoplastic polymers such as polyamide, ethylene vinyl alcohol (EVOH), and modified polyethylene. EFEP can be extruded, injection molded, and blow molded, and it is used in many applications such as those identified in Supporting Information: Chapter 4.7 (Daikin, 2011a). EFEP is a melt-processable resin with good processability because of its low melting point. It also has excellent mechanical properties, provides chemical resistance, low permeability, exceptional weatherability, and good heat resistance. Other prominent features include inherent flame retardancy as well as good optical properties given that EFEP is highly transparent and has both a low dielectric constant and loss tangent.

CPT

Chlorotrifluoroethylene-tetrafluoroethylene is a terpolymer of chlorotrifluoroethylene, tetrafluoroethylene, and perfluoroalkyl-vinyl-ether. It is a melt-processable polymer and resin, which is readily processed because of its lower melting point. It can be melt-molded as a thermoplastic resin by extrusion, injection, and compression molding. CPT

is a modified perfluoroalkoxy fluoropolymer (PFA), which utilizes chlorotrifluoroethylene to provide low permeability to PFA, and it has many outstanding properties as a hybrid polymer of PFA and PCTFE as shown below. It has demonstrated permeation resistance to organic solvent, chemicals, water vapor, and gasoline (Daikin, 2011b). CPT offers superior permeation resistance against gasoline and flexible fuel and can be part of construction meeting the LEV III requirements (US environmental protection regulations in this automotive application). CPT also has notable barrier properties against many kinds of organic solvents and strong acids, especially HF, HCl, and HNO₃. This is very useful for semiconductor applications (Daikin, 2021b). In addition to the features noted above, CPT also provides heat resistance, excellent weatherability, flame retardancy, and good optical properties owing to its high transparency.

THV

THV fluoropolymers are a group of fluorinated thermoplastic polymers composed mainly of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and vinylidene fluoride (VDF; Dominghaus, 1998; Hintzer & Schwertfeger, 2014; Hull et al., 1997). The melting point of the different grades ranges from approximately 100 °C to nearly 250 °C. THV fluoropolymers are easy to process due to their broad processing windows. Different THV grades exhibit high flexibility, high transparency, bondability to fluorinated and nonfluorinated materials, and very good permeation resistance against fuels and other chemicals. The polymers are used as a barrier layer in fuel hoses, for transparent films and tubing, as matrix materials in composites, and the bonding layer in multilayer construction (Dams & Hintzer, 2017; Hull et al., 1997). The high transparency of the special film makes it an ideal adhesive film for laminated glass and the optimal protective film for surfaces. THV grades compete against other fluorothermoplastic materials for applications that require transparency and low refractive index as well as with fuel barrier materials. Commercial nonfluorinated materials cannot be used as substitutes for THV because of the unique combination of properties. Polymethylmethacrylate (PMMA) is used in conjunction with THV to provide differences in refractive index to create the total reflection needed for polymer optical fibers (Park et al., 2008). Transparent polymers, such as PMMA or polycarbonate, do not have the same chemical resistance or UV resistance to compete directly with THV.

FEPM

Trifluoroethylene-propylene copolymer elastomers, ASTM D1418, are high MW fluoropolymers with alternating tetrafluoroethylene and propylene segments (Kojima et al., 1977). They are also known as TFE-P copolymers. Various articles can be produced by means of compression molding, extrusion, injection molding, and calendaring. FEPM elastomers are compounded and cured (cross-linked) to deliver unique and valuable properties by providing exceptional heat resistance with a continuous service temperature higher than

200 °C, outstanding chemical resistance with little or no deterioration even in contact with strong acids, bases, and oxidants at high temperatures, steam resistance, and high electrical resistivity on the order of 10^{15} – 10^{16} Ω/cm (bulk resistivity). Formulated FEPM components are now used worldwide in many critical industrial applications where they must function safely in harsh environments, thereby extending the life of critical components and reducing downtime and costly repairs. FEPM elastomers are used in a range of applications including thermal power plants, oil and gas industry, ocean development, chemical and nuclear plants, automotive, aerospace, heavy-duty diesel, electronics, machinery, renewable energy, food processing, and medical. Their noted heat and chemical resistance make them especially valuable in oil and gas extraction (downhole) applications, where reliability is essential to cost effective and environmentally responsible production (Hull, 1983). FEPM elastomers are also used in high-performance wire and cable applications as insulating materials with the highest heat resistance, for example, lightweight, high-voltage automotive cables and motor cables for Japanese high-speed bullet trains (AGC Chemicals Company, 2021b).

Fluoroelastomers (FKM)

FKM are a family of fluoroelastomer materials defined by ASTM international standard D1418 (ASTM, 2021). FKM fluoroelastomers contain vinylidene fluoride (VDF) as a monomer combined with a variety of other fluoromonomers to create a palette of polymers with properties tailored for specific uses (Dams & Hintzer, 2017; Drobny, 2016; Van Cleeff, 1997; Worm & Grootaert, 2001). Cross-linked FKM fluoroelastomers are amorphous polymers designed for demanding service applications in hostile environments characterized by broad operating temperature ranges in contact with industrial chemicals, oils, or fuels (Worm & Grootaert, 2001). FKM fluoroelastomers are used mainly in fabricated parts (e.g., o-rings, gaskets, seals) to provide barriers against a wide range of fluids under severe service conditions (Drobny, 2016). Their design allows stable extrusion and molding processes and fitting in a wide range of processing constraints, reducing the risk of failure and increasing productivity. FKM fluoroelastomers provide high temperature and aggressive fluids resistance and retention of properties over a wide and demanding range of operating use conditions (high and low temperatures) for sealing and fluid transport applications, offering far superior performance than hydrocarbon elastomers. Applications include aerospace, automotive, oil and gas, chemical processing, electrical, office equipment, food, pharmaceuticals, and consumer wearables. Additionally, uncured FKM fluoroelastomers are used as a polymer processing additive (PPA) or polymer extrusion aids in small amounts (50–2000 ppm) dispersed in polyolefins such as high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), significantly improving their film extrusion characteristics, reducing melt fracture and die build-up, as well as increasing productivity, minimizing energy and

water footprint, and enabling the extrusion of thin films (Lavallée, 2020; Shell, 2020).

FFKM

Perfluoroelastomers, designated by ASTM D1418 as FFKM, are a fully fluorinated class of elastomers that are typically made up of tetrafluoroethylene (TFE), a perfluoro (alkyl vinyl ether; PAVE), and a cure site monomer(s) (Ohkura & Morizawa, 2017). FFKM elastomers offer superior chemical and temperature resistance, excellent resistance to gas and liquid permeation, and resistance to weather and ozone with operating temperatures ranging from –40 °C to 325 °C (Drobny, 2016; Greene-Tweed, 2021a, 2021b). These polymers can also be compounded to meet the special requirements of upstream, midstream, and downstream oil and gas exploration due to their superior properties (Barnwell, 2021; Daemar, 2021). Because of these properties, FFKM elastomers are used in a wide variety of applications such as critical sealing solutions for the aerospace, pharmaceutical, medical, chemical processing, semiconductor, and oilfield industries (Atkinson, 2018; Marshall, 2017).

Amorphous fluoropolymers

Amorphous fluoropolymers are copolymers of TFE and specialty monomers that yield linear, high molar mass non-crystalline polymers (AGC Chemicals Company, 2021c; Gangal & Brothers, 2010; Hintzer et al., 2013; Korinek, 1994; Resnick & Buck, 1997, 1999). Amorphous fluoropolymers have the outstanding chemical and thermal stability and surface properties of semicrystalline perfluoropolymers as well as the unique properties associated with amorphous materials such as optical clarity and high gas permeability. The optical properties are outstanding, with more than 90% transmission, and thereby low dissipation, over a wide range of wavelengths (e.g., 200–2000 nm). TFE/PDD (2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole) copolymers have the lowest refractive index known for a solid organic polymer (Groh & Zimmermann, 1991). This unique combination of properties makes amorphous fluoropolymers unmatched for uses in degassing, fiber optics, photolithography, antireflective coatings, passivation and protective coatings for medical, military, and aerospace devices, as well as electronic applications (Gangal & Brothers, 2010; Hintzer et al., 2013).

Fluorinated ionomers

Fluorinated ionomers are copolymers of TFE and a perfluorovinylether monomer containing an ionic group, typically a sulfonic acid or carboxylic acid (Grot, 2011, 2013). Fluorinated ionomers can be extruded or cast into film and converted into ion exchange materials (IXMs). IXMs come in a variety of useful forms offering a broad range of solutions for different applications (AGC Chemicals Company, 2021d; Asahi-Kasei, 2021; Chemours, 2021a). These forms include ion exchange membranes (IEMs), dispersions, and resins. IEMs must possess the required ion transport properties for the electrochemical cell in which they reside to perform well

and work effectively. Some of these properties include high ionic conductivity, chemical resistance, high operating temperature range, low permeability, and balanced durability and performance (Chemours, 2021b).

Ion exchange membranes (IEMs) stand to play a noteworthy role in today's modern world (Chemours, 2021b) and as such, are utilized in a wide range of applications and end-use industries including electrochemical processing, energy production, and hydrogen production. IEMs revolutionized the chlor-alkali industry (Grot, 2013), the manufacture of primarily caustic soda and chlorine, by eliminating the use of hazardous materials such as mercury and asbestos (Asahi-Kasei, 2021) and, in doing so, reducing energy consumption. Water electrolysis, the process of converting water into hydrogen and oxygen, relies on IEM technology. Although this process requires electricity, renewable energy sources such as solar or wind power can be utilized, allowing the potential for hydrogen to be a “clean” energy source (Science Center, 2021). Hydrogen fuel cells, some of which use a type of IEM known as a proton exchange membrane, can then convert hydrogen to electricity, a crucial technology to reach the stated target of the EU New Green Deal (EC, 2021).

STUDY METHODOLOGY AND DATA

Seven global fluoropolymer manufacturers (AGC Chemicals Americas, Arkema, The Chemours Company, Daikin Industries, Gujarat Fluorochemicals Limited, Solvay Specialty Polymers, and 3M Company) participated in this study and contributed data, writing, critique, and analysis. The companies noted above are members of the US-based Performance Fluoropolymer Partnership (PFP) and/or EU-based Fluoropolymer Product Group (FPG).

This study provides data on 14 fluoropolymers, building on a prior study (Henry et al., 2018). The study was chartered within two global industry groups. Participants put forward candidate fluoropolymers of notable commercial importance for the study and provided company and published data that address the PLC criteria. Thirteen PLC criteria that relate to the polymer structure and properties, including three to physicochemical properties and five to

stability, set forth in BIO by Deloitte (2015) and presented in prior work on four fluoropolymers (Henry et al., 2018), are addressed in this study (Figure 1). These criteria are briefly described in Table 3 with further description provided in Supporting Information: Chapter 3 and in the prior work (Henry et al., 2018). Participants provided company and published data and a description of methods and/or public references to demonstrate the origin of the data provided. These methods and references are provided in detail in Supporting Information: Chapter 4. The PLC criteria data were compiled and are presented in Tables 4 and 5.

The data assessment was done in two ways: Companies could self-assess the PLC data if they had the technical resources to do so or they could submit their PLC data to a third-party contractor for an independent technical review. The third-party consultant hired by PFP was GSI Environmental Inc. The objective was to be able to publish the references and methods behind the PLC data provided for each fluoropolymer in the study. In cases where the data and/or methods contained confidential business information, the third-party consultant independently evaluated the information supplied before it was shared in a blinded, aggregate form with the participating project companies. In several cases—FKM, PVDF, and ionomers—several companies submitted data for the same fluoropolymer. The data were combined and are presented in Tables 4 and 5. There is no intentional company attribution for the data presented.

The following describes further how the study data were generated and compiled.

- A third-party consulting company (GSI) was engaged to comment independently on data, methods, and references initially supplied by study participants for their respective fluoropolymers. Several study participants used this third-party consultant.
- Following the initial third-party assessment and assembly of the master data Tables 4 and 5 as well as the FKM data in Supporting Information: Table 4.11, a series of subsequent assessments were conducted (within PFP)

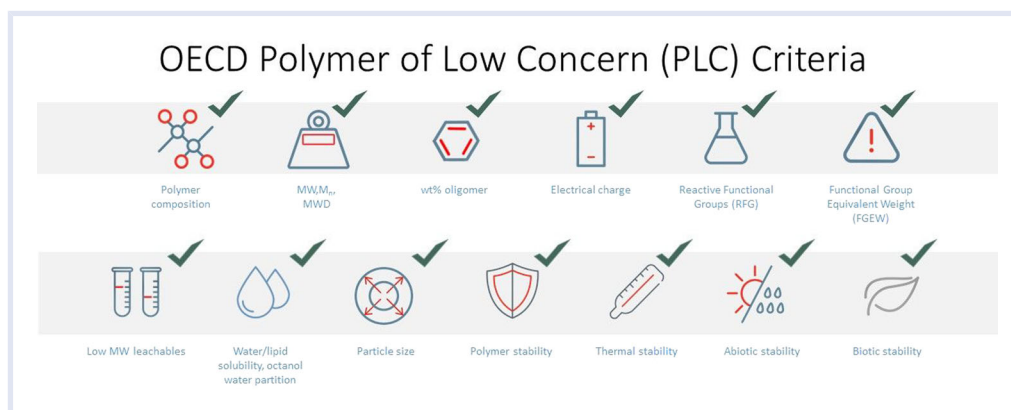


FIGURE 1 OECD polymer of low concern (PLC) criteria add (C) 2021 W.L.Gore & Associates

TABLE 3 Polymer of low concern (PLC) criteria descriptions

(See Supporting Information: Chapter 3 for additional details) Criterion	Description
Polymer composition	The polymer composition criterion requires structure and elemental composition of the polymer be described and identified (e.g., by Chemical Abstracts Service [CAS] number).
Molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da	The number average molecular weight (Mn) and oligomer content are the most commonly used criteria for PLC assessment. The EU assessment report (BIO by Deloitte, 2015) states that the “most potential health concern polymers have a number average molecular weight, Mn, <1000 Da and oligomer content >1%.” The higher the oligomeric content, the more likely a polymer is to be a health or ecotoxicological (OECD, 2009, p. 9). Molecular weight (MW) is an important predictor of biological effect because large molecules (>1000–10 000 Da) are too large to penetrate cell membranes (Supporting Information: in Beyer, 1993, p. 14). Because large molecular weight polymers cannot enter the cell, they cannot react with “target organs,” such as the reproductive system, and are not bioavailable. “Therefore, as the Mn of a polymer increases, a reduced incidence of potential health concern effects might be expected” (OECD, 2009, p. 20). An additional PLC consideration is the weight percentage of oligomers that are <1000 Da. Oligomers may be composed of, for example, dimers, trimers, and tetramers, meaning they have 2- monomer, 3- monomer, and 4-monomer units, respectively. The EU report (BIO by Deloitte, 2015) concluded that most potential health concern polymers have Mn of <1000 Da and oligomer content of >1%: “...the distribution of potential health concern polymers exhibited an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content” (OECD, 2009, p. 24). Molecular weight distribution (MWD), also known as “polydispersity index,” measures the heterogeneity of size of polymer molecules in a polymer. The MWD is an important parameter for predicting potential biological effects of polymers because, although Mn may be a large value, low MW oligomers <1000 Da may be present, which could penetrate the cell.
Ionic character	Electrical charge or ionic character can be anionic, cationic, amphoteric, or nonionic. Specifically, cationic polymers have been associated with aquatic toxicity (Auer et al., 1990; USEPA, 1997a).
Reactive functional groups and RFG ratio to MW	A “reactive functional group” (RFG) is defined as an atom or associated group of atoms in a chemical substance that is intended or can be reasonably expected to undergo facile chemical reaction (USFR, 2012). Some highly reactive functional groups (or a high ratio of RFGs per mole) have been associated with adverse human health and ecotoxicology (e.g., acrylates, methacrylates, isocyanates, anhydrides, aziridines; USEPA, 2010). The functional group equivalent weight (FGEW) is used to determine if the RFGs in a polymer are substantially diluted by polymeric material to allow the polymer to be a PLC (USEPA, 1997). The FGEW of a polymer is defined as the ratio of the Mn to the number of functional groups in the polymer. The FGEW is used as an indication of the degree of reactivity of the polymer; the lower the FGEW, the more reactive the polymer and the greater the potential for health and environmental impact (OECD, 2009, p. 10).
Low MW leachables	Low MW leachables are chemical molecules, either inorganic or organic, that migrate (i.e., leach) out of the polymer. These could be residual monomers or oligomers resulting from incomplete polymerization processes, surface residues, or other chemicals used in the manufacturing processes (e.g., initiators, catalysts, chain transfer agents, surfactants). Low MW leachables are critically important to the potential for a polymer to affect health and the environment, given that they may be able to migrate out of the polymer and cross cell membranes to potentially react with biomolecules. A report to the EU (BIO by Deloitte, 2015) concluded that “Polymers with <1% MW < 1000 Da and low water extractability are not able to cause systemic effects which are toxicologically or ecotoxicologically relevant.” Monomers, by nature, are reactive. Unreacted monomers left in a polymer may migrate out of the polymer to react with biomolecules to cause potential adverse effects. Regulatory authorities (BIO by Deloitte, 2015) and the OECD Expert Group on Polymers (OECD, 2009) agree that the residual monomer content of a polymer is critical to determining if it qualifies as a PLC.

(Continued)

TABLE 3 (Continued)

(See Supporting Information: Chapter 3 for additional details) Criterion		Description
Particle size		Particle size is also a PLC criterion. Particles that are small enough to reach the deep lung upon inhalation are often associated with adverse health effects. Therefore, to qualify as a PLC, median mass aerodynamic diameter (MMAD) of the polymer particle size should be >5 μm .
Structural and elemental composition		In the US, Chemical Categories of Concern are the result of the review of new chemicals by the USEPA under the TSCA (see https://www.epa.gov/reviewing-new-chemicals-under-toxic-substances-control-act-tsca/chemical-categories-used-review-new). The categories describe the molecular structure, boundary conditions such as MW, equivalent weight, the log of the octanol–water partition coefficient, log <i>P</i> , or water solubility, and standard hazard (mammalian and ecological) and (environmental) fate tests to address concerns.
Elemental composition		The elemental composition is a factor in the assessment of the eligibility of polymers for reduced notification requirements. The exclusion of polymers under this step is not a conclusion of hazard but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process. These elemental requirements differ across jurisdictions as covered in the report to the EU on global regulatory approaches to polymer assessment (BIO by Deloitte, 2015). For example, in the EU under REACH it is proposed that polymers composed from among these elements, covalently bound to C, have reduced hazard: H, N, O, Si, S, F, Cl, Br, or I (BIO by Deloitte, 2015). In contrast, the USEPA Polymer Exemption Rule states that a polymer is eligible for reduced agency review when it has at least two of the following elements: C, H, O, N, S, or Si (USFR, 1995).
Water and lipid solubility and the octanol–water partition coefficient		Water solubility is the extent to which a compound will dissolve in water. According to the OECD (2009) meeting of the Expert Group on Polymers, polymers with “negligible” water solubility, or those described as “hydrophobic” have been represented with a water solubility of 0.000001 mg/L (1×10^{-6} mg/L; assigned arbitrarily; OECD, 2009). That is equivalent to 1 ppt, a very conservative definition.
		Polymers with water solubility <10 mg/L showed generally low health concerns.
		The octanol–water partition coefficient (K_{ow}) is another criterion to assess chemicals and their environmental and health impact. The K_{ow} is a physical–chemical property at equilibrium to represent the lipophilic or hydrophilic nature of a chemical, the distribution of a compound in octanol, representing the lipophilic nature, to its solubility in water, representing the aqueous nature. The higher the K_{ow} , the more lipophilic the compound. Typically, a K_{ow} >5000 or a log K_{ow} >5 means high lipophilicity and, thus, a high potential to bioaccumulate or bioconcentrate. According to the Stockholm Convention, a bioconcentration factor of >5000 and a log K_{ow} >5 is used as a criterion for bioaccumulation.
Stability		Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. As was previously described in the Polymer of Low Concern section under the molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da heading, molecules with Mn <1000 Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment.
Abiotic stability		Polymers are stable; monomers are not. Abiotic degradation may involve sunlight, water, or oxygen. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Hydrolytic degradation of polymers is another potential way to break the polymer bonds, creating smaller oligomers that may be bioavailable. Chemical oxidation is a reaction involving the loss of electrons from one atom to another.
Biotic stability: aerobic, anaerobic, and in vivo		Biotic stability is assessed by whether the polymer is degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic) conditions; in vitro and in vivo stability studies demonstrate this. In vivo biodegradation involves the breaking of the polymer bonds by the action of bacteria, enzymes, and oxidants within the organism.
Thermal stability		Thermal stability of a polymer can be assessed when used as intended under normal, foreseeable use conditions or in extreme temperatures during disposal, such as by incineration. Thermal stability testing may involve Thermogravimetric Analysis (TGA), which determines mass loss over time and temperature of a test substance.

TABLE 4 Fluoroplastics and PLC criteria

Supporting Information Data: Chapter	Fluoroplastics			
	4.1 PVDF	4.2 PVDF-HFP copolymer	4.3 ECTFE	4.5 PCTFE
	Polyvinylidene fluoride	Vinylidene fluoride, hexafluoropropene copolymer	Ethylene, chlorotrifluoroethylene copolymer	Polychlorotrifluoroethylene
PLC assessment criterion ^a	CAS 24937-79-9	CAS 9011-17-0	CAS 25101-45-5	CAS 9002-83-9
Structure	$-(CF_2-CH_2)_n-$	$-(CF_2-CH_2)_n-[CF(CF_3)-CF_2]_m-$	$-(CF_2-CFCl-CH_2-CH_2)_n-$	$-(CF_2-CFCl)_n-$
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes
Molecular weight (Mn) ^b (Mn > 1000 Da and oligomer content <1%)	70 000–300 000	80 000–300 000	Mn >50 000	70 000–400 000 average based on grade type
Molecular weight distribution $M_w^c \div$ number average M_n	2–3	2–3	1.1	1.7
Wt% oligomer (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	Negligible	Negligible
Ionic character	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs) ^d and functional group equivalent weight (FGEW)	None and N/A	None and N/A	None and N/A	None and N/A
Low molecular weight leachables	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	Negligible
Residual monomers	<50 ppb	<50 ppb	<50 ppb	<0.1 wt%
Ratio of residual monomers to molecular weight (typical value)	$\sim 10^{-12}$ – $\sim 10^{-13}$	$\sim 10^{-12}$ – $\sim 10^{-14}$	$\sim 10^{-13}$	<10 ⁻⁵
Structural similarities to RFG of concern	None	None	None	None
Reference standard	ASTM D3222-18a	ASTM D5575-18	ASTM D3275-81	ASTM D3275-81

(Continued)

TABLE 4 (Continued)

Fluoroplastics					
Supporting Information Data: Chapter	4.1 PVDF	4.2 PVDF-HFP copolymer	4.3 ECTFE	4.4 ECTFE	4.5 PCTFE
Physical-chemical properties					
Water solubility and octanol/water partition coefficient, K_{ow}	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, MMAD, should be >5 μm)	Powders: 5–300 μm pellets: 2–4 mm	Powders: 5–300 μm pellets: 2–4 mm	D50%: 50–70 μm (typical)	D50%: 50–70 μm (typical)	Pellet: 2–4 μm , flake: 0.54 mm powder: 5–300 micron
Stability					
Hydrolysis, light (hv), Oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp. ($^{\circ}\text{C}$)	150 $^{\circ}\text{C}$	150 $^{\circ}\text{C}$	150 $^{\circ}\text{C}$	150 $^{\circ}\text{C}$	120 $^{\circ}\text{C}$
Meets ^a PLC criteria (Yes or No)	Yes	Yes	Yes	Yes	Yes
Fluorinated polymerization aid (PA) used? (Yes or No)	No	No	No	No	No
Recommended processing/application (use) temperature ($^{\circ}\text{C}$)	Processing: 200 $^{\circ}\text{C}$ –250 $^{\circ}\text{C}$ Use max temp: 150 $^{\circ}\text{C}$	Processing: 180 $^{\circ}\text{C}$ –250 $^{\circ}\text{C}$ Use max temp: 100 $^{\circ}\text{C}$ –140 $^{\circ}\text{C}$ depending on HFP content	Processing: 250 $^{\circ}\text{C}$ –280 $^{\circ}\text{C}$ Use max. Temp: 150 $^{\circ}\text{C}$	Processing: 250 $^{\circ}\text{C}$ –280 $^{\circ}\text{C}$ Use max. Temp: 150 $^{\circ}\text{C}$	Molding: 230 $^{\circ}\text{C}$ –330 $^{\circ}\text{C}$ and Use Max same as above at 120 $^{\circ}\text{C}$
Fluoroplastics					
Supporting Information Data: Chapter	4.6 FEVE	4.7 EFEP	4.8 CPT	4.9 THV	
Fluoroethylene-vinyl ether copolymer	Fluoroethylene-vinyl ether copolymer	1-Propene, 1,1,2,3,3,3-hexafluoro-, polymer with ethylene and 1,1,2,2-tetrafluoroethylene	1,1,1,2,2,3,3-Heptafluoro-3-[(trifluoroethenyl)oxy]propane polymer with chlorotrifluoroethylene and tetrafluoroethylene	1-Propene, 1,1,2,3,3,3-hexafluoro-polymer with difluoroethylene and tetrafluoroethylene	
PLC assessment criterion ^a	cbi	35560-16-8	116018-07-6	25190-89-0	(Continued)

TABLE 4 (Continued)

Supporting Information Data:		Fluoroplastics			
Chapter		4.6 FEVE	4.7 EFEP	4.8 CPT	4.9 THV
Structure		cbi	$-(CH_2-CH_2)_n-(CF_2-CF_2)_m-[CF_2-CF(CF_3)]_l-$	$-(CF_2-CF_2)_n-(CFCI-CF_2)_m-[CF_2-CF(CF_3)]_l-$	$-(CF_2CH_2)_x-(CF_2-CF-CF_3)_y-(CF_2-CF_2)_z$
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)		Yes	Yes	Yes	Yes
Molecular weight (Mn) ^b (Mn > 1000 Da and oligomer content < 1%)		7000–46 000	130 000	200 000–300 000	131 000
Molecular weight distribution Mw ^c ÷ number average M _n		2.0–4.0	4	2–5	1.8
Wt% oligomer (< 5% for < 1000 Da oligomers, < 2% for < 500 Da oligomers)		Mn < 1000 range of < 3.5% and Mn < 500 is < 0.7%	Negligible; < 0.1 wt% oligomer content	Negligible; < 0.1 wt% oligomer content	wt.% < 1000: None
Ionic character		Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs) ^d and functional group equivalent weight (FGEW)		None and N/A	None and N/A	None and N/A	None and N/A
Low molecular weight leachables		Negligible; cross- linked as final product	Negligible	Negligible	No active leachables by USP class VI (121 °C)
Residual monomers		0.12%–1.43% non- fluorinated	Negligible	Negligible	None detected
Ratio of residual monomers to molecular weight (typical value)		10^{-7} – 10^{-8}	< 10^{-5}	< 10^{-5}	$\sim 10^{-13}$
Structural similarities to RFG of concern		None	None	None	None
Reference standard			ASTM D7472	ASTM D7471	

(Continued)

TABLE 4 (Continued)

Supporting Information Data: Chapter		Fluoroplastics				
		4.6 FEVE	4.7 EFEP	4.8 CPT	4.9 THV	
Physical-chemical properties						
Water solubility and octanol/ water partition coefficient, K_{ow}		Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	
Particle size (median mass aerodynamic diameter, MMAD, should be $>5\ \mu\text{m}$)		Solution or flake 150 nm for emulsion	2–4 mm (pellets)	2–4 mm (pellets)	Pellets ~400–750 μm	
Stability						
Hydrolysis, light (hv), oxidation, biodegradation (aerobic and anaerobic)		Stable	Stable	Stable	Stable	
Thermal stability at normal foreseeable use maximum continuous temp. ($^{\circ}\text{C}$)		220 $^{\circ}\text{C}$	130 $^{\circ}\text{C}$; low melting point 160 $^{\circ}\text{C}$ –190 $^{\circ}\text{C}$ and high decomposition temperature of 357 $^{\circ}\text{C}$ –380 $^{\circ}\text{C}$	200 $^{\circ}\text{C}$; low melting point 239 $^{\circ}\text{C}$ –251 $^{\circ}\text{C}$ and high decomposition temperature of $>400\ ^{\circ}\text{C}$	Continuous use is expected ~room T. ($<100\ ^{\circ}\text{C}$ as host resin melts at 120 $^{\circ}\text{C}$); No expected degradation; fluoropolymer degrades $>350\ ^{\circ}\text{C}$ by TGA	
Meets ^a PLC criteria (Yes or No)		Yes	Yes	Yes	Yes	
Fluorinated polymerization aid (PA) used? (Yes or No)		No	No	No	Yes and No	
Recommended processing/ application (use) temperature ($^{\circ}\text{C}$)		180 $^{\circ}\text{C}$ –200 $^{\circ}\text{C}$	Molding temperature: 200 $^{\circ}\text{C}$ –280 $^{\circ}\text{C}$; Use max as noted above	Molding temperature: 310 $^{\circ}\text{C}$ –330 $^{\circ}\text{C}$; Use max as noted above	Melt processing: $<350\ ^{\circ}\text{C}$ Application: $<100\ ^{\circ}\text{C}$ (in LLDPE)	

Abbreviations: ECTFE, ethylene-chlorotrifluoroethylene; HFP, hexafluoropropylene; PCTFE, polychlorotrifluoroethylene; PLC, polymer of low concern; PVDF, polyvinylidene fluoride.

^aSee OECD (2009) and BIO by Deloitte (2015) for details on characteristics of a “Polymer of Low Concern” and Supporting Information: Chapter 3.

^bMolecular Weight is number average molecular weight which is defined as the total weight of the polymer divided by the total number of molecules. It is the mole fraction of molecules in a polymer sample.

^cMolecular weight is weight average molecular weight which is determined by summing the weights of all the chains and then dividing by the total number of chains. It is the weight fraction of molecules in a polymer sample.

^dFor definition of reactive functional group, lists of low-, moderate-, and high-concern functional groups and FGEW limits, see USEPA polymer exemption guidance manual, BIO by Deloitte (2015, pp. 191–192), and USEPA (2010). See Supporting Information.

TABLE 5 Fluoroelastomers and specialty fluoroplastics—PLC criteria

Supporting Information Data: Chapter	Specialty fluoroplastics		Fluoroelastomers		
	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
	Perfluoro(alkenyl vinyl) ether polymer	Sodium or potassium salts of perfluorosulfonic acid/TFE copolymer or perfluorocarboxylic acid/TFE copolymer	Tetrafluoroethylene-propylene copolymer	1-Propene, 1,1,2,3,3,3-hexafluoro-polymer with 1,1-difluoroethylene copolymer and terpolymers	Tetrafluoroethylene-trifluoromethyl trifluorovinyl ether copolymer
PLC assessment criterion ^a	37626-13-4	9002-84-0, 1314-23-4, 409-21-2, 11173-25-2	27029-05-6	9011-17-0, 26425-79-6, 25190-89-0	26425-79-6
Structure	See Supporting Information	See Supporting Information	See Supporting Information	Supporting Information	-(CF ₂ CF ₂) _x -(CF ₂ -CF(OCF ₃)) _y -(Cure Site Monomer) _z
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes	Yes
Molecular weight ^b (M _n > 1000 Da and oligomer content <1%)	150 000–300 000	>100 000	Various grades vary between 146 000–275 000	30 000–340 000	10 000–1 000 000
Molecular weight distribution M _w ^c ÷ number average M _n	1.4–2.5	1.0–2.4	Various grades give various ratios from 1.4 to 3.3	1.2–2.4	1.2–3.5
Wt% oligomer (Figure MWD) (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	<0.01%	Negligible to <1%	Negligible
Ionic character	Neutral	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs) ^d	None and N/A	None and N/A	None and N/A	None and N/A	None and N/A
Functional group equivalent weight (FGEW; typical value)	>10 ⁵	>10 ⁵	>10 ⁵	>10 ⁴ –10 ⁵	>10 ⁴

(Continued)

TABLE 5 (Continued)

Supporting Information Data: Chapter	Specialty fluoroplastics		Fluoroelastomers		
	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
Low molecular weight leachables	<1 ppm	<1 ppm	No active leachables	<0.4 ppm to <1 ppm	No active leachables
Residual monomers	<1 ppm	<1 ppm	No residual monomers Only cross-linking agent at <1 ppm	<50 ppt to <5 ppm	<50 ppb
Ratio of residual monomers to molecular weight (typical value)	>10 ⁻⁵	>10 ⁻⁵	10 ⁻¹¹ –10 ⁻¹²	>10 ⁻¹⁰ –10 ⁻¹³	0.25 ppt as Mn = 10 ⁵ (for representative FKM)
Structural similarities to RFG of concern	None	None	None	None	None
Reference standard	ASTM D 1418				
Physical–chemical properties					
Water solubility and octanol/water partition coefficient, K _{ow}	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, aerodynamic diameter, MMAD, should be >5µm)	Solution, sheet or pellets	(1) Aqueous dispersion casting (as a film) followed by annealing or (2) Melt extrusion as a membrane (reinforced)	Sheet or crumb	Sheet or block; powders 300–350 µm stability increased/enhanced when cross-linked	Sheet or block; or “crumb”
Stability					
Hydrolysis, light (hν), oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable	Stable
(Continued)					

(Continued)

TABLE 5 (Continued)

Supporting Information Data: Chapter	Specialty fluoroplastics		Fluoroelastomers		
	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
Thermal stability at normal foreseeable use maximum continuous Temp (°C)	>250 °C	Sulfonic acid polymer: maximum operating temperature of 175 °C under anhydrous conditions, 220 °C –240 °C in aqueous systems carboxylic acid polymer: use below 120 °C	200 °C	180 °C	200 °C–300 °C
Meets ^a PLC criteria (Yes or No)	Yes	Yes	Yes	Yes	Yes
Fluorinated polymerization aid (PA) used? (Yes or No)	Yes and No	Yes and No	No	Yes and No	Yes and No
Recommended processing/ application (use) temperature (T °C)	<280 °C	Sulfonic acid polymer: maximum operating temperature of 175 °C under anhydrous conditions, 220 °C–240 °C in aqueous systems carboxylic acid polymer: use below 120 °C	–60 °C–204 °C (AFLAS Technical Document)	Melt processing: <300 °C 160 °C–320 °C (cross- linking temperature)	160 °C–320 °C (cross-linking temperature)

Abbreviations: FEPM, trifluoroethylene-propylene copolymer; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMVE perfluoroelastomer; PLC, polymer of low concern.

^aSee OECD (2009) and BIO by Deloitte (2015) for details on characteristics of a “Polymer of Low Concern.”

^bMolecular weight is number average molecular weight.

^cMolecular weight is weight average molecular weight.

^dFor definition of reactive functional group, lists of low-, moderate-, and high-concern functional groups and FGEW limits, see USEPA polymer exemption guidance manual, BIO by Deloitte (2015, pp. 191–192), and USEPA (2010). See Supporting Information.

until all data cells in the tables cited above were backed up with a narrative, a testing method, and/or references where publicly available.

- Where several companies have provided data on the same fluoropolymers, the table data presented provide a multicompany compilation and assessment along with appropriate methods and references.
- Individual companies supplying data are identified as authors, but there is no direct attribution regarding which company supplied which data for this study.

PLC ASSESSMENT RESULTS

This study was conducted on commercial fluoropolymer products using the PLC criteria to characterize their potential hazard. Figure 1 illustrates the PLC criteria used (BIO by Deloitte, 2015; Henry et al., 2018). The pictured criteria encompass structure, physicochemical property, and stability criteria evaluated in the study. Data informing structure criteria, MW, Mn, and MW distribution (MWD), physicochemical property criteria, water and lipid solubility and K_{ow} , and stability criteria are presented in Tables 4 and 5. The study also gathered structural data on (a) residual monomers, (b) ratio of residual monomers to MW, (c) structural similarities to reactive functional groups (RFGs) of concern, and (d) thermal stability at normal foreseeable maximum continuous use temperatures. Brief descriptions of PLC criteria are provided in Table 3 with additional details, including references for each criterion in Supporting Information: Chapter 3. An additional data point gathered was whether the fluoropolymer(s) presented utilized a fluorinated polymerization aid (PA) during manufacture. The study results are presented in Tables 4 and 5 and summarized below.

Polymer composition: Each of the fluoroplastics, specialty fluoroplastics, and fluoroelastomers assessed in this study met the criterion of polymer composition whereby either fluorine (F) and/or chlorine (Cl) must be covalently bound to the carbon-only polymer backbone.

MW and MWD: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the criteria for MW (Mn >1000 Da) and MWD (1–3). The data demonstrate the fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study are high-MW solid polymers with fairly narrow MWD and negligible to low wt% oligomer content. The MW for fluoroplastics in Table 4 and specialty fluoroplastics in Table 5 ranged from 50 000 to 300 000, and the MWD ranged from approximately 1.4 to 3. We note that FEVE was measured in its uncured state and that, upon curing, its MW increased significantly. The MW and MWD were determined in a variety of ways depending on the fluoropolymer and its solubility (or insolubility) in various solvents. The MW and MWD data for fluoroelastomers and specialty fluoroplastics in the study are presented in Table 5. The MW and MWD varied because of the various grades of fluoroelastomers ranging from 100 000 to 250 000 with some less than (down to 10 000) and greater than (up to 500 000). MWD was on

the order of 1.4 to 3.5. Fluoroelastomer MW is lower for uncured fluoroelastomer versus cured fluoroelastomer. Cured fluoroelastomer is the form used in many formed-use applications (e.g., gaskets and o-rings). The methods and references for MW and MWD data are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. Methods included size exclusion chromatography (SEC), gel permeation chromatography (GPC) along with osmotic pressure, and parallel plate rheometry methods.

Weight % oligomer: The criteria for wt% oligomer are less than 5% oligomer content for Mn less than 1000 Da, and less than 2% oligomer content for Mn less than 500 Da (BIO by Deloitte, 2015; Henry et al., 2018; see also the Supporting Information). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the wt% oligomer criteria. Many polymers in the study were reported as “negligible” for oligomers based on analyses conducted. Polymers in the study not cited as negligible have reported numerical data presented in Tables 4 and 5. In addition to SEC and GPC, analytical methods employed included a weight loss upon heating method and the FDA 21 CFR 177.1380 method. The methods and references for wt% oligomer are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5.

Ionic character: The fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study are neutral polymers, either containing no ionic groups or may contain anionic at the terminus of their high MW polymer chains as noted in the prior study of fluoropolymers (Henry et al., 2018). Notably different are fluorinated ionomers, which have neutralized (salts) sulfonic acid or carboxylic acid groups pendant to the polymer backbone and as such are neutral and not ionically charged in their polymeric solid form and are low in toxicity and not dermally irritating on skin contact (USEPA, 1997). None of the evaluated polymers in the study have cationic nature. The methods and references for ionic character are presented in the Supporting Information: Chapter 4 with the specific subchapter noted in Tables 4 and 5.

RFG, functional group equivalent weight (FGEW) and structural similarities to RFG of concern: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the RFG and FGEW criteria. The polymers in this study do not contain the reactive functional groups set forth in the PLC criteria (e.g., acrylates, alkoxysilanes, amines, aziridines, carbodiimides, and so forth; see Supporting Information: Chapter 3). Given that the polymers in this study have no RFGs, the FGEW values in Tables 4 and 5 are very large numbers (such as $>10^4$ – 10^5) or the value given is not applicable due to the lack of RFGs altogether. Even the polymers with some functional groups present (e.g., fluorinated ionomers) are not reactive. For example, the FEVE polymerization process leads by design to a polymer with neutral and/or anionic end groups. FEVE resins do contain a small amount of hydroxyl and carboxyl functional groups. These functional groups are classified as low concern RFG

by the USEPA (1997) and OECD (2009). There are no RFG structural similarities across the polymers in this study.

Low MW leachables (MW < 1000 Da): All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the low MW leachable PLC criteria, which has been widely discussed (see Supporting Information: Chapter 3 for references). Many of the study polymers report no active leachables, whereas the rest cite values less than 1 ppm (Tables 4 and 5). For FEVE, it is reported that some non-fluorinated polymer PA may well remain in the uncured polymer resin. The methods and references for low MW leachables are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. The data presented in Tables 4 and 5 were determined for each of the respective polymers in this study using techniques such as SEC and GPC as the predominant analytical methods along with the use of USP Class VI testing. Additional methods included 21 CFR 177.2600 (USCFR, 2022) and the USEPA's toxicity characteristic leaching procedure (TCLP; SW-846 Test Method 1311; USEPA, 1992).

Residual monomers and ratio of residual monomers to typical MW: PLC criteria of equal interest to the low MW leachables are the residual monomers and the ratio of residual monomers to typical MW (see Supporting Information: Chapter 3 for references). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the residual monomers and ratio of residual monomers to typical MW PLC criteria. The study data presented in Tables 4 and 5 show the polymers in this study have residual monomers ranging from less than 50 ppb for several fluoropolymers and up to less than 0.1% for PCTFE based on the methods utilized. Fluoroelastomers in this study have residual monomers ranging from less than 50 ppb up to less than 5 ppm. Residual monomers were determined in several ways including dynamic and static headspace gas chromatography/mass spectrometry (GC/MS) at 150 °C. The monomers used in most cases have very low boiling points and are thus readily volatilized (and captured or destroyed) during polymer manufacture processing and drying steps. The methods and references for residual monomer determination are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. Given the very low residual monomer levels reported, the ratio of residual monomers to polymer MW range from 10^{-11} to 10^{-13} for the study polymers.

Water solubility and octanol/water partition coefficient (K_{ow}): The fluoroplastics, specialty fluoroplastics, and fluoroelastomers in this study are solids that are hydro- and oleophobic, practically insoluble in both water and n-octanol. Therefore, a K_{ow} cannot be computed and is not applicable to these substances. It is worth noting that the practical lack of solubility in water (<10 mg/L) and n-octanol indicate the inability for the study fluoropolymers to actively or passively cross cell membranes. This does mean there is no indication that these polymers can bioaccumulate or bioconcentrate in biota (Henry et al., 2018 and this study). The methods and references for solubility are presented in the

Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5.

Particle size: To meet the PLC assessment criteria for particle size, a powder must be 5 μ m or greater in size (median mass aerodynamic diameter [MMAD]). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the particle size PLC criterion. As shown in Tables 4 and 5, the fluoroelastomers in this study are provided in sheets, blocks, pellets, or "crumb," and the fluoroplastics and specialty fluoropolymers in this study are provided in the form of powders, pellets, sheets, flake, or in dispersions. References and additional information regarding the form of the study polymers is provided in the Supporting Information: Chapter 4.

Stability: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the PLC criteria for hydrolysis, light stability, oxidative stability, and aerobic and anaerobic biodegradability (e.g., breakdown into species with Mn <1000 Da). Public literature has abundant thermal, chemical, and biological stability data for the polymers in this study as stability is a hallmark property for these polymers (Ebnesajjad, 2017). For biodegradation, the assessments were largely made based on property data of the study polymers demonstrating they are insoluble and stable in environmental media and thus are not expected to be bioavailable and therefore not biodegrade.

Additionally, published literature reports (Drobny, 2016; Ebnesajjad, 2017; Grot, 2013; Henry et al., 2018; Polymer Industry Association [PIA], 2019) that the study polymers are stable at foreseeable maximum continuous use temperatures presented in Tables 4 and 5. All polymers, including fluoropolymers can degrade when misused or when heated above their recommended use temperatures (Fluoropolymer Products Group of Plastics Europe [FPG], 2012; PIA, 2019). Of course, users are expected to follow guidance for use provided by manufacturers. Hence, the recommended temperatures for reasonably foreseeable use for the study substances are presented in Tables 4 and 5. References and additional information regarding the stability of the study polymers is provided in the Supporting Information: Chapter 4.

Fluorinated PA: If a fluorinated PA was used in the manufacture of the polymer, it was reported for each fluoropolymer in this study. Nine of the 14 fluoropolymers in the study were reported not to have used a fluorinated PA in their manufacture. It is industry practice to use fluorinated PAs when it is necessary to obtain specific end-use property or performance requirements generally related to very high-polymer MWs (see also Supporting Information: Chapter 7). For five study polymers, THV, FKM, FFKM, fluorinated ionomers, and amorphous fluoropolymers, a response of "Yes and No" was provided indicating that for some polymer grades a fluorinated PA is used, but not for others. See Supporting Information: Chapter 4 for additional information.

Results summary: This study examined three fluoroelastomers, nine fluoroplastics, and two specialty fluoroplastics:

ionomers and amorphous. Data for each were gathered from the author companies and assessed by the PLC criteria applicable to the polymer itself “in use” (BIO by Deloitte, 2015; Henry et al., 2018; OECD, 2009). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the PLC criteria based on the data presented in Tables 4 and 5 with additional details provided describing methods and references in the Supporting Information: Chapter 4.

Including the four fluoroplastics in the prior study (Henry et al., 2018), data for 18 fluoropolymers have been provided for PLC assessment. These polymers have a wide range of compositions and structures and represent most of the global commercial fluoropolymer market (see additional text in the Discussion). These 18 fluoropolymers represent the major fluoropolymers manufactured and are used worldwide in innumerable critical end-use products and applications. Tables 1 and 2 highlight examples of the end-use markets as well as critical functionality and benefits these polymers provide.

Each of the assessed polymers in this study are insoluble in both water and *n*-octanol, and thus K_{ow} is not applicable. This lack of solubility in water and octanol confirms that fluoropolymers are not mobile in the environment and are not bioaccumulative and not able to bioconcentrate. The stability studies reported here on each of the study fluoropolymers reveal their stability in terms of light, hydrolysis, heat, oxidation, and biodegradation. When coupled with the lack of solubility, these fluoropolymers are most often characterized as relatively inert materials in the environment. Like any other chemical material or product, it is important to follow the fluoropolymer manufacturer's recommended use and temperature conditions. Tables 4 and 5 describe these recommendations for each fluoropolymer. As reported, the physical forms of the fluoropolymers are largely pellets, blocks, crumb, sheets, some powders (all with MMAD >5 μ m). The solid fluoropolymers are not nanoparticles, and concerns related to nanoparticles do not apply during normal product use. Due to the properties described above for the assessed fluoropolymers—large molecules with no water solubility—the fluoropolymers are biologically inert without the practical ability to cross cell membranes.

During the evaluation of the study fluoropolymers, there was a conscious focus on several core PLC parameters: MW, low MW leachables, % oligomers, and residual monomers, which are direct outcomes related to fluoropolymer manufacturing. In addition to what is reported here in Tables 4 and 5 for the fluoropolymers themselves, industry efforts to manage emissions during manufacturing are discussed below.

DISCUSSION

Fluoropolymers have substantial, unique societal value: Fluoropolymers possess a remarkable combination of properties and functional characteristics, as shown in Tables 1 and 2, that make them valued materials of choice in a broad range of industries and applications critical to life

and a sustainable environment in the 21st century. Their unparalleled combination of properties and performance characteristics deliver functionality to a wide variety of products and systems critical to achieving important societal goals (Amcham, 2020c; FPG, 2021a; Wood, 2020b). They are strategically important to innovation in vital sectors of the global economy requiring high-speed, high-volume data transmission, miniaturization, or operations in extreme temperatures. Moreover, they are crucial to achieving important societal goals such as decarbonization, renewable energies, and/or competitiveness in the digital transition (FPG, 2021a). Fluoropolymers are indispensable for critical applications in the chemical, electronic, semiconductor, healthcare, and transport sectors and the deployment of 5G networks (FPG, 2021a). For many critical applications, fluoropolymers are the material of choice because alternatives are unable to provide the full complement of performance and functionality required. As such, there are currently no viable commercial alternatives to fluoropolymers in virtually every critical application in which they are used (FPG, 2021a, 2017; PFP, 2020).

Commercial fluoropolymers in this study meet the PLC criteria: Widely used by regulators, PLC criteria have been established around the world and documented by OECD expert groups as an appropriate hazard assessment methodology for polymers in-use and can effectively identify low risk fluoropolymers to help prioritize regulatory action (BIO by Deloitte, 2015; OECD, 1993, 2009). Here, we present PLC data, for hazard assessment, that define a group of fluoropolymers' “in-use” properties. PLC is not a comprehensive life-cycle assessment tool. Full life-cycle assessments consider all phases of product “life” including creation (manufacturing) and end-of-life (disposal). Information on manufacture and end-of-life is provided later in this study. Recently, polymers have been under increased regulatory scrutiny. In 2019, the industry-led European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a Conceptual Framework for Polymer Risk Assessment (“CF4Polymers”; ECETOC, 2019). CF4Polymers provides guiding elements to be considered in assessing potential ecological and human health hazards and risks posed by polymer substances. CF4Polymers also considers specific life-cycle stages of polymer products and their associated routes of exposure. The authors of the CF4Polymers framework support the PLC approach as a means to accomplish polymer risk assessment. They specifically support the findings of Henry et al. (2018) and state that they are “unaware of scientific evidence to justify generally assigning fluoropolymers the same level of regulatory concern as other PFAS” (ECETOC, 2019). In 2020, the European Commission contracted a study to propose criteria to identify PRR under REACH (Wood, 2020a). The report states that the authors consider fluoropolymers meeting the criteria to be considered PLC, “following the recommendations of Henry et al. (2018).”

The properties and characteristics of fluoropolymers are anchored in the strength of the carbon–fluorine bond, which

render them highly stable (thermally, chemically, and biologically), inert, and durable—long lasting in use—under exacting and high-performance conditions. Physical, chemical, thermal, and biological stability are important criteria for a polymer to be considered a PLC. The data presented in Tables 4 and 5 demonstrate that commercial fluoropolymers from the author companies meet the criteria to be considered PLC. The PLC criteria for physicochemical properties reflect the state of the polymers in this study, solids, as well as their inertness and stability. None of the fluoropolymers assessed in this study were soluble in water or octanol. They are biologically inert, insoluble in water and octanol, and not expected to move in or between environmental media. Fluoropolymers are also twice as dense as water. These properties and water insolubility mean fluoropolymers are not mobile in the environment and therefore would not be expected to be found in sources of drinking water. Fluoropolymers are neither bioavailable nor bioaccumulative. These solid polymers cannot be absorbed through a cell membrane via passive or active transport and do not bind or interact with the cell surface (see also Supporting Information: Chapter 8). In addition, whereas aquatic and mammalian toxicology studies of fluoropolymers may be desirable for some, they are technically difficult for insoluble, solid, high-MW polymers. The OECD test guidelines reiterate this in many cases. This is confirmed for example in REACH Annex VII guidance, which repeatedly states toxicity is unlikely to occur “if a substance is highly insoluble in water or the substance is unlikely to cross biological membranes” (see Supporting Information: Chapter 9).

Finally, structure criteria including MW, MWD, residual monomer(s), oligomers, and other synthesis by-products, as represented by low MW extractables and leachables have been determined for the fluoropolymers presented and meet values established for the PLC criteria and regulated uses (e.g., USP). The concentrations in the fluoropolymer that have been evaluated are extremely low, reflective of effective manufacturing processes that minimize these compounds complemented by capture and/or destruction systems for such materials. For additional information, see the section below discussing responsible manufacturing. This study and prior work (Henry et al., 2018) provide a guide for other global fluoropolymer manufacturers to gather and present data on additional commercial fluoropolymers to determine if they too meet the PLC criteria.

Fluoropolymer stability, aka persistence, is not an intrinsic hazard: Fluoropolymers are stable, inert, solid materials. Fluoropolymers resist degradation by acids, bases, oxidants, reductants, photolytic processes, microbes, and metabolic processes; for this reason, they are thermally, chemically, and biologically highly inert. Fluoropolymer stability was presented in the introduction and is further considered in the Supporting Information: Chapters 4 and 5. Fluoropolymers are not expected to degrade under environmental conditions or normal use and processing conditions (Wood, 2020a). They are stable and remarkably durable and are

therefore persistent. However, persistence alone does not imply that there is a present or future risk to human health or the environment (Rüdel et al., 2020). Persistence itself is not an intrinsic hazard, as it does not in itself imply or inform the potential for an adverse effect (aka toxicity). There is no language in REACH supporting the notion that persistence alone justifies risk-management measures. REACH has regulated persistence in combination with other properties that do inform potential hazards. In fact, REACH combines persistence with bioaccumulation and toxicity (or “very persistent” with “very bioaccumulative/very mobile” vPvB/vPvM) to justify designation as a substance of very high concern (SVHC) and consideration of potential risk-management measures for uses associated with unacceptable risk. Therefore, persistence on its own does not justify the need for specific risk-management measures. Fluoropolymers themselves are persistent, but they are not bioaccumulative, not mobile, and not toxic and therefore not SVHCs from a regulatory perspective (Ruwona and Henry, 2021).

PFAS grouping and segmentation—Scope of regulatory measures: The OECD definition of PFAS is based only on chemical structure (OECD, 2021). It describes a universe of fluorinated organic substances with vastly different physical, chemical, and biological properties, including polymers and nonpolymers; solids, liquids, and gases; highly reactive and inert substances; soluble and insoluble substances; and volatile and involatile substances and is too broad to allow effective, science-based assessment and regulation of chemical compounds as an entire group (Amcham 2020a; BDI, 2021; Buck et al., 2021; Orgalim, 2021; Wallington et al., 2021). A 2021 OECD report states: “it is highly recommended that such diversity be properly recognized and communicated in a clear, specific and descriptive manner” and “the term ‘PFASs’ does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene aliphatic carbon moiety” (OECD, 2021).

In this context, the available property data (Tables 4 and 5) reveal that fluoropolymers have distinctly different properties from nonpolymeric PFAS and from SCFPs that have a polymeric backbone that does not contain C–F bonds directly attached to it. The perfluoroalkyl moiety in SCFPs is found in a side-chain connected via a functional group to the polymer backbone and “can potentially lead to the formation of nonpolymer PFAS as a result of degradation” (Fluoropolymer Products Group of Plastics Europe [FPG], 2021b; Wood, 2020a; see Supporting Information: Chapter 6). Segmentation that clearly differentiates the broad PFAS family according to their properties, rather than using a structure-based classification alone (OECD, 2021), is needed for a scientifically sound, risk-based regulatory approach. Regulating all PFAS as one homogenous group (ECHA, 2020) absent consideration of their properties, particularly when the properties are so demonstrably different, neglects basic scientific consideration of these properties,

which are the foundation of substance differentiation. The USEPA does not consider all PFAS to have similar risk profiles and therefore they are following a categorical grouping approach based on information about similarities in structure, physicochemical properties, and existing test data on the toxicity of PFAS (USEPA, 2021b). Therefore, segmentation based on properties should be conducted before performing any grouping-based risk assessment, placing stable, nonhazardous fluoropolymers that meet the criteria to be considered PLC in a separate category (see also Supporting Information: Chapter 6).

Fluoropolymer market perspective: The commercial fluoropolymer global market sales have been reported to be approximately 230 000 MT (Dams & Hintzer, 2017). Given the expected fluoropolymer market growth, ranging from approximately 4%–5% to 7%–8% (Allied Market Research [AMR], 2022; Future Market Insights [FMI], 2022; FPG, 2021a; Globe Newswire, 2021), a pro forma market table was created for 2021 using a 5% growth rate. Adding ionomers as well as updated amorphous market information (company data) to the above, the total commercial fluoropolymer market sales is estimated to be approximately 330 000 MT in 2021 (see Supporting Information: Chapter 10). Four fluoropolymers: PTFE, FEP, PFA, and ETFE, were the focus of the first fluoropolymer PLC paper (Henry et al., 2018) and account for approximately 64% of fluoropolymers sold globally in 2021 (pro forma basis). The sales volume of these four fluoropolymers is represented by the first four bars in Figure 10.1 in Supporting Information: Chapter 10. This study discusses 14 fluoropolymers representing an additional 32% (pro forma basis) of the global fluoropolymer market. Therefore, this study, in combination with Henry et al. (2018), presents PLC data from the cited manufacturers of commercial fluoropolymers representing approximately 96% of the global commercial fluoropolymer market that meet the criteria to be considered PLC. The projected 2021 sales volume of the major types of commercial fluoropolymers covered in this study (PVDF, FKM, FEPM, amorphous, ionomers, THV, ECTFE, PCTFE, and FFKM, EFEP, CTP, and FEVE) are also represented in Figure 10.1 in Supporting Information: Chapter 10. As noted, estimated market volumes were provided for the sum of FEPM, CPT, EFEP, and FEVE as well as a small “others” category. The fluoropolymer polyvinyl fluoride (PVF) was not covered by these two papers but is also shown in Figure 10.1 in Supporting Information: Chapter 10. Other fluorinated polymers, perfluoropolyethers, and SCFPs are not addressed in this study (see Supporting Information: Chapter 6).

FLUOROPOLYMER LIFE-CYCLE CONSIDERATIONS

This study focuses on the properties of the 14 selected commercial fluoropolymers themselves in-use providing data that demonstrate they meet the criteria to be considered PLC. Additionally, the life-cycle stages of fluoropolymer creation (manufacturing) and disposal at the end of industrial or consumer use (end-of-life) are important to

consider. The primary focus in these life-cycle stages is generally nonpolymer PFAS from the manufacturing process or fluoropolymer degradation in end-of-life disposal (ECHA, 2020; FPG, 2021a; Guelfo et al., 2021; Lohmann et al., 2020).

The long-established life-cycle assessment approach to environmental protection and risk management first considers the extent of emissions, their toxicity, and their exposure potential (Guinee et al., 2011). When emissions are sufficiently large in scope, toxicity, and exposure potential, emission-management methods are then considered, including process input changes and emission controls to reduce or eliminate the risk of the emissions. Fluoropolymer manufacturing and disposal life-cycle stages were discussed in the paper that first presented fluoropolymer PLC data (Henry et al., 2018). Here we provide an update and current perspective.

Responsible manufacturing: As corroborated by the data presented here and in prior work (Henry et al., 2018), a large volume percentage and number of commercial fluoropolymers are manufactured that meet the criteria to be considered PLC. Emissions from fluoropolymer manufacture are a key product life-cycle focus. The main focus during the manufacturing phase is not directly related to fluoropolymers but from emissions. Emissions of concern may include nonpolymer PFAS such as fluorinated PAs, unreacted monomers, oligomers, or other unintended by-products formed during manufacturing. It is important to note that, although some high-MW fluoropolymers require use of a fluorinated PA in manufacturing (see also Supporting Information: Chapter 10), it has been reported that at least 50% of commercial fluoropolymers are made without one (Pro-K Fluoropolymer Group, 2021).

Recently, a group of fluoropolymer member companies of FPG voluntarily committed to responsible manufacturing principles through the commissioning of a Regulatory Management Option Analysis, developed by independent consulting firm Chemservices (FPG, 2021a). Member companies of this group are working on individual projects and joint projects at the trade association level with third-party experts. Specifically, companies have committed to continuously improving and/or developing the best available techniques in the manufacturing process, managing environmental emissions, developing R&D programs for the advancement of technologies allowing for the replacement of nonpolymer PFAS PAs and/or working with downstream users to increase the recyclability and reuse of its products in line with the objectives of circular economy (FPG, 2021a). Implementation of this voluntary industry initiative to address concerns relating to fluoropolymers will strengthen already ongoing efforts performed by the fluoropolymer industry promoting responsible manufacturing practices. In addition, member companies are committed to working with EU authorities to establish and implement technical actions to guarantee adequate control of the risks derived from the manufacture and use of fluoropolymers to mitigate such risks wherever possible. This will be done following

transparency principles and agreements to monitor progress. For example, important emission reduction has been demonstrated by major fluoropolymer manufacturers including fluorinated PA recovery for reuse, 99% removal of fluorinated PA in wastewater treatment, and 99.99% capture and destruction efficiency of gaseous emissions routed to a thermal oxidizer (Chemours, 2021c), as well as 99–99.9 plant emission reductions (Daikin, 2021c, 2022). Four other companies have reported replacement of fluorinated PAs with nonfluorinated PAs (Arkema, 2008, 2021b; Chemours, 2022; Gujarat Fluorochemicals Limited, 2022; Solvay, 2022). These are substantial efforts toward mitigating emissions associated with fluoropolymer manufacturing being worked on by fluoropolymer manufacturers. This study and the prior study (Henry et al., 2018) provide a guide for other global fluoropolymer manufacturers to gather and present data on their commercial fluoropolymers in-use demonstrating that they meet the PLC criteria.

End-of-use: At the end of industrial or consumer use, fluoropolymers may be disposed via the following routes: landfill, incineration (e.g., waste-to-energy [WTE] facilities), or reuse/recycling. There is considerable data demonstrating that fluoropolymers such as PTFE do not degrade in the environment or release substances of toxicological or environmental concern (FPG, 2021a; Hintzer & Schwertfeger, 2014). FPG member companies are working with the industry and end users on this subject and are engaged in a research project aimed at identifying conditions required for proper disposal (incineration) of fluoropolymers (FPG, 2021a).

Fluoropolymers are chemically, thermally, and biologically stable (Henry et al., 2018; this study) and therefore are not expected to transform to dispersive nonpolymeric PFAS when disposed of in a landfill. A recent study presented results from OECD guideline biodegradation studies demonstrating that PTFE is stable and does not degrade under environmentally relevant conditions (Ruwona and Henry, 2021). Further, fluoropolymers that meet the criteria to be considered PLC, such as those in this study and prior work (Henry et al., 2018), have negligible leachables, unreacted monomers, and oligomers most likely destroyed in fluoropolymer use processing and would therefore not be expected to significantly contribute to landfill leachate (Ruwona and Henry, 2021).

Available data reveal that fluoropolymers are mineralized (i.e., all C–F bonds broken, hydrofluoric acid generated, and scrubbed to calcium fluoride) under commercial WTE incineration operating conditions (Aleksandrov et al., 2019; Bakker et al., 2021; DEC, 2021; Giraud et al., 2021a, 2021b). In recent pilot scale studies representative of full-scale WTE facilities, the most common form of end-of-life destruction conducted on PTFE found that combustion converted the fluorine into controllable hydrogen fluoride gas and that, of the 31 PFAS studied, no fluorine-containing products of incomplete combustion were produced above background levels (Aleksandrov et al., 2019). Further, a recent study investigating the presence of PFAS in waste incinerator flue

gas stated: “based on a literature review, RIVM expects that most of the PFASs will largely degrade during the incineration process and then be removed when the flue gases are cleaned. The remaining PFASs are expected to be removed during the recovery of the carbon dioxide” (Bakker et al., 2021). The RIVM report affirmed that PTFE is the most stable fluorine-containing polymer. For PTFE, the RIVM report concluded that complete thermal decomposition is achieved at a temperature of approximately 800 °C. It was therefore assumed that other fluorine-containing polymers also thermally decompose completely at a temperature of 800 °C. Temperatures at the pyrolysis front and the combustion front in the waste-burning bed range from 900 °C to 1100 °C (Asthana et al., 2006; Ménard et al., 2006), which is well above 800 °C, the temperature at which the complete thermal decomposition of PTFE is achieved (Bakker et al., 2021). Studies for additional fluoropolymers and those with additional pilot and/or full-scale fluoropolymer studies would contribute to this body of data and further affirm their results. The PFP and FPG currently have joint projects working on these potential contributions.

Recycling of fluoropolymer products and articles containing fluoropolymers is difficult because separation of the fluoropolymer from the end products is not always possible (FPG, 2021a; Hintzer & Schwertfeger, 2014; Pro-K Fluoropolymer Group, 2018). This is because fluoropolymers are used predominantly in small components of larger finished articles involving a wide variety of materials. There are several options to recycle fluoropolymer products. In primary recycling, solid fluoropolymer waste is ground and later fed back into the manufacturing cycle of some fluoropolymer products. Recycled fluoropolymers may be used in high-end applications when correctly collected, cleaned, and reprocessed. In secondary recycling, solid fluoropolymer waste is ground, followed by degradation to approximately 1% of the original degree of polymerization by using electron beams, gamma rays, or thermomechanical degradation. The recovered material can be used in the manufacturing of new fluoropolymer products. Lastly, in tertiary recycling or upcycling, solid fluoropolymer is ground, then decomposed into the starting monomers at temperatures higher than 600 °C (pyrolysis) to obtain the same chemical components from which the fluoropolymer was manufactured; monomers, such as tetrafluoroethylene, are purified by distillation, and can then be reused to manufacture new fluoropolymer (3M, 2021; Schlipf & Schwalm, 2014). For the primary and secondary schemes, recycling treatments can be undertaken by the manufacturers of fluoropolymers themselves (onsite), or at a larger scale, mainly by specialist recycling companies. The upcycling needs to be colocated to a fluoropolymer manufacturing plant that can use tetrafluoroethylene.

Primary and secondary recycling is limited because of the presence of fillers, colorants, and other materials in the composition of their final articles. Further, recycling might not work for all end-of-life components, as they are used predominantly in small components of larger

finished articles involving a wide variety of materials. Therefore, collecting and dismantling for recycling might not be feasible for all products (FPG, 2021a; Hintzer & Schwertfeger, 2014; Pro-K Fluoropolymer Group, 2018). However, it should be noted that upcycling treatment is applicable to some articles containing fluoropolymers, such as pipe liners in chemical plants, as well as other plant components such as pumps, tank liners, seals, hoses, compensators, and many other fluoropolymer components and systems. These are the products for which the high quantities of fluoropolymers are used offering significant recycling potential.

SUMMARY

This study has described the composition, uses, performance properties, and functionalities of 14 commercially available fluoropolymers, including fluoroplastics and fluoroelastomers. Fluoropolymers are the preferred material of choice because of their unique combination of properties, which are not achievable from other materials or via other functions. As a result, fluoropolymers have become a critical mainstay for society and are useful to modern living, as they provide vital, reliable functionality to a broad range of industrial and consumer products. Further, the study has presented data demonstrating the subject fluoropolymers satisfy the widely accepted polymer hazard assessment criteria to be considered PLC. The data presented demonstrate the fluoropolymers in the study are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic, and contain low levels of impurities. These results further demonstrate that the fluoropolymer class should be considered distinctly different and should not be grouped with other PFAS for hazard assessment or regulatory purposes. When combined with earlier work (Henry et al., 2018), the study demonstrates that commercial fluoropolymers are available that meet the criteria to be considered PLC, which represent approximately 96% of the global fluoropolymer market. Lastly, emissions from fluoropolymer manufacture and disposal at end-of-use are a product life-cycle focus. Emissions may include nonpolymer PFAS such as fluorinated PAs, unreacted monomers, oligomers, or other unintended by-products formed during manufacturing. Fluoropolymer manufacturers recently committed voluntarily to responsible manufacturing principles by continuously improving and/or developing the best available techniques in the manufacturing process, managing environmental emissions, developing R&D programs for the advancement of technologies allowing for the replacement of fluorinated PAs, and/or increasing recyclability and reusing fluoropolymers in line with the objectives of circular economy.

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CONFLICT OF INTEREST

The authors are employed by companies that commercially manufacture fluoropolymers. SHK is an independent fluorotechnology consultant working on behalf of AGC Chemicals Americas Inc. and principal of BeachEdge Consulting LLC.

DATA AVAILABILITY STATEMENT

Data gathered for this paper is presented in the paper itself and the Supporting Information: Data file provided. Additional data are available upon request from the corresponding author Stephen Korzeniowski (shkorzo@gmail.com).

SUPPORTING INFORMATION

The Supplement contains a glossary of terms as well as additional information on the study of fluoropolymers properties and functionalities, polymer of low concern (PLC) background and criteria, references and methods for the PLC data for the study of fluoropolymers, benefits, features and alternatives assessment for the study of fluoropolymers, the differences between fluoropolymers and side-chain fluorinated polymers, fluoropolymer bioavailability and toxicity studies, fluoropolymer global market information, fluoropolymer socioeconomic analyses and risk-management options analysis (RMOA).

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Why Does PTFE Still Matter? Revisiting Its
Structure–Property–Performance–Applications Relationships Beyond
the PFAS Debate

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Why Does PTFE Still Matter? Revisiting Its Structure–Property–Performance–Applications Relationships Beyond the PFAS Debate

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Abstract

This review aims to present polytetrafluoroethylene (PTFE), its recent syntheses and processes, properties, applications, and its position in the per- and polyfluoroalkyl substances (PFAS) context. It is the most widely produced fluoropolymer, with production volumes increasing every year. In this review, this specialty polymer is described as endowing exceptional characteristics (chemical, thermal, UV, and aging resistance, waterproofness, rheological, mechanical, tribological, surface properties, and moisture vapor permeability). These outstanding features are well explained by numerous studies linking them to their crystallinity and packing structure, which are closely associated with a constantly evolving chemical synthesis process (fluorinated surfactants are no longer used nowadays). Moreover, the high molar mass of PTFE (several million $\text{g}\cdot\text{mol}^{-1}$) prevents its penetration through the human membrane, in addition to its insolubility in all solvents, non-toxicity, and non-bioaccumulation, showing its safe behavior (i.e., biocompatible) and Food and Drug Administration (FDA) approval. Furthermore, although considered a PFAS, this material meets the 13 Organization for Economic Co-operation and Development (OECD) polymer of low concern (PLC) criteria and, so far, is not subject to regulatory restrictions. Because of such features, PTFE can be used in many advanced applications satisfying stringent requirements (in terms of durability, safety, operational efficiency, and sustainability). Then, PTFE is a must-have material in the medical field and in transportation (aerospace, aircraft, railway, and automotive). It is also essential in electronics, the Internet of Things, clean energy storage and conversion, and other high-tech applications, making it an irreplaceable material in many areas of daily life.

Keywords: applications; chemistry; fluorinated polymers; physical properties; PTFE; structure-properties relationships.

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Abbreviations

AlN aluminum nitride

BNNB-G glycine-functionalized boron nitride nanobarbs

BfR German Agency for Risk Assessment

CAGR Compound Annual Growth Rate

CEPA Canadian Environmental Protection Act

CTFE chlorotrifluoroethylene

CTE coefficient of thermal expansion

CT computed tomography

CF carbon fibers

CNTs carbon nanotubes

CIR Cosmetic Ingredient Review

DTG derivative thermogravimetric curve

DLP digital light processing

E_a activation energies

ePTFE Expanded PTFE

EWG Environmental Working Group

ETFE poly(ethylene-co-tetrafluoroethylene) copolymer

ECTFE poly(ethylene-co-chlorotrifluoroethylene) copolymer

ECHA European Chemicals Agency

FKM poly(vinylidene fluoride-co-hexafluoropropylene) copolymer

FDA Food and Drug Administration

GWP global warming potential

GF glass fibers

hBN Hexagonal boron nitride

HSP Hansen Solubility Parameters

ILSS interlaminar shear strength

MAF mobile amorphous fraction

mPTFE modified polytetrafluoroethylene

MRI magnetic resonance imaging

MPs microplastics

OECD Organization for Economic Co-operation and Development

ODP ozone depletion potential

PCTFE Poly(chlorotrifluoroethylene)

PFAS per- or polyfluoroalkyl substance

PFOA perfluorooctanoic acid

PFOS perfluorooctanesulfonic acid

PFSA perfluorosulfonic acid

PLC polymer of low concern

PE polyethylene

PEGDA polyethylene glycol diacrylate

PTFE poly(tetrafluoroethylene)

PEMFCs Proton Exchange Membrane Fuel Cell

PVDF poly(vinylidene fluoride)

PVF poly(vinyl fluoride)

PFIB perfluoroisobutylene

PFSA perfluoroalkyl sulphonic acid

REACH Registration, Evaluation, Authorization and Restriction of Chemicals

RAF rigid amorphous fraction

SR-PTFE self-reinforced PTFE

THz terahertz

TFE tetrafluoroethylene

T_g glass transition temperature

TG-MS thermogravimetric–mass spectrometric

T_m melting temperature

VDF vinylidene fluoride

VCRP Voluntary Cosmetic Registration Program

μ friction coefficient

1. Introduction

Fluoropolymers represent a class of specialty polymers (Fig. 1) known for their excellent properties, including remarkable chemical resistance, weather and aging stability, low surface energy, coefficient of friction, and dielectric constant. These exceptional properties arise from the strong and stable carbon-fluorine covalent bond, which is widely present in their chemical structures. Due to their unique chemical and physical properties, these technical polymers have found many applications in various fields such as electronics, construction, architecture, aerospace, automotive, and medical industries (Fig. 2) [1–5].

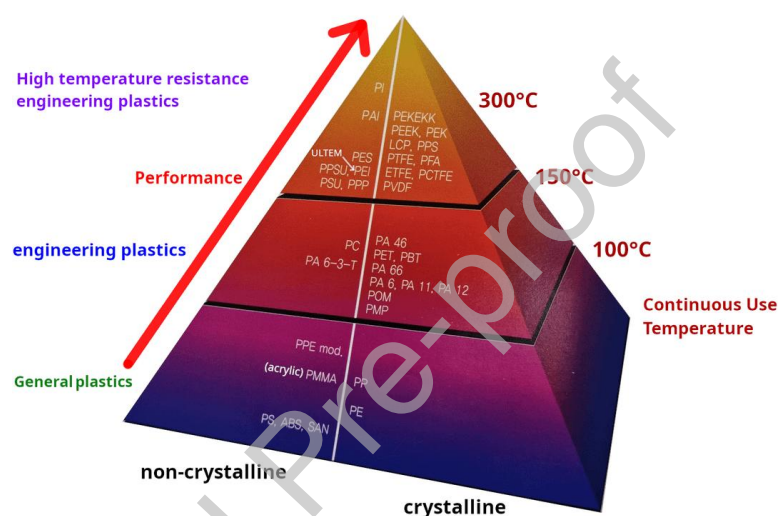


Fig. 1 : Pyramid of features, volume of production, and price of three kinds of polymers separating semi-crystalline and amorphous polymers).

Among fluoropolymers, polytetrafluoroethylene (PTFE) is one of the oldest produced after polychlorotrifluoroethylene (PCTFE) [6]. Discovered unexpectedly by Plunkett in 1938 [7–10] as a white powder insoluble in all solvents and thermostable, this specialty polymer has quickly been investigated and industrially implemented by the Dupont de Nemours Company. This was a real milestone in the development of fluoropolymers. Owing to its exceptional properties [11], it plays a significant role across a wide range of applications [12]. It is worth noting that PTFE was used during the Manhattan Project for handling uranium hexafluoride in the development of nuclear weapons.

Surprisingly, from the current terminology, PTFE is now classified as per- or polyfluoroalkyl substance (PFAS) and is expected to be restricted by the European Chemicals Agency (ECHA) [13] and Registration, Evaluation, Authorization and Restriction of Chemicals Regulation

(REACH), despite its high molar mass and the fact that it is insoluble, non-mobile, non-toxic, and non-bioaccumulative [14].

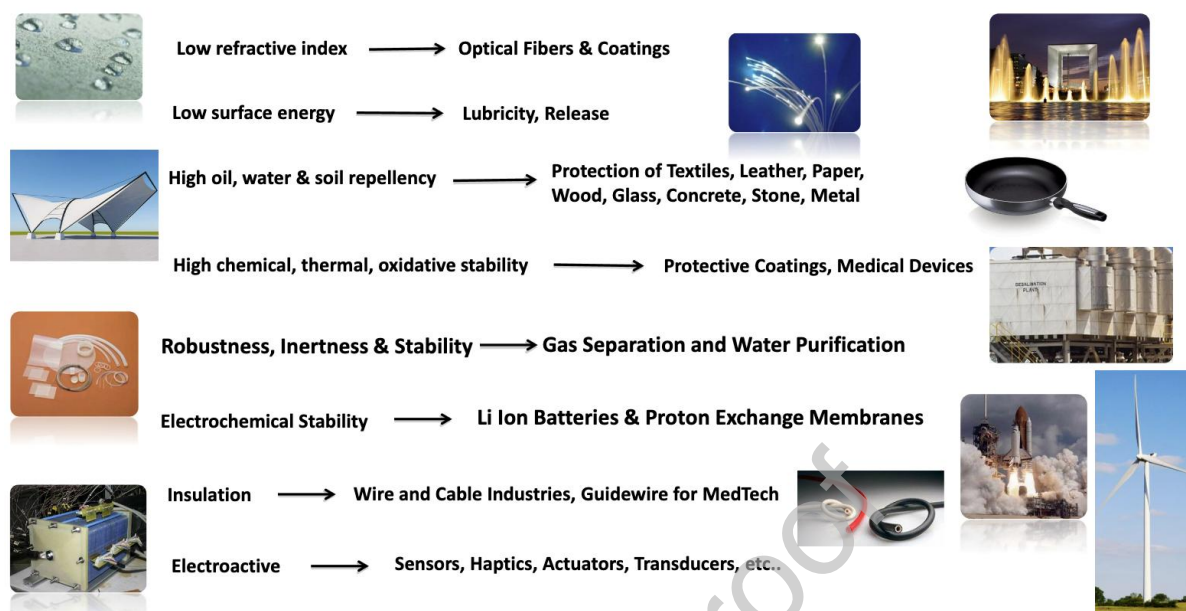


Fig. 2 : Application fields of fluoropolymers, including automotive and aerospace.

The objective of this study is to review recent articles and publications dealing with modern syntheses of PTFE, currently produced in aqueous medium without any surfactants, and to highlight recent characterizations of its molar masses as well as its thermal, dielectric, tribological, and mechanical properties, without neglecting its applications. Furthermore, since PTFE may be regarded as a PFAS, arguments will be presented demonstrating that, unlike low-molar-mass organic compounds, it displays a behavior consistent with materials considered to raise minimal environmental or health concerns dictated by regulation agencies. Indeed, PTFE satisfies the 13 criteria of the OECD as a “polymer of low concern”. Moreover, studies on recycling and degradation — including more recently by mechanochemistry in the presence of specific activators — will further illustrate this review. These recent developments have not been addressed or summarized in any previously published reviews or book chapters.

2. Synthesis

2.1. Synthetic routes and recent processes

As with many fluorochemicals, calcium fluoride (CaF_2), commonly known as fluorite or fluorspar, is a naturally occurring mineral found on Earth's surface, making fluorine the 13th most abundant element on Earth. Its reaction with sulfuric acid yields HF, which enables the fluorination of various compounds. The production of tetrafluoroethylene (TFE) starts with the

fluorination of chloroform, yielding CHF_2Cl , more commonly known as R-22 (Fig. 3). Such a derivative undergoes pyrolysis, producing difluorocarbene, which dimerizes to TFE via recombination (Fig. 3) [1,11,15,16]. The advantage of this process is the ability to obtain highly pure TFE. Other academic reactions leading to TFE have also been reported [17,18].

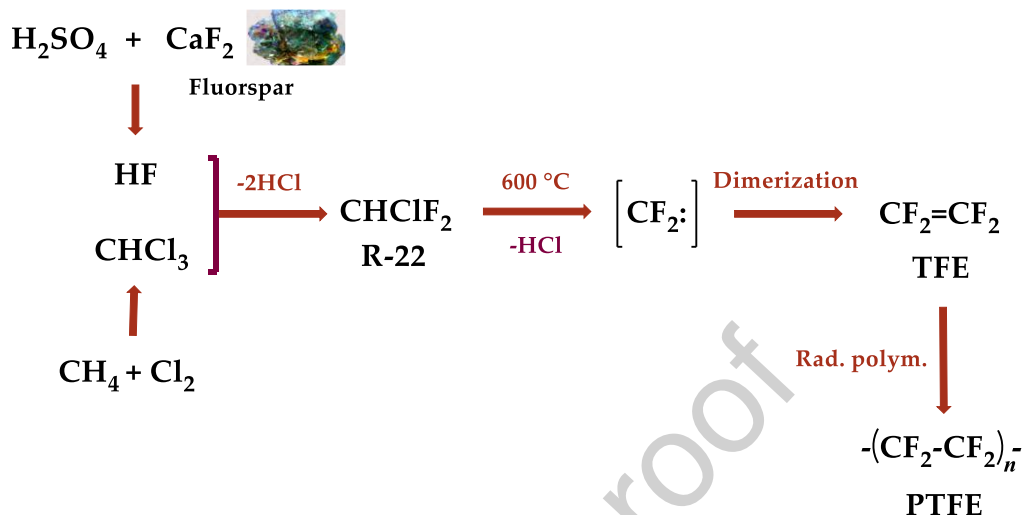


Fig. 3 : Synthetic route of tetrafluoroethylene (TFE) from CaF_2 and PTFE.

TFE is a hazardous and explosive gas (b.p. = -75°C) [18], and can undergo a radical polymerization to give PTFE that usually occurs in three steps (Fig. 4). In the first one, free radicals are generated from the thermal degradation of the initiator (potassium persulfate in the case of Fig. 4). These radicals react onto TFE, forming a new free radical ($^{\bullet}\text{O}_3\text{SOCF}_2\text{CF}_2^{\bullet}$). In the second step (propagation), macroradicals (polymer chains) grow by successive additions of TFE units from the active radical centers [16]. Lastly, termination of such macroradicals occurs exclusively *via* recombination [1]. Sometimes, transfer reactions may occur if the medium contains a chain-transfer agent or reactants with labile bonds.

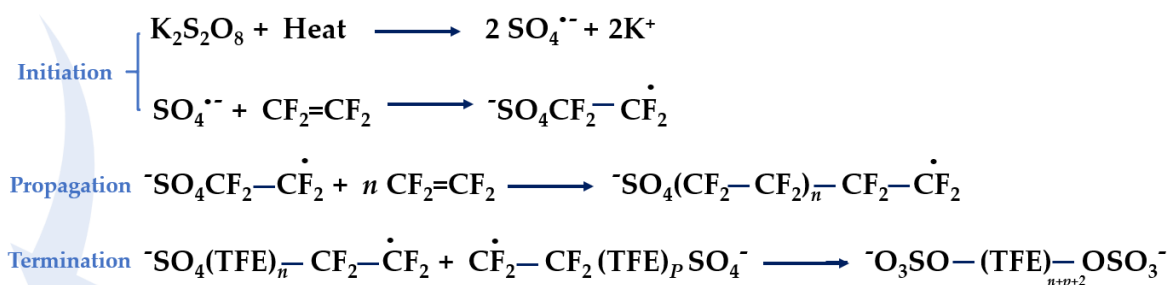


Fig. 4 : Mechanism of radical polymerization of tetrafluoroethylene (TFE).

Industrially, the polymerization happens in aqueous media (suspension, dispersion, or emulsion processes) [11]. In the final step, because TFE is highly hydrophobic, a surface-active reactant (or surfactant) is required to ensure the formation of micelles in which polymerization occurs [19]. After the discovery of Teflon® at DuPont (Fig. 3), the first generation of surfactants used was fluorinated [20], using perfluorooctanoic acid ($C_7F_{15}CO_2H$, PFOA) or perfluorooctane sulfonic acid ($C_8F_{17}SO_3H$, PFOS). Both of these compounds led to severe issues in the early 2000s (toxicity, bioaccumulation, persistence, and water solubility, thus spreading in creeks, rivers, and oceans) [21].

Table 1 : Non-exhaustive list of identified patents on PTFE produced in the presence of hydrocarbon surfactants

Title of the patent	Company	Patent number	Reference
Method for producing modified polytetrafluoroethylene, method for producing modified polytetrafluoroethylene powder, and method for producing stretched porous material	AGC	Higuchi et al., US 2020/0207880 A1	[22]
Aqueous polymerization of perfluoromonomer using hydrocarbon surfactant	CHEMOURS	Brothers et al., US 2016/0122509 A1	[23]
Employing polyalkylene oxides for nucleation in aqueous polymerization of fluoromonomer	CHEMOURS	Brothers et Gangal al., EP 2019/ 3 074 430 B1	[24]
Polytetrafluoroethylene production method	DAIKIN	Kato et al., US 2021/0340290 A1	[25]
Process for preparing fluoropolymers and fluoroelastomers in presence of a non-fluorinated sulfonate type hydrocarbon containing surfactant thereof	GUJARAT FLUOROCHEMICALS	Chauhan et al., US 2022/0372179 A1	[26]
PTFE-based formulation for the insulation of integrated circuits	SYENSQO	Kapeliouchko et al., US 2006/ 6,982,308 B2	[27]

So, many countries and companies no longer use them [28]. Under the EU Regulation on Persistent Organic Pollutants (REACH and ECHA), PFOS has been restricted since 2019, while PFOA has been banned since 2006 [21]. These surfactants were replaced by fluorinated ones with shorter fluorinated group ($C_5F_{11}CO_2H$, $C_4F_9SO_3H$ or $C_3F_7CO_2H$) [29] or bearing ether group (e.g., $C_3F_7OCF(CF_3)CO_2NH_4$ Gen®X or $CF_3OC_3F_6OCHF_2CF_2CO_2NH_4$ Adona®) [30]. However, reversed effects of both last ones were noted, showing even more toxicity [21,30–33]. After many years of efforts, the PTFE manufacturers used hydrocarbon surfactants for the production of PTFEs which are claimed to have the same properties as those produced with fluorinated surfactants [21–27,34].

Table 2 : Main PTFE suppliers and their trademarks

Trademarks	Suppliers
Teflon®	Chemours (formerly DuPont)
Hostaflon®	Manufactured by Dyneon and later part of Celanese
Fluon®	AGC Chemicals
Polyflon®	Daikin
Dyneon™	Dyneon
Various series as DF®-201, DF®-16	Dongyue Group
Polymist® and Algoflon®	Syensqo (ex-Solvay Solexis)
Soreflon®	Arkema
Inoflon®	Gujarat Fluorochemicals Limited (INOX Group(GFL))
Heroflon®	Heroflon USA (Daikin)
FluoroPlast™	Halopolymer
Various series as CGF®218, CGF®238, CGF®2021, CGF®219	Haohua Chemical Science
Flontech®	Flontech USA LLC
Various series as MF®-4DW, MF®-4DA, MF®-4DM	Fujian Sannong
Various series as LM®-PSR102, LM®-PSR104	Lee and Man Chemical
PTFE ROD ML01	Luxi Chemical
Various series as SFN®-1, SFN®-2, SFN®-1002, SFN®-2301, etc.	Sinochem
Various series as CGM®031, CGM®021, CGM®-16 (F), CGM®3101, CGM®3102, CGM®1101	Sinochem
3F® FR002A	Shanghai Huayi 3F New Materials Technology
Various series as 4S01-B, 4S02-A	Shandong Huafu Chem
Various series as 3M™ PTFE Film Tape 5490, 3M™ PTFE Film Electrical Tape 60	3M
Various series as Gr® - C525	Zhejiang Juhua
Niflon®	Jinhua Yonghe Fluorochemical

A non-exhaustive list of patents deposited by various companies is given in Table 1. Finally, and more recently, several companies manufacturing FPs announced that they would not use any surfactants in their TFE polymerization processes, *e.g.*, AGC, Syensqo and Arkema. The main PTFE suppliers and their trademarks are listed in Table 2.

Indeed, it appears reasonable to claim that fluoropolymers, which are manufactured without the use of PFAS polymerization aids, should be exempted from any regulatory initiative and that their uses should be allowed without any unjustified restriction [14,35].

In addition, fluoropolymer manufacturers have made stringent efforts to control PFAS emissions from their production processes. Such progress is based on improvements in abatement techniques, but, more importantly, on the removal of PFAS polymerization aids and the introduction of alternative technologies that do not require these chemicals [21]. Nowadays, most fluoropolymer productions are developed completely free from PFAS polymerization aids [21]. A brief historical overview illustrating the evolution of PFAS, from the discovery of PTFE to REACH regulations, is presented in Fig. 5 [36].



Fig. 5 : Historical timeline of the emergence and prohibition of PFAS and the rise of their alternatives (reprinted with permission from Elsevier [36]).

2.2. Chemical structure, molecular organization, and morphology

PTFE has a chemical structure composed of carbon and fluorine atoms, represented by the CF_2 - CF_2 repeating unit. Commercially available PTFE is generally described as predominantly linear and unbranched. However, branching and network formation can be introduced intentionally (e.g., via irradiation-assisted routes) or in specific solid-state polymerization pathways [37,38]. As a result, the linear PTFE is semi-crystalline, exhibiting a high degree of crystallinity, typically reported in the 93–98% range depending on grade and thermal history [1,37]. The structure of PTFE is like that of polyethylene (PE), except that fluorine atoms have replaced all hydrogen atoms. Since the size of the fluorine atom is larger than that of the hydrogen atom (0.064 nm *versus* 0.028 nm, respectively), steric hindrance increases along the carbon backbone. Consequently, the fully extended planar zigzag conformation characteristic of PE (the pitch of which is 1.68 nm) is replaced by a helical chain conformation in PTFE

(pitch of 1.95 nm), shielded by a fluorine-rich sheath surrounding the carbon backbone. This fluorinated sheath reduces polarizability and interfacial cohesive interactions, which underlie PTFE's exceptionally low surface energy, weak adhesion, and outstanding chemical resistance [39].

Additionally, the C-F bond is among the strongest single bonds in polymers (460.2 kJ/mol against 410 kJ/mol and 372 kJ/mol for C-H and C-C, respectively), contributing to the high thermal stability and chemical inertness of PTFE relative to hydrocarbon polymers [1,7,11,15,40]. The high chain symmetry and stiffness also favor high crystallinity, but at the expense of melt processability [39]. Commercial PTFE is marketed with a reported number average molar mass range of 10^6 - 10^7 g.mol⁻¹ [11]. Based on Suwa's equation [41], the molar mass of PTFE can be estimated from the heat of crystallization measured by DSC, which establishes an empirical relationship between the enthalpy of crystallization and the polymer's molar mass [41,42].

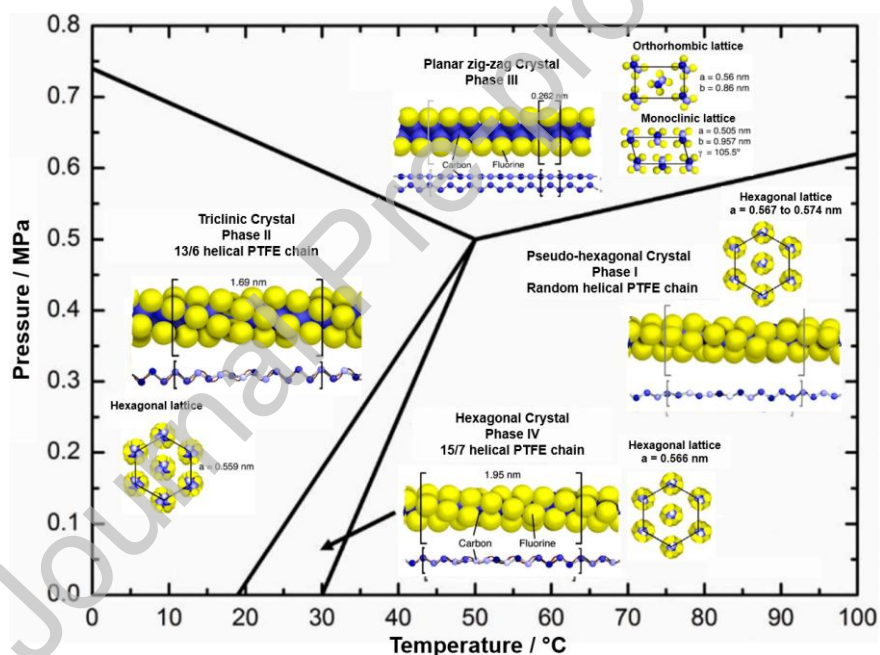


Fig. 6 : Molecular structures and phase transition diagram of PTFE crystallization zone at different temperatures and pressures. Adapted from Brown et al. [43–47].

PTFE is a semi-crystalline polymer composed of crystalline and amorphous regions. Its crystalline fraction undergoes two solid-solid phase transitions near 19 °C and 30 °C [11,37,48–51] (Fig. 6). At atmospheric pressure, upon heating, PTFE transforms from a well-ordered triclinic crystal (phase II, $T < 19$ °C) with a 13/6 helical chain conformation (i.e., 13 CF₂ units complete six turns to recover the initial fluorine registry) [48], to a partially ordered hexagonal phase (phase IV, 19 °C–30 °C). In this intermediate phase, the chains adopt a 15/7 helical

conformation, with a repeating distance (pitch) of ca. 1.95 nm along the molecular axis and an interchain spacing of ca. 0.566 nm [52]. Above ca. 30 °C, PTFE evolves toward a pseudo-hexagonal phase (phase I), often described as rotationally disordered, in which the chain conformation is commonly reported as 13/6 [11,50] (Fig. 6). Under high pressure, PTFE can undergo a distinct conformation/packing change towards a planar zig-zag arrangement (phase III) [43,53]. The four crystalline phases of PTFE are summarized in Fig. 6, with phase I predominating at ambient conditions above ca. 30 °C [11,49] (Fig. 6). In addition, in 1975 Young [54] discovered that PTFE nascent crystals deform mostly by crystallographic slips along macromolecular chains under a very low shear of 2.5 MPa.

The helical arrangement imparts a relatively stiff, rod-like character to PTFE chains, favoring crystallites composed of extended-chain segments (stems) and highly ordered packing. Diffraction analyses confirm that PTFE crystallites consistently exhibit this packing, which contributes to the high crystallinity observed in both virgin and sintered materials [55]. However, alternative routes, such as radiation-induced solid-state polymerization, can introduce branching or network points, yielding microstructures reminiscent of electron-beam-modified PTFE [38,56,57] with direct implications for relaxation dynamics, sintering behavior, and radiation response.

The amorphous phase of PTFE is composed of two types of disordered macromolecular populations. Chains located near regions of high crystallinity exhibit lower molecular mobility than that characteristic of more distant chains. The former defines a so-called rigid amorphous fraction, often abbreviated as RAF. The latter, which possesses increased molecular mobility, defines the mobile amorphous fraction, denoted MAF (Fig. 7). Due to their significant differences in molecular mobility, all regions (crystalline and amorphous) exhibit markedly different critical temperatures, as discussed in the following section.

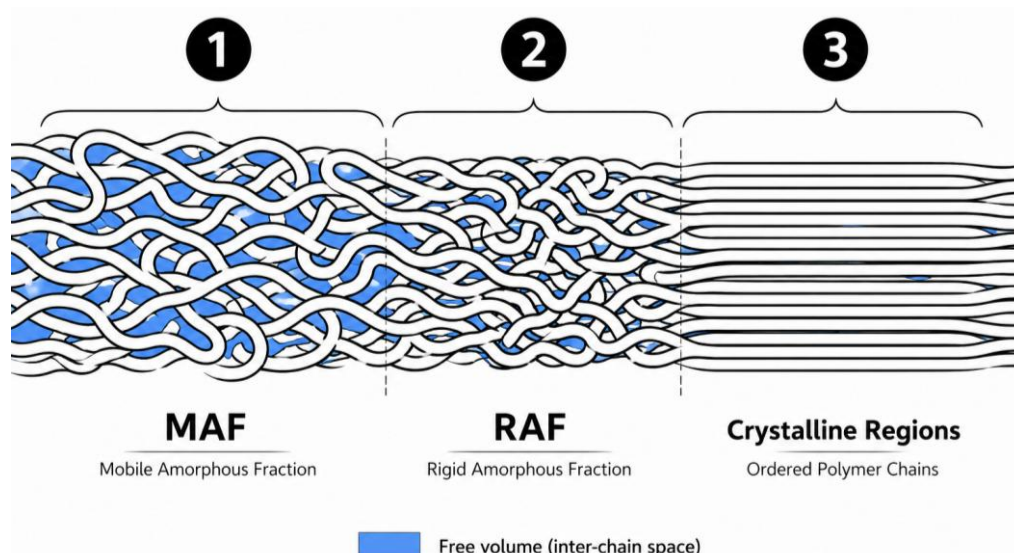


Fig. 7 : Schematic illustration of PTFE structure. (1): mobile amorphous phase; (2): rigid amorphous phase; (3): crystalline phase (inspired by ELSEVIER from Calleja et al., 2013 [58]).

3. Thermal properties of PTFE

3.1. Melting behavior: a history-dependent thermal hallmark of semi-crystalline PTFE

As discussed in the preceding morphology section, PTFE is a semi-crystalline fluoropolymer with high crystallinity. Then, its thermal response is logically dominated by melting. Although a melting temperature near 327 °C is frequently reported [1], a critical examination of calorimetric studies indicates that PTFE does not exhibit a single universal melting point. Instead, reported melting temperatures and peak shapes depend strongly on thermal history, crystal perfection, and kinetic superheating [41,59,60].

DSC measurements on virgin (i.e., “never melted”) PTFE powders typically exhibit two melting endotherms in the 320-350 °C temperature range (Fig. 8). In contrast, PTFE that has been melted and recrystallized generally displays a single melting peak at a lower temperature (Fig. 8), [41]. This behavior has been interpreted as reflecting distinct crystalline populations, with highly perfect chain-extended crystals present in virgin powders being progressively replaced by less perfect lamellar morphologies after melting and recrystallization [41,60].

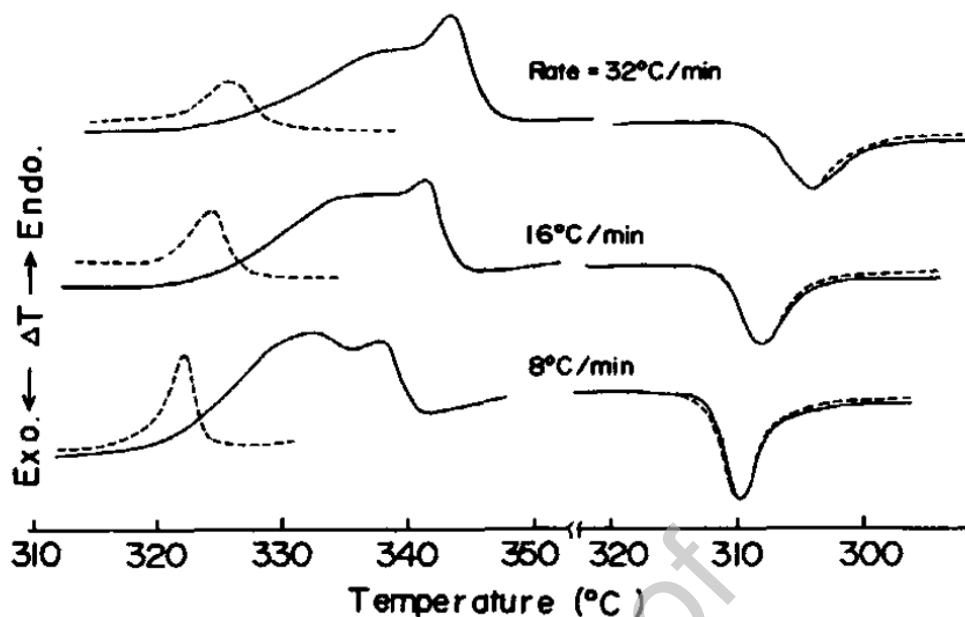


Fig. 8 : DSC thermograms of PTFE at various heating and cooling rates, where the solid line corresponds to the melting of virgin polymer and its first crystallization from the melt. The dotted line is specific to the sample after melting and crystallization, consecutive to the first run (reprinted with permission from WILEY [41]).

The strong dependence of the melting signature on the calorimetric protocol was convincingly established by Starkweather [59], who highlighted that the relative intensity of the high-temperature melting event increases with heating rate, consistent with pronounced superheating effects in PTFE and non-equilibrium melting behavior [59]. Quantitatively, Huang et al. [60] reported an apparent melting temperature of approximately 342 °C for “never-melted” PTFE *versus* 327 °C for melt-processed material, confirming that the widely cited 327 °C value corresponds primarily to melt-crystallized states rather than to the most perfect native crystals [60].

Previous thermodynamic analyses can support this distinction. Indeed, using perfluoro-*n*-alkane analogs, Starkweather [61] estimated an equilibrium melting temperature for virgin PTFE close to 340 °C and discussed an extended-chain upper bound of ca. 347 °C for highly perfect crystals [61]. In agreement, dissolution and gelation studies in perfluorinated media also distinguished “virgin” PTFE melting around 345 °C from pre-melted PTFE melting near 327 °C, reinforcing that PTFE melting must be interpreted as a history-dependent response rather than as a single intrinsic material constant [62].

Using temperature-modulated DSC, Pucciariello and Villani [63] provided additional evidence that the melting behavior of PTFE can involve partially reversible contributions, particularly in

native specimens. By separating the reversing and non-reversing heat-flow components, they highlighted a broad reversible signal in the melting/crystallization region, which they interpreted as surface melting/crystallization processes. Further, they reinforced the strong dependence of calorimetric signatures on thermal history [63].

Because DSC traces of PTFE may be strongly influenced by morphology, thermal lag, and kinetic superheating, reliable thermodynamic comparisons benefit from robust calorimetric baselines. Recommended thermodynamic datasets and transition reconstructions have been discussed based on adiabatic calorimetry and calorimetric rationalizations [64,65].

Although PTFE exhibits a first-order endothermic transition near ca. 327–335 °C, it remains essentially non-melt-processable under conventional flow conditions because the melt viscosity is extremely high [11,63]. PTFE components fabricated by powder-processing are therefore sintered at or slightly above this temperature to promote particle coalescence. The apparent melting point depends strongly on molar mass and crystallinity [66,67], typically falling between ca. 300 and ca. 335 °C, with values near 327 °C often cited for common grades, and approaching ca. 335 °C in highly crystalline materials [66,67]. PTFE produced by solid-state polymerization exhibits a decrease in this transition temperature with increasing radiation dose, consistent with the corresponding loss of crystallinity [38].

3.2. Glass transition: brief note on DSC limitations and literature scatter

The glass-transition behavior of PTFE is considerably more complex [11,58] than that of conventional semi-crystalline polymers. On one hand, its calorimetric detectability is limited by its very high crystallinity. Consequently, DSC signatures corresponding to T_g may be weak and broadened, and reported values have historically exhibited large scatter [65,68]. On the other hand, the coexistence of different amorphous fractions (RAF and MAF, respectively), as well as the use of various experimental techniques, has led to a wide range of T_g values reported in the literature. For instance, some reports indicate a low T_g (ca. -100 °C) while others claim a high temperature transition (ca. +100 °C) [58] (Table 3). More recent analyses using rheometry and dynamic mechanical methods indicate that PTFE exhibits two distinct amorphous-phase relaxation signatures [58]. The lower-temperature transition is attributed to the mobile amorphous fraction (MAF) (Fig. 7), in which chain segments retain substantial mobility and display a relaxation analogous to the conventional T_g of many polymers.

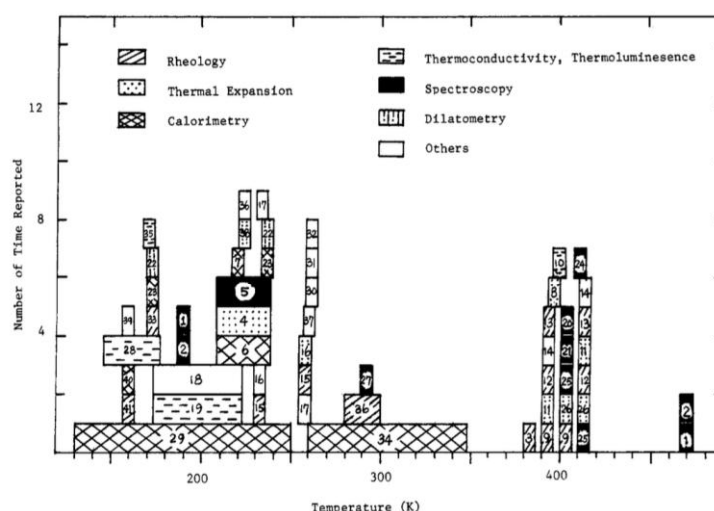


Fig. 9 : Reported glass transition temperatures in the literature and registered with different experimental techniques (reprinted with permission from ACS [65]).

The higher-temperature signature is associated with the rigid amorphous fraction (RAF) located in the crystal–amorphous interphase (Fig. 7). The nearby lamellae constrain chain segments and therefore relax at higher temperatures. Within this framework, the T_g most consistently associated with the MAF is near $-103\text{ }^{\circ}\text{C}$ [58]. A glass transition has long been discussed in PTFE (Table 3). However, its calorimetric detectability is limited by its very high crystallinity and a constrained amorphous fraction. Consequently, DSC signatures corresponding to T_g may be weak and broadened, and reported values have historically exhibited large scatter [65,68].

In the present review, T_g is therefore mentioned only to prevent confusion between thermodynamic transitions and relaxational phenomena: PTFE does not exhibit a single sharp T_g readily detected by DSC, and the interpretation in terms of mobile/rigid amorphous fractions (MAF/RAF) and multiple glass-like transitions is more convincingly addressed *via* thermomechanical and dielectric methods. These aspects are therefore treated in detail in the dedicated sections on viscoelasticity (sections 4.2 and 4.7) and electrical properties (section 8) (Fig. 9).

3.3. Crystalline solid–solid transitions near ambient temperature

Besides fusion, PTFE exhibits reproducible crystalline transitions at temperatures close to ambient conditions. Adiabatic calorimetry provided early rigorous evidence for the two first-order transitions at approximately 293 K and 303 K (i.e., around $20\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$), associated with rearrangements in crystalline packing [64]. Calorimetric studies subsequently confirmed these transitions and remain a thermodynamic hallmark of PTFE [59,65].

Table 3. Reported apparent glass-transition/ α -relaxation temperatures for PTFE across techniques. The dispersion reflects (i) different probed length/time scales and (ii) the coexistence of a mobile amorphous fraction (MAF) and a rigid amorphous fraction (RAF), which can yield distinct relaxation signatures rather than a single, universal T_g .

Technique	T_g value ($^{\circ}\text{C}$)	Author and reference
Dynamic mechanical analysis (DMAs)	-110	McCrum [69]
	-103	Calleja [58]
	+116	Calleja [58]
	+130	Starkweather [70]
	+130	Wortmann [71]
Steady or transient rheometry	+110	Tobolsky [72]
	+110	Araki [73]
Mechanical measurements	-110	Woodward and Sauer [74]
	-110	Rae and Dattelbaum [75]
Dilatometry (CTE)	+123	Araki [76]
Thermally stimulated currents (TSCs)	+130	Sauer [77]
Calorimetry and thermodynamics	-50	Durrell [68]
	-110	Lau [78]
Calculational methods	-75	Marchionni [79]
Acoustic	-110	Kvacheva and Perepechko [80]
Permeability measurement	<20	Fossati [81]

Although their enthalpic magnitude is modest relative to melting, these transitions are technologically important because they occur within typical service temperature ranges and can affect dimensional stability and thermal expansion. Their detailed manifestations in the thermo-mechanical response and their coupling with viscoelastic phenomena are discussed in the dedicated PTFE rheology section to avoid redundancy.

3.4. Thermal expansion and dimensional stability

PTFE is characterized by a high coefficient of thermal expansion (CTE) and a strong sensitivity of its dimensional response to morphology and thermal transitions. Typical engineering values

are on the order of $(10\text{--}15)\times 10^{-5} \text{ K}^{-1}$, although significant variability exists depending on temperature, crystallinity, and prior thermal history. Araki [76] provided early quantitative evidence that PTFE expansion behavior depends strongly on the amorphous fraction and exhibits marked changes around 388–402 K (averaging 396 K), emphasizing the need to interpret CTE values as morphology-dependent rather than universal constants [76] (Fig. 10).

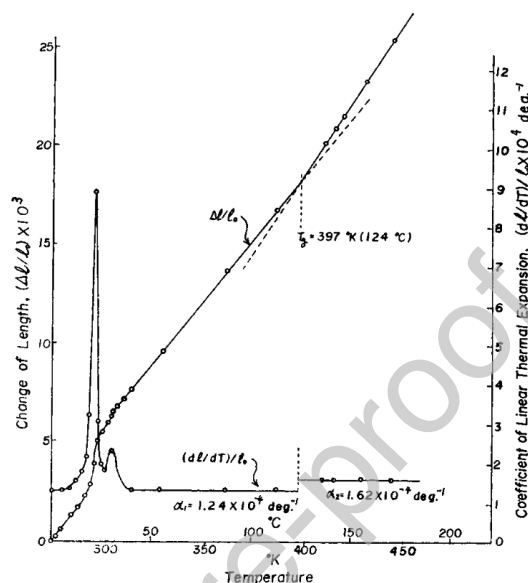


Fig. 10 : Experimental variations of PTFE linear expansion coefficient (reprinted with permission from WILEY [76]).

Reducing thermal expansion and improving dimensional stability under thermal cycling are central motivations for PTFE compounding. Chen et al. [82] investigated PTFE/silica composites and showed that filler incorporation can reduce the CTE. However, effectiveness depends on filler dispersion and interfacial quality, as weak adhesion may limit the expected constraining effect of microfillers. These results highlight that dimensional stability in PTFE composites cannot be predicted solely from filler fraction. It must also account for constraints imposed on the amorphous regions, stress transfer, and microstructural continuity.

3.5. Thermal transport properties and strategies to enhance conductivity

Neat PTFE exhibits a low thermal conductivity (ca. $0.2\text{--}0.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), which may limit heat dissipation in applications involving frictional heating or thermal management under electrical insulation requirements [83]. Notably, heat transport is influenced by microstructure. For instance, Price and Jarratt reported that the thermal conductivity of PTFE increases approximately linearly with crystallinity, underscoring that processing history affects not only fusion signatures but also transport properties [84].

Several studies have therefore explored PTFE-based thermally conductive composites. Hexagonal boron nitride (hBN) is a particularly attractive filler due to its high intrinsic thermal conductivity and dielectric character [85]. However, in hBN/PTFE systems, effective conductivity is frequently limited by platelet alignment and interfacial thermal resistance. Pan et al. [86] demonstrated that hybrid filler architectures can mitigate anisotropy. Indeed, combining hBN platelets with aluminum nitride (AlN) particles reduced preferential in-plane alignment and promoted through-plane pathways, yielding a through-plane thermal conductivity of ca. $1.04 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 30 vol % total filler (Fig. 11) [86]. In the same study, the authors reported that, at 30 vol % filler loading, the through-plane thermal conductivity reached $0.723 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the hBN-only composite, compared with $0.680 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for AlN-only and $1.04 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the hybrid hBN/AlN formulation, highlighting the central role of orientation and filler–filler connectivity in determining thermal transport.

Beyond BN-based approaches, alternative thermally conductive fillers have also been evaluated in PTFE. Ferenc Tóth et al. [83] investigated graphene-, alumina-, boehmite-, and hydrotalcite-filled PTFE composites prepared by pressing and free sintering. They reported that graphene provided the most significant enhancement. Indeed, at 16 wt.% graphene, the thermal conductivity increased from 0.24 to $0.62 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [83]. Complementary approaches have been reported using other fillers and architectures, including halloysite nanotubes and related strategies to control dispersion and interfacial heat transfer in PTFE matrices [87,88].

At higher filler contents, thermal conduction may further increase, but typically at the expense of processability. Yuan et al. [89] reported high-volume-fraction Si_3N_4 /PTFE composites (ca. 62 vol %) yielding thermal conductivities ca. $1.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, illustrating the need for high filler connectivity and percolation to reach the $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ regime [89]. Overall, improving thermal transport in PTFE requires simultaneous control of filler network formation, orientation anisotropy, and interfacial thermal resistance, rather than relying solely on filler fraction.

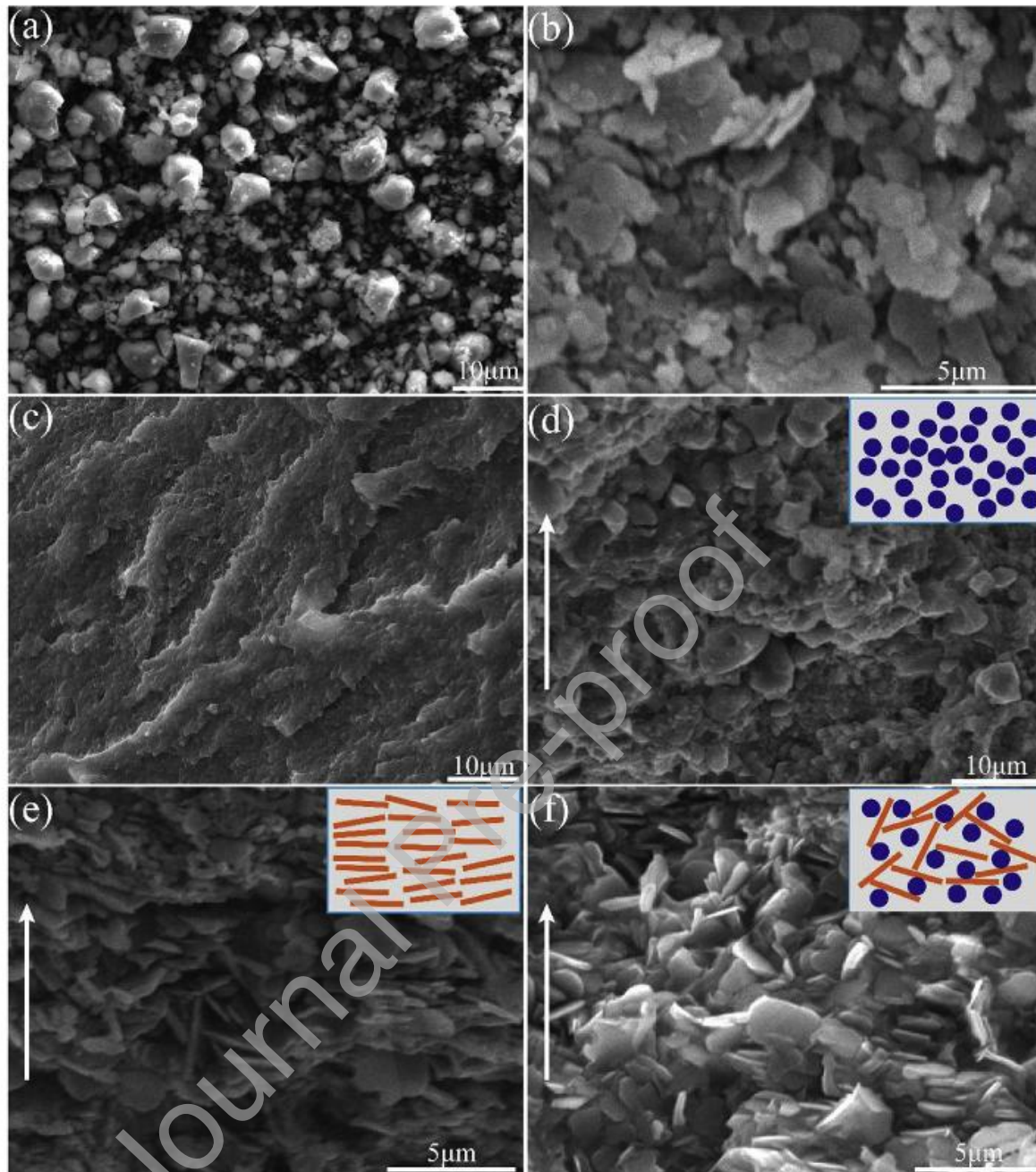


Fig. 11 : Illustration of the interest in combining spherical aluminum nitride (AlN) fillers with hexagonal boron nitride (hBN) tablets for improving thermal conductivity of PTFE (reprinted with permission from ELSEVIER [86]).

3.6. Thermal stability and degradation

PTFE is often regarded as thermally stable. Actually, its degradation behavior depends strongly on the atmosphere, heating rate, specimen geometry, and chemical history. Conesa and Font [90] provided a detailed thermoanalytical assessment of PTFE decomposition under different atmospheres using coupled thermogravimetric–mass spectrometric (TG–MS) analysis. They identified multiple fluorinated products and emphasized the formation of hazardous species such as perfluoroisobutylene (PFIB) under severe overheating or combustion conditions [90].

A key methodological conclusion emerging from the literature is that kinetic insights cannot be derived from single-rate TGA alone. Hondred et al. [91] compared PTFE and ETFE at multiple heating rates and applied isoconversional analysis, providing evidence that PTFE degradation can be described by a global autocatalytic framework across broad conversion windows, whereas copolymers often require multistep descriptions (Fig. 12) [91]. Such multi-ramp experiments are particularly informative because they enable the determination of conversion-dependent activation energies (E_a) and the verification of the extent to which PTFE degradation can be approximated by a global single-step representation *versus* an evolving multistep pathway. Such an observation was confirmed in 2025 [92].

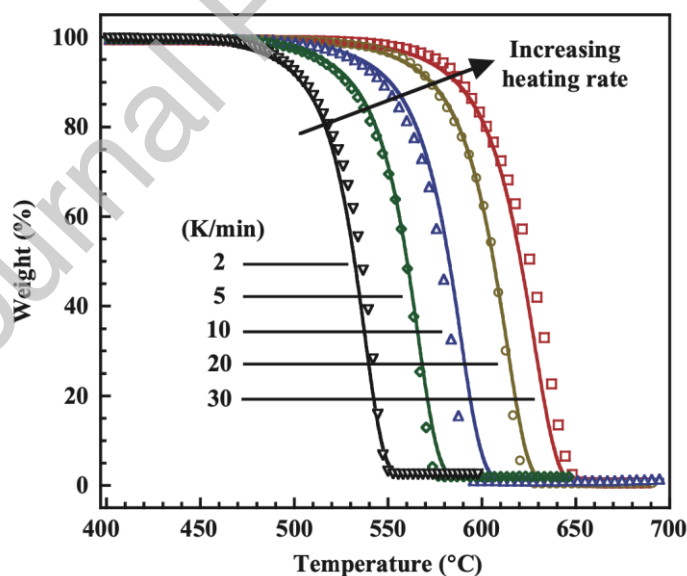


Fig. 12 : Influence of the heating rate on the TGA data of PTFE degradation in air. Symbols: experiments; lines: n^{th} -order, single-step autocatalytic reaction model (reprinted with permission from SAGE [91]).

Abiodun et al. [92] extended this kinetic framework to PTFE composites and provided a robust example of modern methodology. They investigated PTFE and modified

polytetrafluoroethylene (mPTFE, containing less than 1 wt.% perfluoropropyl-vinyl ether, PPVE, comonomer), as well as their nanocomposites containing 20 wt.% glycine-functionalized boron nitride nanobarbs (BNNB-G). The materials were examined under nitrogen using multi-heating-rate TGA at heating rates of 2, 5, 10, and 20 °C min⁻¹, coupled with evolved-gas analysis (TGA–MS). A suite of isoconversional methods (Friedman, OFW, and KAS) was also employed, complemented by numerical optimization using Vyazovkin's method and its advanced variant. The latter enables the extraction of $E_a(\alpha)$ without imposing an *a priori* reaction model and is especially useful when kinetics are multistep. At 5 °C·min⁻¹, the BN nanofiller produced a modest increase in the onset temperature, defined as the temperature at which the relative mass loss reaches 5%. At the same time, it induced a more pronounced upward shift in $T_{\max}$ from 579.0 °C (PTFE) to 591.4 °C (PTFE/BNNB-G). Here, $T_{\max}$ corresponds to the temperature of the maximum weight-loss rate, i.e., the peak temperature of the derivative thermogravimetric curve (DTG). At low conversion, the apparent activation energy related to thermal degradation increased substantially from 256 kJ·mol⁻¹ (PTFE) to 316 kJ·mol⁻¹ (PTFE/BNNB-G) at 5 % weight loss, resulting in lifetime predictions increased by ca. one order of magnitude depending on the selected temperature window. Importantly, conversion-dependent $E_a(\alpha)$ profiles highlighted three conversion regimes, supporting a multistep degradation scenario. This kinetic interpretation was consistent with the evolved-gas analysis, which was dominated by CF_x and C_nF_m fragments (e.g., CF, CF₂, CF₃, C₂F₃, C₂F₄), whose relative intensities were altered by the nanofiller.

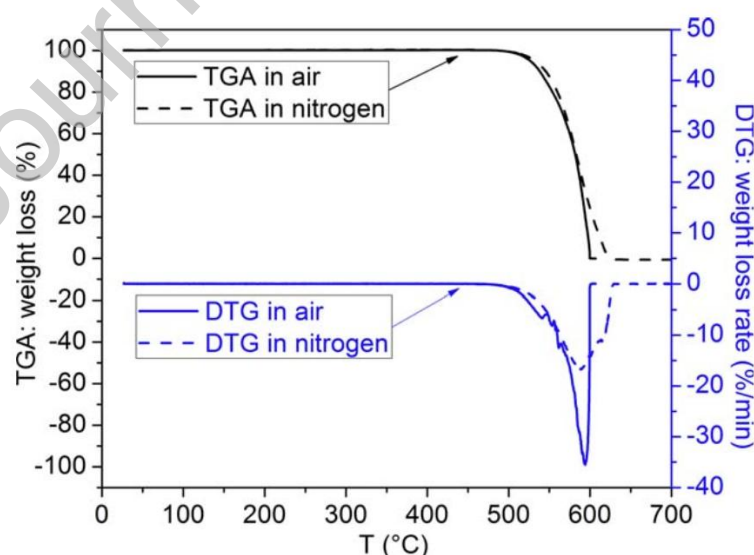


Fig. 13 : TGA and DTG curves of virgin PTFE under different atmospheres (reprinted with permission from WILEY [93]).

Degradation profiles are also affected by oxidative conditions. Huang et al. [93] studied the thermal aging and degradation of PTFE in the 340-450 °C range. They reported that, while PTFE remains essentially stable up to very high temperatures in air or an inert atmosphere, the degradation profiles diverge once weight loss begins, with oxidative environments leading to more pronounced weight loss than nitrogen (Fig. 13). This should not be interpreted as a drastically lower onset temperature in air, but rather as a modification of degradation pathways and apparent kinetics once decomposition is triggered [60].

This atmosphere dependence is consistent with conclusions from evolved-gas studies: under inert conditions, PTFE degradation is dominated by fluorocarbon depolymerization/fragmentation, whereas oxidative environments enable secondary oxidation of fluorocarbon fragments, producing lighter oxygenated species such as CO, CO₂, or COF₂, thereby altering apparent weight-loss kinetics [90,94]. Chemical history and defect chemistry may also affect apparent stability. Electron-beam irradiation studies have revealed that oxidative irradiation can generate peroxide species and oxygen-containing functionalities, which evolve upon annealing, thereby modifying the early thermal response and the onset of degradation [95,96].

A further key parameter for filled grades is the influence of inorganic phases. Puts and Crouse [97,98] systematically demonstrated that contact with metal sulfates, fluorides, or oxides may lower degradation onset temperatures and shift product distributions, indicating that degradation can be catalytically accelerated or chemically redirected depending on mineral surface chemistry [97,98]. Using TG-FTIR, Odochian et al. [94] observed that bronze or carbon additives affected the initiation range and CO/CO₂ ratio resulting from PTFE thermal degradation. In contrast, these authors reported that the prevailing monomer release remained essentially unchanged [94].

Finally, macroscopic transport may influence apparent kinetics. Van der Walt et al. [99] investigated the pyrolysis of PTFE granules (800-1000 µm). They proposed a shrinking-particle model, showing that the degradation behavior may be controlled by surface availability and heat transfer, thereby depending on particle geometry and characteristic length scales [99]. This framework implies that surface-to-volume ratio can affect apparent degradation rates, which is especially relevant for extrapolating laboratory-scale TGA to practical overheating scenarios.

3.7. Concluding remarks and transition to viscoelastic properties

From a thermal standpoint, PTFE combines (i) a high-temperature melting behavior strongly controlled by crystal perfection and processing history, (ii) crystalline solid–solid transitions near ambient temperature that can influence dimensional response, (iii) a low intrinsic thermal conductivity that can nevertheless be improved through rational composite compositions, and (iv) a high apparent thermal stability whose assessment requires careful kinetic methodology, atmosphere control and consideration of inorganic surfaces.

Because thermal transitions and thermal history strongly condition chain mobility and constrained amorphous fractions, they also govern the viscoelastic response. The following section, therefore, focuses on the viscoelastic properties of PTFE and discusses relaxation phenomena and flow-related behavior in relation to morphology and processing conditions.

4. Rheology and Processing of PTFE: Governing Mechanisms

4.1. Absence of actual melt flow

Unlike most thermoplastics, PTFE cannot be shaped by conventional melt-processing techniques because of its exceptionally high melt viscosity above its crystalline melting temperature. Consequently, industrial PTFE components are generally manufactured using powder-processing routes. Depending on the geometry of the final component, the most widely used industrial processes include compression molding followed by free sintering, ram extrusion, paste extrusion, and, for selected complex geometries, isostatic pressing. Although the specific processing parameters vary considerably with component dimensions, PTFE grade, fillers and industrial practice, these manufacturing routes all rely on the same fundamental mechanisms involving powder compaction, particle coalescence during sintering, and crystallization during cooling. Understanding these mechanisms is essential because they ultimately govern the microstructure and therefore the final physical and mechanical properties of PTFE components.

Among all synthetic polymers, PTFE occupies a unique rheological domain. Above its crystalline melting point (T_m about 327 °C), it does not exhibit actual viscous flow [1]. Apparent melt viscosities range from 10^{11} to 10^{15} Pa·s, depending on the measurement technique [72,100,101], which is far beyond the measurable range of conventional rheometers. This non-flow behavior is not a consequence of degradation or experimental limitations—it is an intrinsic property of PTFE's molecular architecture.

The chain structure, composed exclusively of $-\text{CF}_2-\text{CF}_2-$ units, forms an extraordinarily regular backbone stabilized by strong intrachain F–F repulsion and dense interchain packing [101,102]. The resulting crystallinity often exceeds 90 %, forming lamellar stacks that resist disentanglement even above T_m . Early investigators interpreted this “solid-like melt” as the persistence of metastable crystallites embedded in a highly viscous matrix [100]. However, later studies demonstrated that the phenomenon is not due to incomplete melting but to restricted chain mobility arising from extreme molar mass (10^7 - 10^8 g·mol⁻¹) and strong interchain cohesion [103].

Above T_m , PTFE enters a metastable short-range ordered state. This regime appears like a melt but differs in molecular mobility [104]. From a thermodynamic standpoint, the enthalpic stabilization of the CF_2 crystal lattice (ΔH_m about 31–42 J·g⁻¹) outweighs the entropy gain associated with amorphous disordering. The exact enthalpy value varies with processing history, crystalline perfection, and purity [92]. As a result, the free-energy barrier for long-range reptation remains prohibitive, even at 30–50 °C above T_m . PTFE thus behaves as a viscoelastic solid, deforming by creep, surface diffusion, or localized slip rather than by continuous viscous flow (Fig. 14) [105].

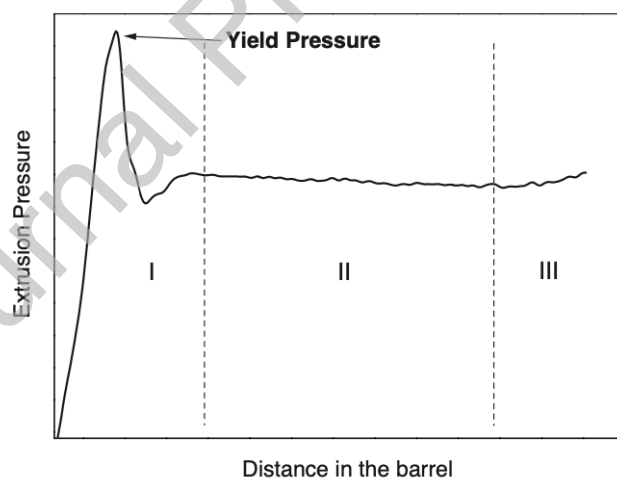


Fig. 14 : Typical behavior of a pressure transient during PTFE paste extrusion (reprinted with permission from ELSEVIER [105]).

Comparisons with melt-processable copolymers such as PFA or FEP highlight this exceptional behavior (Fig. 15). In those systems, incorporation of small comonomer units disrupts the chain regularity, reduces crystallinity to 40–60 %, and decreases molar mass, thereby allowing measurable viscosities (10^3 - 10^4 Pa·s) near 300 °C [106]. These structural “defects” introduce chain-mobility pathways that are absent in PTFE. Yet, such modifications invariably sacrifice some of the chemical inertness and dielectric purity that define PTFE’s technological value.

The classical interpretation that PTFE lacks an actual liquid phase is now widely accepted, but it has occasionally been challenged. Some DSC and rheo-optical studies report transient softening or shear-thinning near 345–355 °C, interpreted as partial chain slippage or mesophase formation. However, these phenomena represent localized viscoelastic relaxation rather than bulk flow: no steady-state shear is sustained once stress is removed. The distinction is subtle but crucial: PTFE deforms but does not flow [92,103].

This unique rheological identity underpins all industrial shaping processes: cold compaction, paste extrusion, and sintering. Each relies on manipulating PTFE in its viscoelastic-solid regime, exploiting plastic deformation, particle rearrangement, or solid-state diffusion rather than liquid-phase viscosity.

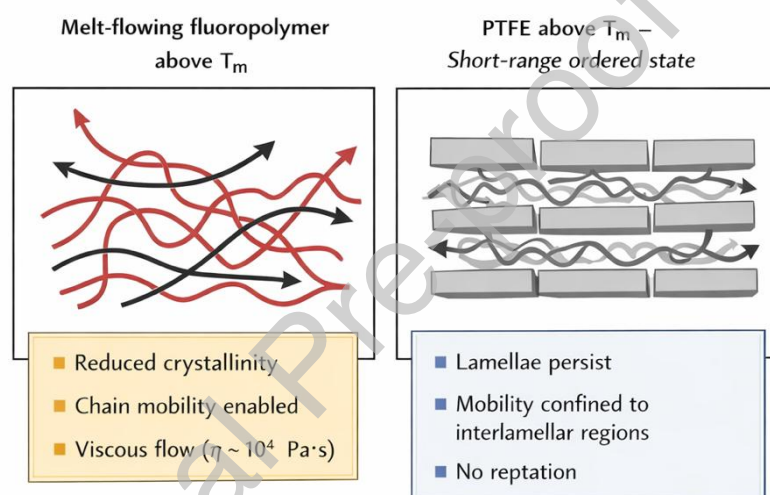


Fig. 15 : Schematic comparison between melt-flowing fluoropolymers and PTFE behavior above T_m .

4.2. Solid-state viscoelasticity and relaxation spectrum

The viscoelastic spectrum of PTFE extends over a wide temperature range, spanning more than 500 K, i.e., from cryogenic to pre-decomposition conditions. This vast range reflects the complex interplay between crystalline lamellae and amorphous domains, as well as between local CF_2 rotations and collective chain slip (Fig. 16).

Early dynamic mechanical and internal friction studies [69,103,107] identified at least three reproducible relaxation processes:

- γ relaxation (about -100 °C): local reorientation of CF_2 groups within the amorphous fraction but linked to restricted segmental motion;

- β relaxation (about 25 °C): disordering of crystalline phase II and transition to phase IV, involving limited cooperative motion of chains;
- α relaxation (about 120 °C): large-scale interlamellar slip and interface softening within the crystalline stacks.

Subsequent studies added nuance to this picture. Sasuga & Takehisa [108,109] reported that unsintered PTFE, containing a higher fraction of amorphous material, exhibits much stronger γ and β peaks. In contrast, sintered samples with increased crystallinity display reduced low-temperature mobility. Such a behavior was attributed to restricted segmental motion as crystallites coalesce during annealing.

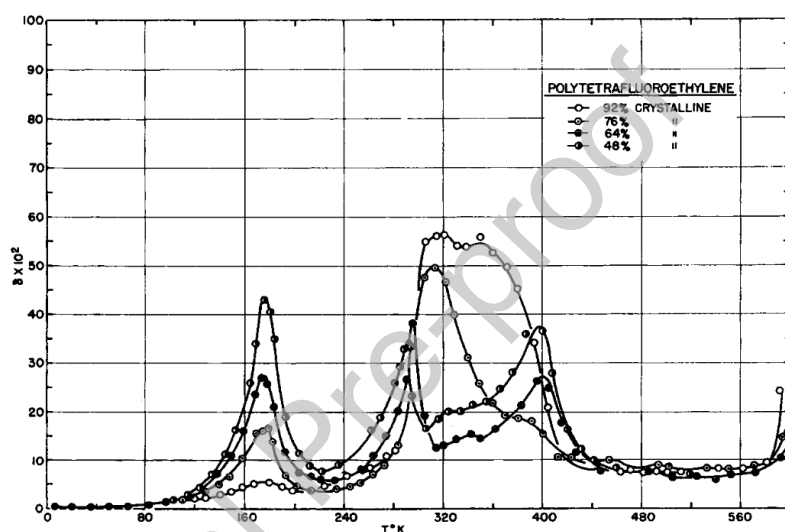


Fig. 16 : Influence of temperature on the logarithmic decrement (internal friction) of several PTFE samples with specific crystallinities (reprinted with permission from WILEY [69]).

The interpretation of these relaxations, however, remains a subject of debate. Some authors (Table 4) [69,107–111] proposed that β and α relaxations correspond to crystalline transitions, while others [103,112,113] argued for a dominant interlamellar mechanism, whereby amorphous tie chains slip between ordered lamellae. More recent positron-annihilation and dielectric studies [112] introduced the concept of dual amorphous fractions: MAF and RAF (as seen in section 2.2.). The MAF exhibits glass-transition-like mobility (with a mean free-volume hole volume V_h about 120 Å³), while the RAF, constrained by adjacent crystallites, highlights limited segmental freedom (V_h close to 80 Å³).

This dual-phase view provides a unifying framework for PTFE's distributed relaxation spectrum. The γ -process originates from local motion within the MAF, the β -process from coupling between RAF and imperfect crystallites, and the α -process from collective slip at the crystal–amorphous interface [58].

However, this interpretation is not universally accepted. For instance, Lau et al. [65] previously reported a broad calorimetric transition around 200 K, suggesting that PTFE exhibits a continuous rather than a discrete glass transition. Similarly, Hu [111] questioned whether distinct RAF/MAF phases can exist in such a highly crystalline polymer, arguing instead for a continuous gradient of chain constraint. This controversy is partly methodological, since crystallinity quantified by DSC does not capture the lamellar connectivity that governs relaxation.

Table 4 : Summary of γ , β , and α relaxations in PTFE with associated phase origins and activation energies.

Relaxation	Typical temperature (°C)	Phase origin	Molecular mechanism	Activation energy (kJ·mol ⁻¹)	Sensitivity to crystallinity	Key references
γ	-120 to -80	Mobile amorphous fraction (MAF)	Local CF ₂ segmental motions; glass-transition-like mobility in unconstrained amorphous domains	40–70	Increases with amorphous content; attenuated after sintering or annealing	[58,69,107,112]
β	15–30	Crystalline phase transitions (phase II → IV)	Rotational disordering within crystalline lamellae; lattice rearrangement	80–120	More pronounced in paracrystalline or defect-rich PTFE; reduced in highly annealed samples	[107–110]
α	100–130	Interlamellar / rigid amorphous fraction (RAF)	Cooperative slip of constrained amorphous chains between lamellae; interlamellar shear	150–250	Shifts to higher temperature with increasing crystalline perfection; linked to lamellar thickness	[58,65,103]
Pre-melting process	120–150	Lamellar interface	Lamellar coalescence and defect annealing prior to melting	>250	Strongly dependent on thermal history; associated with recrystallization phenomena	[101,111]

Despite these divergences, consensus has emerged on several points:

- PTFE lacks a sharp glass transition and exhibits distributed segmental mobility;
- The relaxation hierarchy ($\gamma \rightarrow \beta \rightarrow \alpha$) reflects increasing cooperativity of motion;
- Crystallinity and thermal history dictate the relative amplitude of these processes.

At room temperature, the storage modulus (E') lies near 1 GPa, decreasing gradually to ca. 0.6 GPa at 100 °C before a marked drop near 150 °C [101]. Loss tangent values ($\tan \delta < 0.05$) confirm predominantly elastic behavior. This limited energy dissipation directly stems from the scarcity of interlamellar tie chains, which restricts large-scale viscoelastic flow while enabling limited micro-slip under load. Creep tests [113,114] reveal substantial strain accumulation over long times even below T_m , consistent with solid-state viscoelasticity rather than plastic yielding. Fractional Maxwell and Burgers models [115,116] successfully capture this broad spectrum, with characteristic time constants ranging from 10^2 to 10^5 s.

Importantly, low-frequency experiments indicate non-linear compliance: strain increases *quasi-linearly* with applied stress once a micro-slip threshold is exceeded. This transition marks the onset of lamellar shear, a phenomenon more reminiscent of crystalline plasticity than of amorphous flow. PTFE, therefore, combines the time dependence of viscoelastic materials with the structural anisotropy of semicrystalline solids. This underscores that PTFE's time-dependent deformation is governed not by viscous flow but by discrete structural events—slip, rotation, and constraint release—within a rigid lamellar network.

4.3. Influence of microstructure and thermal history

The rheological and relaxation behaviors of PTFE depend sensitively on its microstructure, particularly crystallinity, lamellar thickness, and defect density. Thermal annealing, irradiation, and mechanical deformation can each alter the balance between crystalline, rigid amorphous, and mobile amorphous regions.

4.4. Annealing and recrystallization.

Takenaga et al. [110], using dynamic mechanical relaxation measurements (internal-friction/damping spectra), reported that annealing at 300 °C converts paracrystalline zones into well-ordered lamellae, thereby sharpening the β -transition and eliminating low-temperature anomalies near 208 K.

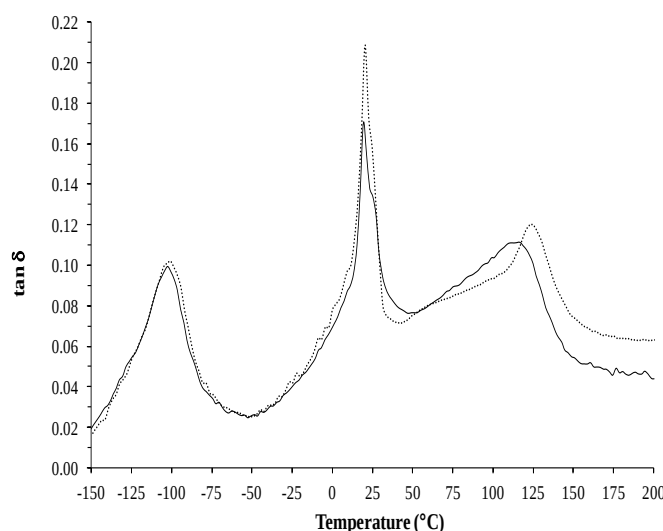


Fig. 17 : Non-isothermal $\tan \delta$ curves of the initial PTFE (solid line) and after annealing at 105 °C for 3 days (dotted line) (reprinted with permission from ELSEVIER [58]).

This process increases stiffness but suppresses mobility within amorphous domains. Similarly, Calleja et al. [58] observed that annealing at 105 °C increases the melting enthalpy (from 31 to 37 J·g⁻¹) based on DSC measurement, while the thermomechanical α -relaxation is shifted from 116 °C to 124 °C, consistent with stronger crystalline–amorphous coupling (Fig. 17).

4.5. Irradiation and defect formation.

In contrast, γ -irradiation experiments, typically performed using a ⁶⁰Co source, promote chain scission and, depending on dose and irradiation atmosphere, competing crosslinking reactions. These radiation-induced defects reduce crystalline perfection and may enhance low-temperature relaxations in dynamic mechanical spectra [108,109]. In parallel, crosslinked PTFE has been reported to exhibit the disappearance of β/β' relaxations, with shifts in the γ and α peaks [56], supporting the view that each process originates from molecular or structural mechanisms. More generally, defect-rich materials tend to exhibit higher damping but lower modulus, illustrating the classic stiffness–mobility trade-off in semicrystalline polymers. Reported irradiation effects on PTFE relaxation behavior nevertheless remain scattered, as they depend strongly on irradiation conditions (dose, temperature, oxygen availability, and post-irradiation thermal history [117]), making direct comparison across studies inherently difficult [118].

4.6. Interpretative challenges.

Despite decades of study, the relationship between crystallinity and viscoelastic response remains controversial. Some authors [103,107] considered relaxation shifts purely thermodynamic, controlled by the amorphous/crystalline fractions ratio, while others [58,112] argued that the degree of interfacial coupling between lamellae and amorphous tie chains is the genuine governing factor. Indeed, even two samples with identical crystallinity may exhibit different mechanical damping if their interfacial morphology and molar mass differ. This may explain why reports of glass-transition-like steps [65] vary widely among laboratories.

4.7. Anisotropy and processing effects.

Mechanical orientation during extrusion or stretching introduces lamellar alignment and fibrillation [119]. Aligned structures exhibit enhanced modulus and creep resistance along the flow direction but increased transverse compliance, consistent with interlamellar slip dominating deformation.

In extreme cases (e.g., expanded PTFE membranes), the fibrillar network allows significant extensibility and a near-zero Poisson's ratio, a unique mechanical response attributed to rotation and reorientation of elongated nodes.

Taken together, these findings portray PTFE not as a “frozen” polymer from a rheological standpoint but as a dynamically heterogeneous solid whose viscoelasticity can be tuned by its structural history. The RAF counterpart acts as a load-bearing skeleton, transferring stress between lamellae, while the MAF provides limited relaxation and energy dissipation. Understanding this coupling is key to explaining why PTFE can deform plastically without melting and why its long-term dimensional stability is simultaneously exceptional and history-dependent (Fig. 18).

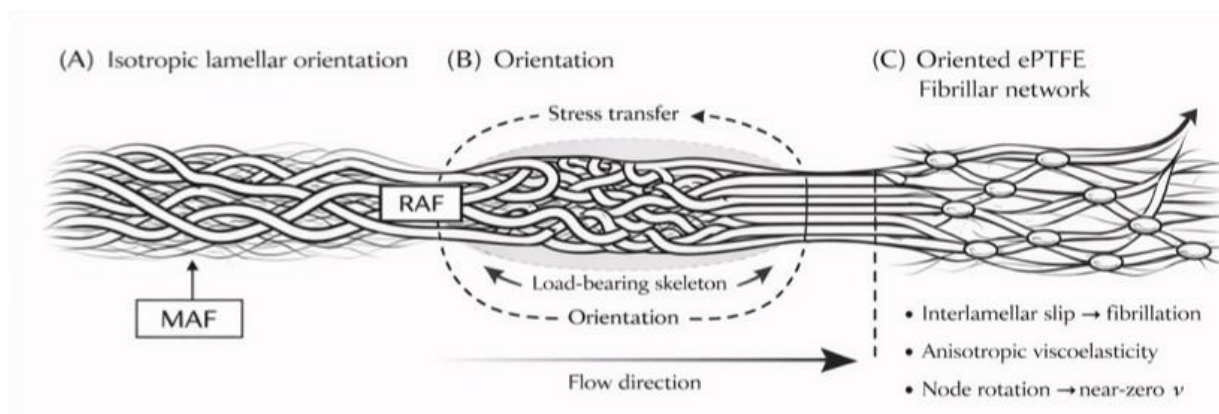


Fig. 18 : Schematic representation of the structural origin of PTFE viscoelasticity heterogeneity and anisotropy.

4.8. Sintering mechanisms

Because PTFE cannot be processed through melt flow, solid-state sintering remains the principal route for obtaining dense, defect-free parts [1,3,9,51]. Yet, despite decades of industrial practice, the mechanism of PTFE sintering remains the subject of persistent debate.

The classical description proposed by Airolidi et al. [100] and refined by Briscoe et al. [120] portrays sintering as a four-stage process:

- (1) particle rearrangement;
- (2) neck growth by surface diffusion;
- (3) plastic deformation under pressure.
- (4) pore elimination through chain interdiffusion.

This framework, inspired by ceramic sintering, has been widely adopted. However, it oversimplifies the molecular-scale complexity of PTFE densification, in which crystalline–amorphous interplay governs diffusion kinetics far more than particle geometry.

Experimental studies using dilatometry, DSC, and SEM reveal that densification begins around 340 °C and is complete near 380 °C, slightly above the nominal melting temperature [58,101].

Instead, sintering relies on localized viscous deformation and segmental diffusion within constrained amorphous regions. This has been modeled as an Arrhenius-type process with an activation energy of ca. 480 kJ·mol⁻¹, comparable to the C–C bond energy, indicating that large-

scale reptation is thermally inaccessible. This latter value reflects cooperative segmental motion rather than bond dissociation.

Nevertheless, alternative interpretations have been proposed. Some authors, such as Hu [111], observed small but reproducible endothermic shoulders in DSC thermograms near 350 °C and argued for the existence of a transient “mesomorphic” phase enabling limited slippage of lamellae. Others [103] proposed that these anomalies reflect partial recrystallization rather than actual melting. Recent *in situ* X-ray diffraction [92] supports the latter interpretation, showing that the (100) and (110) reflections sharpen continuously during sintering rather than disappearing, as they would do in a liquid.

A further controversy concerns the role of pressure. Under uniaxial compression, sintering proceeds much faster, and densification kinetics often fit a Coble-type model where the rate scales as:

$$(\sigma/\eta) \times (1/r^2) \quad (\text{eq 1})$$

suggesting that stress-assisted diffusion accelerates neck formation. In this latter expression, σ , η and r denotes the applied uniaxial stress, the effective viscosity reflecting the resistance to viscoelastic deformation and interfacial diffusion, and the characteristic pore radius, respectively. The $1/r^2$ dependence highlights the strong acceleration of densification for finer PTFE powders. However, pressureless sintering, which is relevant to many industrial processes, relies almost entirely on interfacial diffusion and is significantly slower. Some reports claim that moderate pressure (ca. 10 MPa) reduces porosity from 3% to <0.5% within a few minutes, whereas pressureless sintering requires hours for similar densification [120].

The above studies raised an ongoing question: is PTFE sintering predominantly diffusion-controlled or creep-controlled? Most modern interpretations acknowledge that both contribute, with diffusion dominating in the early stages and viscoelastic creep in the later stages, when the interfacial area becomes continuous [100,120]. Morphologically, sintering induces lamellar thickening and increased crystalline perfection, as evidenced by narrowing of XRD peaks and sharpening of DSC endotherms [101,103,111]. This recrystallization explains why sintered PTFE often exhibits a higher modulus and lower damping than its pre-sintered counterpart [101,108–110].

However, excessive annealing can generate internal stresses and warpage due to non-uniform contraction upon cooling, an effect often misinterpreted as “dimensional instability.” This is a

manifestation of viscoelastic stress relaxation within the RAF during post-crystallization shrinkage [112,113].

Thus, sintering of PTFE remains a striking example of a non-classical rheological transformation: the material densifies and coalesces without melting, driven by the diffusion of chain segments through narrow amorphous channels [100,103,120–122].

The process sits at the intersection of solid mechanics and rheology: a slow, diffusion-limited viscoelastic flow occurring in the absence of a liquid phase [100,121–123] (Fig. 19).

4.9. Paste extrusion and fibrillation.

Among the peculiarities of PTFE, its ability to be paste-extruded is perhaps the most technologically remarkable feature. Paste extrusion converts fine PTFE powders, nominally non-flowing, into continuous, fibrillated structures with controlled anisotropy. The process, though superficially mechanical, is profoundly rheological.

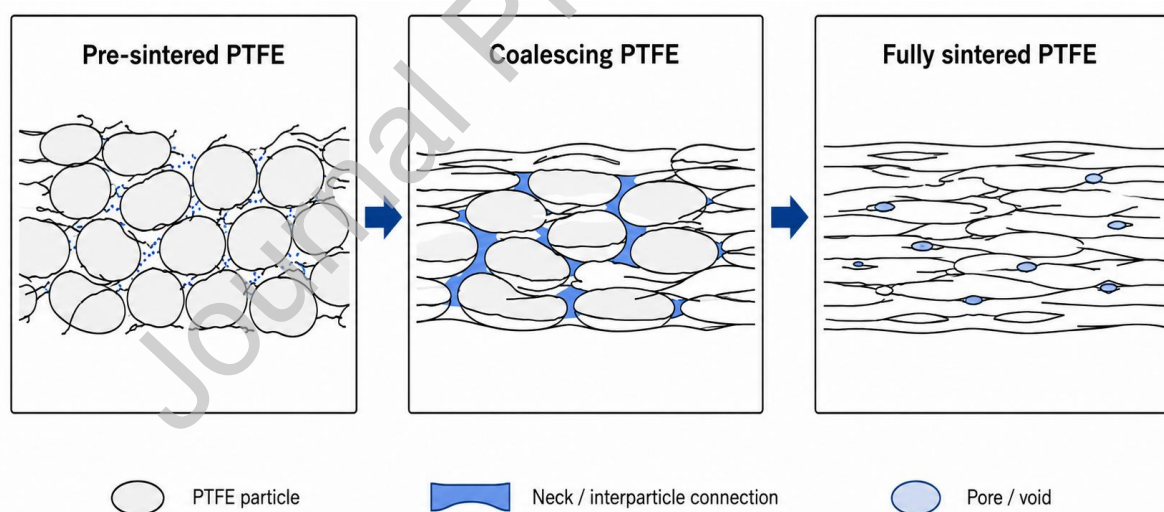


Fig. 19 : Schematic illustration of the successive stages involved in PTFE particle coalescence during sintering. This figure (created with assistance of AI tools) is a conceptual representation rather than a quantitative description of molecular orientation or stress distribution.

PTFE fine powders consist of submicron particles (0.2–0.5 μm) with extremely high surface area and strong interparticle friction [124–126]. To enable deformation, a hydrocarbon lubricant (15–25 wt. %, typically C11-12 isoparaffin, also known under the trademark Isopar H®) is incorporated, forming a deformable “wet paste” [105,106,127]. This paste behaves as a *pseudo-*

viscoplastic material, with a yield-like stress and pronounced wall slip [105,106,123,128]. The constitutive relationship between shear stress (τ) and shear rate ($\dot{\gamma}$) follows a power law:

$$\tau = K \dot{\gamma}^n \quad (\text{eq 2})$$

with K a constant and n is about 0.5 (i.e., characteristic of a rheothinning behavior). The apparent viscosities often exceed 10^8 Pa·s. Such parameters place paste extrusion firmly in the solid-like flow regime rather than in fluid mechanics [128].

During extrusion, the PTFE particles align along the flow direction and coalesce into fibrillar aggregates under compressive stress [127] (Fig. 20). This fibrillation is the origin of PTFE's unique anisotropy: mechanical strength and modulus increase parallel to flow but decrease transversely. For instance, longitudinal tensile strength can exceed 30 MPa, whereas transverse tensile strength remains below 20 MPa [119]. After extrusion, controlled heating removes the lubricant (<200 °C), followed by sintering at 340–380 °C to fuse the fibrils into a coherent structure.

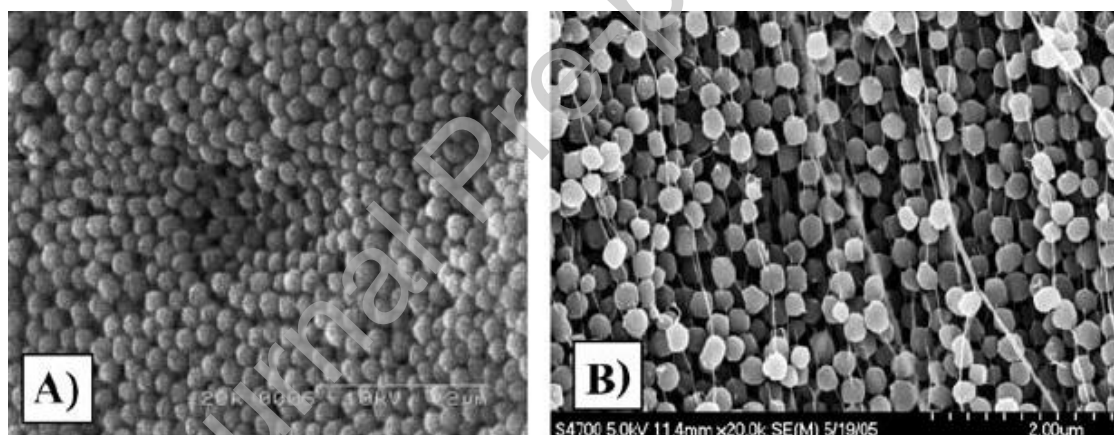


Fig. 20 : SEM micrographs of PTFE paste: (A) before extrusion and (B) after extrusion, illustrating shear alignment and fibril formation (the scale bar is 2 μ m) (reprinted with permission from Walter de Gruyter GmbH [127]).

A long-standing question concerns the mechanism of fibril formation [105,127]. Briscoe et al. [120] attribute it to the mechanical interlocking of partially crystalline particles, while Ariawan et al. [106] suggested that oriented sintering of surface amorphous layers produces continuous fibrils. The reality likely involves both effects: local shear during extrusion induces orientation in the amorphous fraction, while subsequent sintering locks in this anisotropy through recrystallization.

Interestingly, paste extrusion transforms what is often viewed as a processing limitation (i.e., PTFE's inability to flow) into a structural advantage. Indeed, the resulting fibrillar texture

confers a combination of high toughness, low density, and directional stiffness unmatched by any other polymer. Expanded PTFE (ePTFE), obtained by post-stretching extruded billets, displays a near-zero Poisson's ratio, enabling use in biomedical implants and high-performance membranes [119,129].

However, the microstructural control of this process remains largely empirical. While shear-thinning and wall slip are well documented, the roles of lubricant migration, interfacial adhesion, and particle morphology remain underexplored [105,127,128]. Recent rheo-visualization studies [123] reveal that lubricant depletion near the die wall induces velocity gradients akin to plug flow, explaining both the uniform fibrillation and the tendency toward “sharkskin”-like instabilities. A comprehensive rheological model of PTFE paste extrusion must therefore integrate particle–lubricant interactions, pressure-dependent slip, and anisotropic densification, elements absent from conventional polymer melt theories [123,127].

4.10. Modeling viscoelastic and creep behaviors

The viscoelasticity of PTFE has inspired more than six decades of modeling efforts, ranging from classical spring–dashpot analogs to modern fractional-derivative frameworks. While these models reproduce experimental data with remarkable accuracy, they often obscure the underlying physics. A critical examination reveals both their utility and their limitations.

Early studies by McCrum [69] and Tobolsky et al. [72] modeled creep and stress relaxation using simple Maxwell or Voigt–Kelvin elements. These works captured the qualitative time dependence but failed to account for the extensive relaxation spectrum observed experimentally. The problem lies in PTFE's hierarchical structure: multiple relaxation modes (γ , β , α) span time constants from milliseconds to days, corresponding to motions ranging from local CF_2 rotations to collective lamellar slip. No finite number of discrete elements can capture such a continuum.

To address this, researchers introduced Burgers-type models that combine the Maxwell and Kelvin branches to account for both instantaneous and delayed deformation [114,115]. The strain response under constant stress is expressed as:

$$\varepsilon(t) = \sigma_0 \left(\frac{1}{E_1} + \frac{t}{\eta_1} + \frac{1}{E_2} (1 - e^{-t E_2 / \eta_2}) \right) \quad (\text{eq 3})$$

under an applied constant stress σ_0 within the linear viscoelastic regime [130,131].

Typical parameters at 25 °C: $E_1 \approx 0.9$ GPa, $E_2 \approx 0.4$ GPa, $\eta_1, \eta_2 \approx 10^{10} - 10^{12}$ Pa·s [114].

While such models fit short-term data well, they lack predictive power outside the experimental window because their parameters depend strongly on the temperature, crystallinity, and loading history. A significant advance came with fractional viscoelastic models, where non-integer derivatives relate stress and strain [115,116]. These models naturally reproduce power-law relaxation ($G(t) \propto t^{-\alpha}$, with $\alpha \approx 0.3 - 0.6$) without invoking discrete time constants. They also continuously bridge the gap between elasticity and viscosity, reflecting the “memory” behavior intrinsic to semicrystalline solids. However, fractional models remain phenomenological. In other words, they describe how PTFE relaxes but not why. Their parameters (α, E_0, η_0) cannot be directly linked to physical microstructure without auxiliary assumptions.

More physically grounded approaches couple viscoelasticity with the evolution of microstructure. Wang et al. [116] combined fractional rheology with temperature-dependent crystallinity, reproducing both creep and recovery behavior up to 260 °C. Their model predicts an activation energy (ca. 140 kJ·mol⁻¹) corresponding to cooperative motion within the RAF. This aligns well with DMA evidence indicating that RAF-mediated slip predominates in long-term relaxation.

Despite these advances, several challenges remain unresolved. First, anisotropy arising from extrusion or stretching renders isotropic models inadequate: the relaxation modulus differs between orientations parallel and perpendicular to the orientation [119]. Second, the interplay between crystallization and relaxation complicates time–temperature superposition, often invalidating WLF-type scaling. Third, viscoelastic models rarely capture irreversible strain recovery or plastic flow, phenomena clearly observed in long-term creep experiments (Fig. 21) [114].

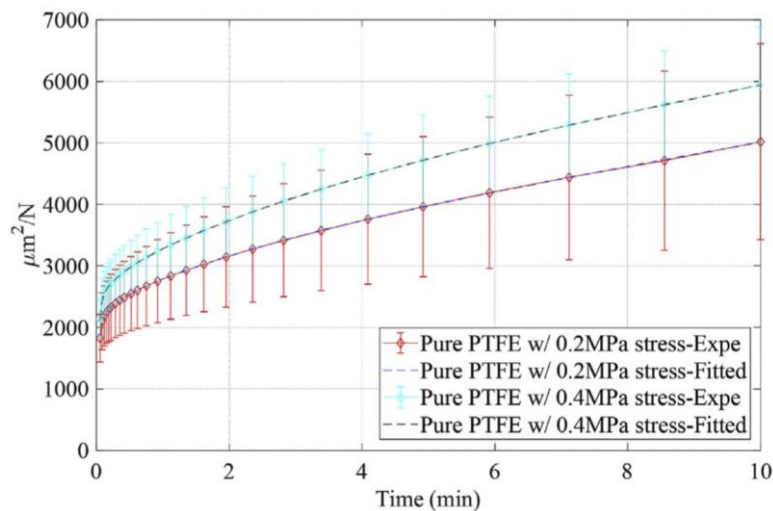


Fig. 21 : Creep compliances of PTFE-based materials under constant stress 0.2 MPa and 0.4 MPa *versus* time. The experimental data are fitted using a linear viscoelastic Prony-series model (reprinted with permission from ELSEVIER [114]).

In this context, the ongoing development of multiscale frameworks that couple fractional rheology, crystal plasticity, and diffusion-based sintering kinetics appears to be the most promising path forward [132]. Such integrative models can reconcile the disparate time and length scales governing PTFE deformation: molecular mobility, lamellar slip, and macroscopic creep. Ultimately, understanding PTFE's viscoelasticity is less about curve-fitting than about uncovering the subtle coupling between its hierarchical structure and its solid-state rheology.

4.11. Structure–rheology–processing correlations

Understanding PTFE's behavior requires a multi-scale view in which structure, rheology, and processing are inseparable. Each level of organization, from molecular conformation to particle morphology, imposes constraints that determine how the material deforms and consolidates. The processing routes developed for PTFE are, in fact, direct technological responses to its rheological singularity: the absence of actual melt flow.

At the molecular level, as mentioned above, the extraordinary regularity of the $-\text{CF}_2-\text{CF}_2-$ backbone and the 13/6 helical conformation create both high stiffness and limited chain mobility. The crystalline lamellae act as quasi-rigid plates, while amorphous tie chains form narrow interfacial zones that mediate deformation through shear and creep. Here, the RAF transmits stress between lamellae, and the MAF governs relaxation and damping. Both these sub-fractions behave cooperatively: when the RAF thickens upon annealing, mobility within the MAF decreases, shifting the α -relaxation to higher temperature. This interplay explains why

the rheological response of PTFE cannot be described by a single glass-transition-like event but rather by a continuum of coupled relaxations. At the mesoscopic level, the powder particle (an aggregate of lamellae and amorphous layers) constitutes the elementary rheological unit. Its surface amorphous layer dictates sintering kinetics, while its crystalline core determines dimensional stability.

During paste extrusion or compression, deformation is localized within these amorphous interfacial regions. This is why even “powder compaction” of PTFE displays viscoelastic hysteresis rather than purely plastic yield. As sintering proceeds, particle boundaries vanish through diffusion across the MAF, producing a continuous microstructure whose residual porosity reflects the efficiency of this interfacial coalescence.

At the macroscopic level, the cumulative effect of lamellar slip, interfacial diffusion, and anisotropic recrystallization produces the well-known directional mechanical behavior of sintered and extruded PTFE.

Creep and stress-relaxation data show a strong dependence on both processing route and orientation. For instance, extruded billets exhibit a storage modulus of up to 1.2 GPa parallel to the flow but only ca. 0.6 GPa transverse to the flow, confirming that processing history becomes an intrinsic structural variable. Expanded PTFE (ePTFE) membranes, created by cold stretching, represent an extreme case in which the lamellar network reorganizes into a fibrillar, node-and-fibril structure with near-zero Poisson’s ratio [119,133]. Such an architecture offers high toughness and tear resistance but also introduces permanent anisotropy, influencing dielectric and tribological behavior.

This hierarchy can be summarized in Table 5. While such a table is convenient, it can mask a more profound truth: the same structural parameters that ensure PTFE’s chemical inertness also induce its rheological rigidity. The dense C–F lattice, which enables resistances to solvents, oxidation, and aging, also prevents from chain interdiffusion. Thus, the processing challenge of PTFE is the direct corollary of its unrivaled stability.

A recurrent misconception in the literature is to treat the PTFE rheology as an anomaly to be circumvented, when in fact it represents a design principle: a material whose thermodynamic stability inherently dictates its deformation mechanisms. This viewpoint reframes PTFE not as a problematic material but as a benchmark for understanding how extreme crystallinity and molecular regularity dictate deformation mechanisms in semi-crystalline solids.

Table 5 : Various processing techniques of PTFE and related characteristics

Processing stage	Dominant structural feature	Rheological regime	Resulting morphology / property
Cold compaction	Semi-crystalline powder	Elastic–plastic	Green density formation
Paste extrusion	Oriented particle aggregate + lubricant	Pseudo-viscoplastic (yield + slip)	Fibrillation, alignment
Sintering (340–380 °C)	Lamellar coalescence via RAF diffusion	Diffusion / creep-controlled	Densification, recrystallization
Cooling / annealing	Crystallization shrinkage	Stress relaxation	Dimensional stability

5. Mechanical properties of PTFE

5.1. Temperature- and rate-dependent solid mechanics

The mechanical behavior of PTFE is dominated by temperature and strain-rate effects and cannot be reduced to a single set of “room-temperature properties”. This point is not related to experimental scatter but rather reflects the intrinsic deformation mechanisms of PTFE as a highly crystalline polymer. Reference datasets reported by Rae and Brown [134] in tension demonstrated that stress levels in the flow regime increase with strain rate [134]) (Fig. 22). In contrast, increasing temperature progressively reduces the resistance to deformation and enables large strains. Almost concomitantly, Rae and Dattelbaum [75] established a comprehensive compression dataset across cryogenic-to-high-temperature ranges and spanning quasi-static to dynamic loading, confirming that PTFE exhibits a similarly strong time–temperature sensitivity under compressive stress. Taken together, these studies provide a robust mechanical basis for evaluating PTFE properties, clearly placing it in the class of strongly rate-sensitive semicrystalline materials.

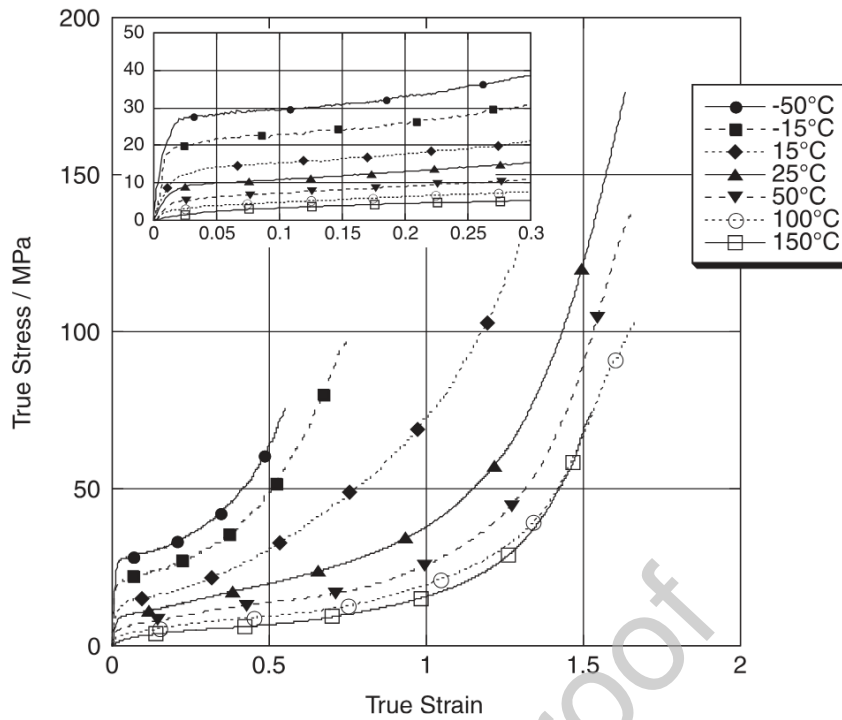


Fig. 22 : Influence of temperature on the tensile behavior of PTFE, referenced as 7C in the publication, under a strain rate of $5 \cdot 10^{-3} \text{ s}^{-1}$ (reprinted with permission from ELSEVIER [134]).

A practical implication is that PTFE is generally ductile at ambient temperature. In support of this view, Calleja et al. [58] reported a tensile experiment conducted at room temperature that evidenced a ductile response. This observation is consistent with the thermomechanical framework in which relaxation associated with the mobile amorphous fraction occurs well below ambient temperature (approximately -100°C). In other words, at room temperature, PTFE does not behave as a glassy polymer; it deforms as a viscoplastic, semicrystalline solid, whose microstructure governs the accessible deformation mechanisms.

5.2. Room-temperature transition and yielding

Early tensile investigations also indicated that PTFE exhibits mechanically detectable changes near room temperature due to solid-state transitions. Koo and Andrews [135] investigated tensile behavior near the room-temperature first-order transition and reported that the yield characteristics vary measurably in that temperature range [135]. Their analysis highlighted that the yield response is also sensitive to strain rate and thermal history, as evidenced by comparing quenched and slowly cooled materials, indicating that the transition cannot be treated merely as a thermal detail. It can directly translate into macroscopic changes in yield stress and yield strain near ambient temperature. Such results provide a clear reminder that PTFE yielding

around room temperature is not expected to vary smoothly with temperature, because phase-state rearrangements may locally modify the deformation mechanisms.

Subsequent studies extended this pattern by providing more comprehensive tensile maps. In particular, Rae and Brown [134] suggested a systematic dataset spanning both the temperature and strain-rate domains, in which the combined effects of these variables on the overall stress–strain response could be observed. Their work is particularly interesting because it reports full stress–strain curves across a wide range of temperatures and strain rates, thereby documenting not only yielding but also the subsequent flow regime and large-strain deformation of PTFE.

5.3. Strain-rate sensitivity and constitutive descriptions

Once PTFE is regarded as a strongly rate-dependent solid, it becomes natural to seek compact constitutive descriptions suitable for engineering use.

i) In tension, Nunes et al. [136] performed mechanical tests under different strain rates and confirmed that the flow stress increases with strain rate. They also emphasized the relevance of non-contact strain measurements and proposed a phenomenological modeling approach calibrated from a limited number of experiments. Although such models are not intended to represent molecular-scale mechanisms, their merit lies in providing a practical representation of PTFE rate sensitivity for design-level predictions.

ii) In compression, dynamic regimes have been investigated in detail. Rae and Dattelbaum [75] combined quasi-static and high-rate compression data to establish a temperature–rate map that explicitly displays the strong dependence of compressive modulus and flow behavior on both variables. Later, Jordan et al. [137] extended this approach to extruded PTFE by combining quasi-static and Hopkinson-type compression experiments (Fig. 23). Their study further demonstrated that processing history (extruded vs. annealed) can alter the response and should therefore be accounted for when comparing datasets. In addition, they discussed modeling strategies, including a Zerilli–Armstrong-type approach, and highlighted the importance of incorporating strain rate into constitutive frameworks for PTFE.

Rae and Dattelbaum [75] combined quasi-static and high-rate compression data over a broad temperature range and established a temperature–strain-rate map showing that both compressive modulus and flow behavior depend strongly on these variables. Their dataset remains a key reference because it documents PTFE response from cryogenic to elevated temperatures under both slow and dynamic loading conditions.

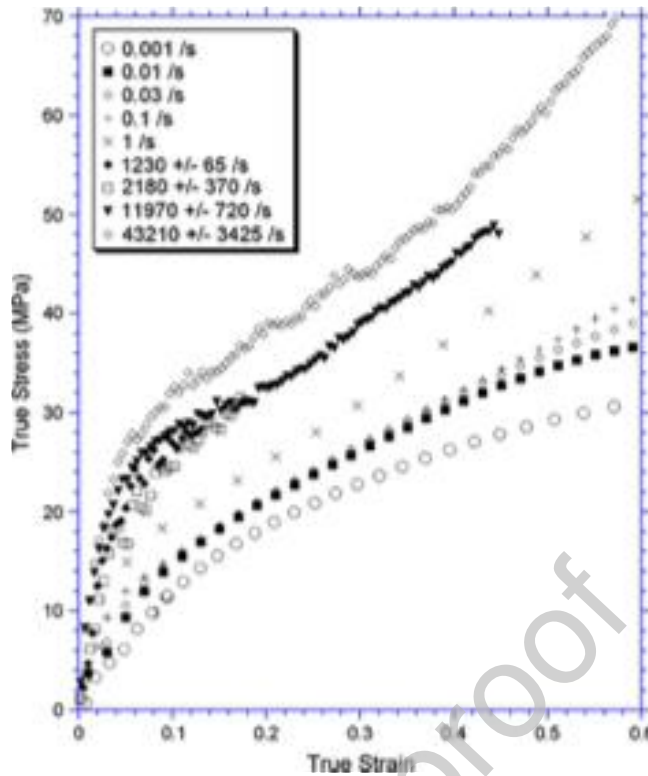


Fig. 23 : Polytetrafluoroethylene tested in compression across a range of strain rates at room temperature (reprinted with permission from ELSEVIER [137]).

5.4. Microstructure-controlled plasticity: band morphology and deformation modes

Early investigators recognized that the mechanics of PTFE cannot be understood without considering its characteristic semicrystalline morphology. Speerschneider and Li [138] proposed one of the most influential mechanistic correlations by linking macroscopic flow behavior to microstructure and temperature. Using tensile experiments performed from cryogenic conditions (i.e., about $-196\text{ }^{\circ}\text{C}$) to $100\text{ }^{\circ}\text{C}$, together with electron microscopy, these authors reported that PTFE transitions from a high-strength, low-ductility regime at low temperatures to a low-strength, highly ductile regime at higher temperatures. Importantly, their analysis did not treat this transition as a purely thermal softening effect. Instead, it was interpreted as a change in deformation mechanisms. At low temperatures, crystalline deformation modes (including bowing and kinking) were reported to dominate, whereas at higher temperatures, non-crystalline modes such as sliding and rotation were predominant [138] (Fig. 24).

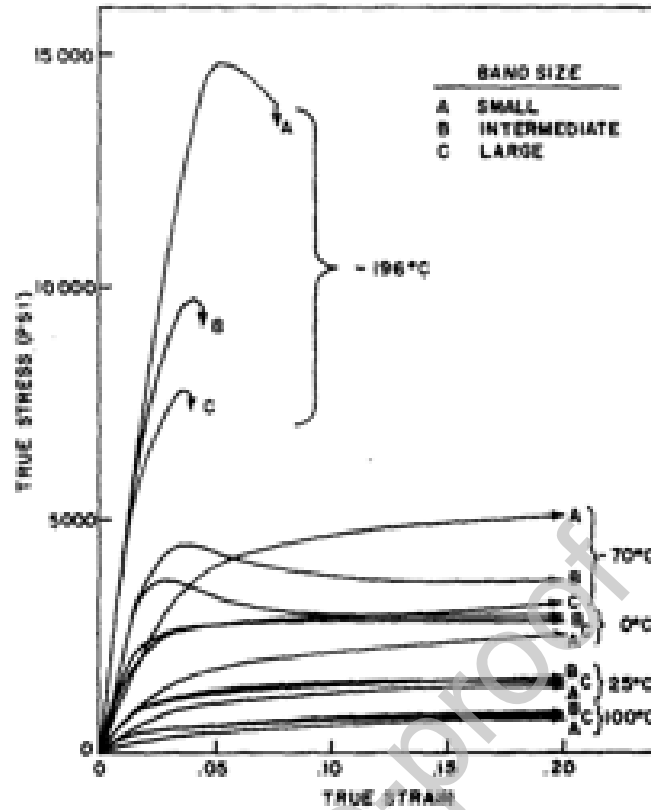


Fig. 24 : Effect of temperature and band size on flow stress of PTFE measured with traction experiments (reprinted with permission from AIP Publishing [138]).

In addition, Speerschnieder and Li [138] introduced a microstructural variable, named “band size”, controlled by cooling rate from the sintering temperature. They revealed that band size affects flow stress at low temperatures and reported a stress-drop phenomenon in the flow-stress relations under cryogenic conditions. These results indicate that PTFE plasticity is controlled not only by the amount of crystalline phase but also by which deformation mechanisms are active, crystalline modes dominating at low temperature and non-crystalline modes at higher temperature. Subsequent works on room-temperature behavior further supported that PTFE’s response may change abruptly when transitions are crossed. As discussed above, Koo and Andrews [135] observed measurable changes in yielding characteristics around the room-temperature first-order transition, together with sensitivity to strain rate and cooling history. When combined with microstructure-driven interpretations, these observations reinforce the trend that seemingly moderate temperature changes around ambient conditions may translate into detectable changes in yield and flow response in PTFE.

5.5. Crystallinity and fracture: limitations of ductile mechanisms

Whereas stress–strain maps characterize PTFE plasticity in terms of flow stress and deformability, fracture studies highlight more directly how microstructure governs damage evolution. Brown and colleagues [139] investigated the effect of crystallinity on PTFE fracture behavior and demonstrated that ductile mechanisms, such as plastic deformation and fibrillation, contribute significantly to fracture resistance. Their analysis also indicated that increased crystallinity may restrict these ductile mechanisms, thereby reducing the fracture resistance. From a structure–property perspective, this provides a key complement to flow-stress descriptions: crystallinity not only alters stiffness and yield but also constrains the mechanisms that enable energy dissipation at the crack tip.

A further interest of the study by Brown et al. lies in the explicit consideration of solid-state transitions around room temperature. Their discussion supports the idea that transitions may influence deformation and fracture behavior, consistent with earlier studies on yielding. The overall message is that PTFE mechanical integrity should not be assessed solely by tensile strength or ductility but must also account for microstructure-controlled fracture mechanisms, particularly in applications involving notch sensitivity, crack propagation, or repeated loading.

5.6. Molar mass as a mechanical lever

Chain architecture provides another way to understand and tailor PTFE mechanics. Włochowicz and Śacigala [140] examined the influence of molar mass on mechanical properties. They reported correlations between number-average molar mass and tensile behavior, including strength and elongation at break, as well as density trends; as expected, after high molar mass, these features no longer change. Their work is valuable because it explicitly treats PTFE as a family of materials rather than as a single reference polymer. Indeed, variations in molar mass translate into measurable shifts in the strength–ductility balance. In the context of a review, this provides a valuable framework to rationalize differences reported across datasets and grades, even when processing routes appear similar [140] (Fig. 25).

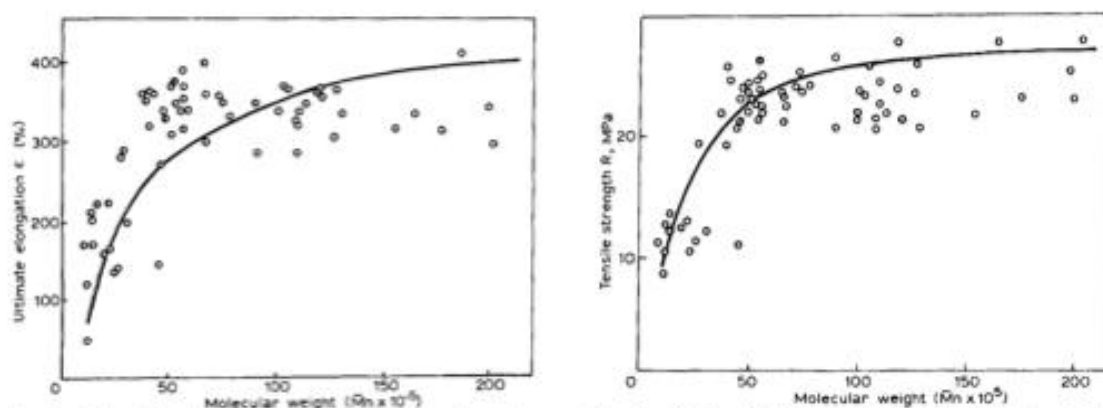


Fig. 25 : Effect of molar mass on the ultimate elongation for PTFE (left) and on the tensile strength (right) (reprinted with permission from WILEY [140]).

5.7. Post-treatments and microstructure tailoring: irradiation effects

In addition to molar mass and cooling history, mechanical response can be modified by post-treatments. In graphite-filled PTFE composites, Barylski et al. [141] investigated the combined effects of graphite content and electron-beam irradiation. These authors reported improvements in mechanical properties, as measured by compression and hardness tests, and discussed an optimal irradiation dose window. Such results indicate that irradiation can be used as a microstructure-modifying tool to enhance deformation resistance under appropriate conditions. However, this effect should not be interpreted as monotonic: as in many polymers, excessive irradiation doses may trigger degradation processes, such as chain scission, which can ultimately reduce mechanical integrity. The mechanical performance of PTFE must therefore be considered as resulting from a balance between beneficial microstructural modifications at moderate doses and degradation at higher doses.

5.8. Large-strain deformation, fibrillation, and non-classical kinematics

While tensile strength and modulus are commonly used to rank polymer performance, PTFE often operates in regimes in which large-strain deformation and microstructural reorganization dominate the response. In this context, paste-extruded PTFE provides a particularly instructive example. Vavlekas and co-workers [119] investigated paste-extruded PTFE under uniaxial extension using a Sentmanat extensional rheometer configuration and reported several distinctive features. First, the ultimate tensile strength increased with extrusion temperature and reduction ratio, while decreasing with testing temperature. Second, the tensile strength followed a power-law dependence on Hencky strain rate. Beyond these strength trends, the same work

revealed an unusual deformation kinematics: the specimen diameter remained approximately constant during extension, implying a near-zero Poisson's ratio ($\nu \approx 0$) under the studied conditions.

A key contribution of these authors [119] is their linking of these macroscopic features to microstructural evolution during stretching. Density measurements indicated a decrease in relative density with increasing extension, suggesting that stretching is accompanied by porosification (Fig. 26). SEM observations were discussed in relation to fibrillation processes, providing a physically consistent picture in which PTFE elongational deformation produces a reorganized, fibrillar architecture rather than a classical incompressible rubber-like response. This study is quite helpful because it emphasizes that PTFE mechanics at large strains can involve volume changes and the development of microstructural damage, which must be accounted for when PTFE is used in membrane-like components or subjected to elongational flow paths (Fig. 26).

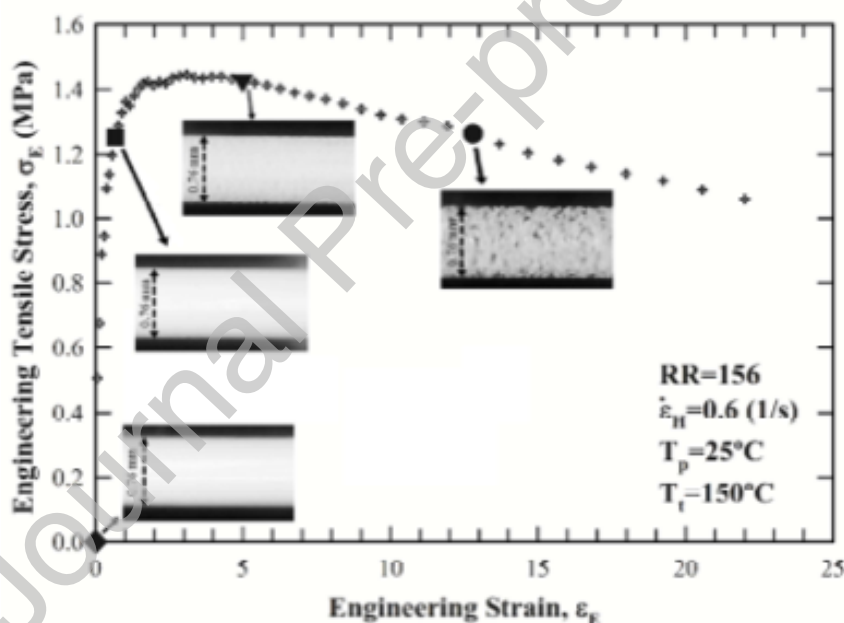


Fig. 26 : Experiments on PTFE (0.6 s^{-1} , 150°C): evidence for porosification at large strain values (reprinted with permission from ELSEVIER [119]).

5.9. Processing routes as primary features of mechanical performance

Processing plays a central role in PTFE mechanics because it governs porosity, interparticle adhesion, crystalline morphology, and molecular orientation. This feature is not limited to composites: in pure PTFE, processing may induce mechanical properties that rival those of reinforced systems. An obvious demonstration was provided by Uehara and co-workers [142], who applied biaxial melt-drawing to prepare void-free PTFE membranes with high

transparency and enhanced mechanical properties. Their strategy combined a two-step molding process designed to improve adhesion between PTFE powder particles and minimize residual voids, followed by simultaneous biaxial drawing from the molten state. Under these conditions, the resulting membranes achieved a tensile strength of up to 120 MPa, i.e., approximately five times higher than that of a commercially available PTFE film. The interest of the study by Uehara et al. lies in its direct, processing-based pathway to “structural PTFE” that relies on the absence of fillers. The authors explicitly attributed the combination of strength and transparency to defect-free structures produced by controlled preform consolidation and low-stress melt drawing. In contrast, films containing residual voids (e.g., those associated with lubricant-assisted processing routes) were shown to retain or amplify scattering defects during drawing, limiting both transparency and mechanical integrity. Such comparisons reinforce a broader observation across several PTFE systems: porosity and interfacial defects are critical structural flaws that govern mechanical performance, and their control is therefore a primary requirement rather than a secondary processing detail [142,143].

5.10. Processing history and high-rate response: extrusion and annealing effects

Processing sensitivity is also apparent in the mechanical response under compressive stress states and dynamic loading. As discussed previously, Jordan and co-workers [137] examined extruded PTFE and compared the “as-received” and annealed states. Their study combined quasi-static and high-rate compression experiments and discussed constitutive descriptions, including a Zerilli–Armstrong-type approach that captures rate sensitivity. Notably, the authors emphasized that the processing route (i.e., extruded condition and post-annealing) can alter the measured response. This reinforces the idea that PTFE datasets should not be compared without at least minimal information on processing history, since microstructural differences induced during extrusion and annealing may influence compressive stiffness and flow behavior, particularly when the strain-rate domain is extended to dynamic conditions [138].

5.11. Filled PTFE: stiffening mechanisms and modulus–ductility trade-offs

The most widely used strategy to improve the mechanical performance of PTFE is to incorporate fillers and reinforcements [144]. Although specific goals may vary (e.g., wear, dielectric stability, thermal conductivity), the mechanical trends are often systematic. In a comprehensive comparative study, Tóth et al. [83] prepared neat and mono-filled PTFE with several nanoparticle types (graphene, alumina, boehmite, hydrotalcite) and varying filler

contents [83]. Their mechanical characterization included tensile, compressive, and shear testing, as well as DMA and hardness measurements. A central result is that all fillers increased the storage modulus and the tensile/shear moduli, whereas ductility decreased relative to neat PTFE. Such results support a general view of nanoparticle reinforcement in PTFE: increased stiffness is typically achieved at the expense of extensibility, likely due to restricted chain mobility and earlier activation of damage mechanisms such as micro-voids at the interfaces. At higher filler fractions, porosity and interfacial quality often become decisive. Sasikala and Sebastian [143] investigated Mg_2SiO_4 -filled PTFE composites, including micro- and nanosized fillers (Fig. 27) [143]. They evaluated mechanical properties using microhardness and strength measurements obtained from flexural and diametrical compressive tests. Their work evidenced that hardness increases with increasing filler content. Notably, the authors highlighted that silane treatment reduces porosity and increases microhardness, demonstrating that interfacial engineering can mitigate void-driven mechanical degradation under high loading (Fig. 27).

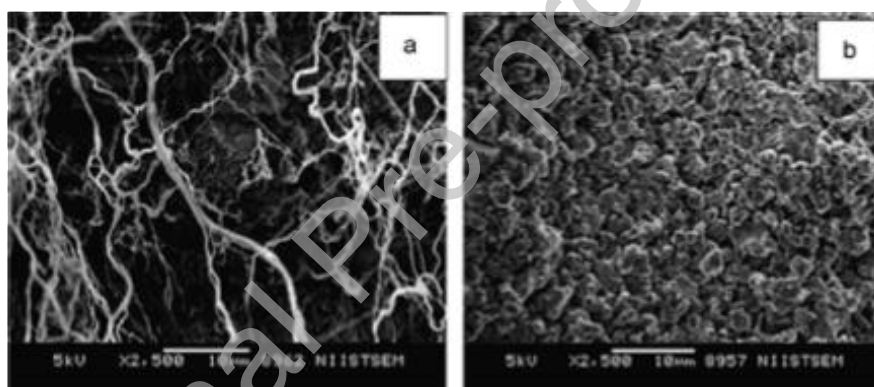


Fig. 27 : SEM images of fractured surfaces of PTFE loaded with (a) 40 vol% untreated Mg_2SiO_4 (b) 40 vol% silane-treated Mg_2SiO_4 (the scale bar is 10 μm) (reprinted with permission from ELSEVIER [143]).

A similar “functionality–mechanics compromise” is observed in composites filled with plate-like ceramic fillers intended for thermal or dielectric applications. Zimmermann-Ptacek et al. [145] studied h-BN-filled PTFE composites across a broad range of volume fractions and reported tensile properties such as modulus, tensile strength, and elongation [145]. They observed that mechanical properties are negatively affected by ceramic loading. However, they also noted that ca. 40% of the tensile strength can be preserved at filler fractions up to 30 vol%. This type of quantitative boundary is particularly valuable for engineering design, as it explicitly specifies the mechanical cost associated with incorporating functional fillers. In practical terms, such a limit is relevant for PTFE-based substrates or insulating components that require enhanced thermal conductivity or dielectric performance without sacrificing mechanical integrity. For example, in electronic packaging or high-frequency circuit substrates, filler

loadings must remain compatible with handling, machining, and assembly stresses. The identification of a filler fraction window in which functional gains are obtained while retaining a defined fraction of tensile strength, therefore, provides a direct guideline for balancing mechanical reliability against thermal or dielectric performance [146].

5.12. Structural PTFE composites: continuous fiber laminates and interlaminar integrity

In addition to particulate fillers, continuous fiber reinforcement enables PTFE-based structural composites with significantly enhanced stiffness and strength. In an interesting study, Riul et al. [147] reported the processing and mechanical evaluation of glass fiber-reinforced PTFE laminates [147]. They measured tensile and flexural properties using full-field strain analysis (named DIC). The reported tensile modulus and strength ($E = 14.2$ GPa and $\sigma = 165$ MPa, respectively) confirm that PTFE can serve as a matrix for load-bearing laminates when architecture and processing are suitably controlled. In addition, they highlighted that sintering time influences fiber–matrix adhesion, highlighting that interface development during sintering is a key parameter controlling laminate integrity.

Interlaminar properties, such as interlaminar shear strength, represent a key aspect of mechanical performance in PTFE laminates, particularly when PTFE is used as a coating or matrix in textile-based composite structures. Bandaru and co-workers [148] investigated PTFE-coated glass fabric composites and evaluated interlaminar shear strength (ILSS) as a function of textile architecture and surface hybridization. They reported that adding metallic mesh in surface layers improves ILSS, with gains depending on the fabric structure. These results illustrate that architectural design and interlayer engineering can enhance load transfer and delamination resistance in PTFE-based laminates.

5.13. Durability under cyclic loading

For many PTFE applications (e.g., bearings, seals, sliding parts, structural composites in service), the relevant mechanical performance is not only a *quasi*-static strength but also durability under repeated loading. Mazur et al. [149] produced PTFE composites filled with bronze, glass fibers, coke, and graphite under static compression and compression–compression fatigue up to 100,000 cycles. Their analysis revealed that filler type and morphology influence both modulus, dispersion energy, and cyclic mechanical response, supported by morphological observations. Such studies support the general conclusion that reinforcement strategies must be

evaluated under service-like loading modes, since fillers which improve stiffness or wear resistance do not necessarily optimize fatigue behavior (Fig. 28).

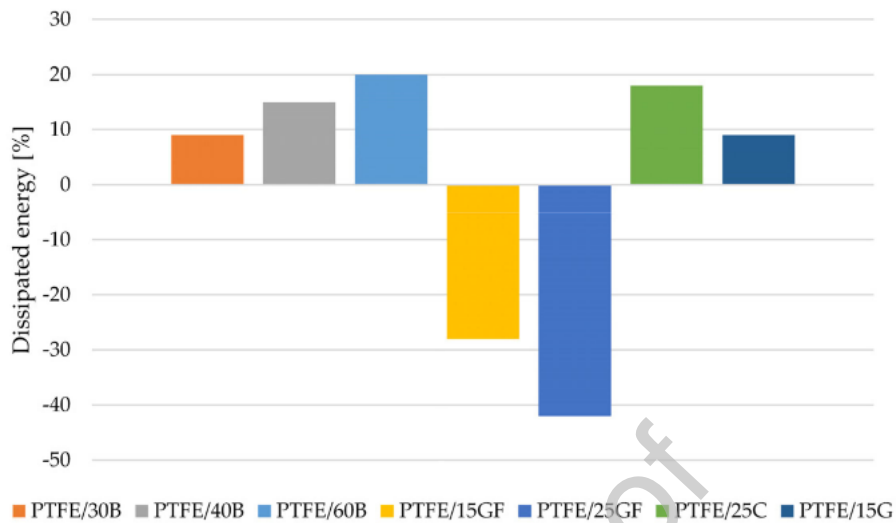


Fig. 28 : Change of the dispersion energy of composites based on PTFE filled with different weight percentages of particles: B=bronze; GF=glass fiber; C=coke and G=graphite (reprinted with permission from MDPI [149]).

5.14. Time-dependent response: creep and hysteresis in PTFE composites

Time-dependent mechanical response is another recurrent feature of PTFE systems, particularly when both reinforcement and processing induce anisotropy. Martins et al. [132] provided a focused mechanical characterization of silica-reinforced PTFE matrix composites, explicitly addressing the influence of strain rate, creep loading, and cyclic loading–unloading sequences [132]. Their results underscore that the mechanical response depends on the loading history (i.e., rate effects and creep). Significant hysteresis is observed upon cycling, reflecting the viscoelastic/viscoplastic nature of the PTFE matrix and the role of composite architecture, including directional effects in processed plates.

6. Tribological and surface behavior of PTFE

6.1. Intrinsic Tribological Behavior of Virgin PTFE

6.1.1. Frictional response, microstructure, and chain orientation

The intrinsic tribological behavior of virgin PTFE results from the interplay between its low surface energy and the weak intermolecular cohesion associated with its *quasi*-cylindrical CF₂ helices. These molecular features yield a very low friction coefficient, μ , (typically ranging

from 0.04 to 0.10) but also a high wear rate, typically on the order of $10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ under dry sliding [150,151]).

The microstructure of PTFE is a central parameter governing its frictional response, in particular its degree of crystallinity, fibrillation, and chain orientation. Drawing-induced fibrillation, as reported by Liu et al. [152], increases crystallinity and promotes the formation of more cohesive transfer films as described later. Orientation effects have been demonstrated at multiple scales. Jang et al. [153], using AFM and microtribometry, observed a strong anisotropy, with friction coefficients of 0.05 along the orientation direction and 0.15 perpendicular to it. Molecular-dynamics simulations further support the role of the chain alignment: Barry et al. [154] showed that the interfacial shear is accommodated by rotational motions of CF_2 units and local chain rearrangements, consistent with experimentally measured low shear strengths. More recently, Cai et al. [155] reported that PTFE drawn by factors of 2–5 exhibits μ values in the 0.03–0.06 range and a much more stable sliding trace, attributed to homogenized molecular alignment.

A defining feature of PTFE tribology is the formation of a transfer film, which enables low friction but remains mechanically fragile. The mechanisms governing its formation, chemical stabilization, and long-term durability are detailed in Section 6.2.2.

The frictional response of PTFE depends on normal load and sliding speed. Ünal et al. [156,157] found that increasing the load from 0.2 to 7.0 MPa reduces μ from 0.16 to 0.08 while simultaneously increasing wear.

These observations highlight that the outstanding lubricity of PTFE originates from its molecular mobility and orientation, while its poor wear resistance reflects the mechanical fragility of the interfacial layer formed during sliding. The thermomechanical and tribochemical processes governing this behavior are examined in the following sections.

6.1.2. Thermomechanical and viscoelastic coupling

The tribological behavior of PTFE cannot be fully described without accounting for its pronounced viscoelasticity. Internal mechanical losses, arising from molecular relaxations in both amorphous and crystalline fractions, play a central role in frictional heating and energy dissipation during sliding. Wieleba et al. [158] demonstrated that PTFE exhibits significant internal friction ($\tan \delta$ of about 0.16 at 3 MPa), which leads to local flash-temperature rises well above the bulk temperature.

Temperature acts as a dual factor, lubricating and degrading the interface simultaneously. Burris et al. [159,160] identified a thermally activated friction mechanism with activation energies of 3-5 kJ mol⁻¹, consistent with shear accommodated by local chain mobility. At moderate temperatures (<100 °C), enhanced segmental motion reduces friction, whereas excessive heating increases wear exponentially as the polymer approaches the onset of crystalline melting near 327 °C (Fig. 29).

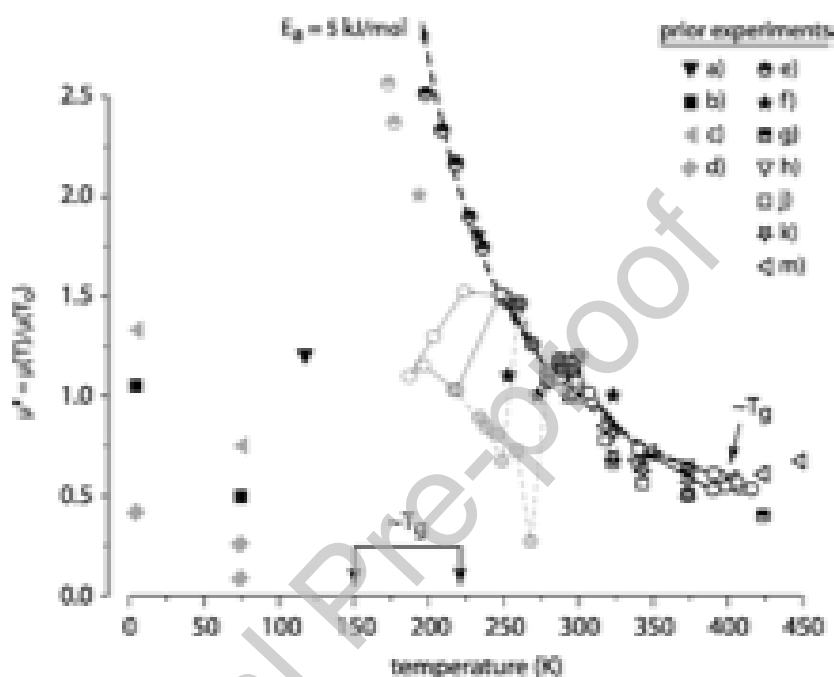


Fig. 29 : Normalized friction coefficient plotted *versus* interface temperature for variable temperature studies of PTFE in the literature from various sources (reprinted with permission from Taylor & Francis [160]).

Thermal effects also interact with molecular relaxations. Babuska et al. [161] mentioned that changes in friction and damping across a wide temperature range (from -150 °C to +175 °C) coincide with the activation of distinct modes of molecular motion (Fig. 30). These transitions reflect the various mobilities of the MAF and the RAF [58]. This interplay defines an operational window in which PTFE maintains a self-replenishing transfer layer without catastrophic softening or brittle failure.

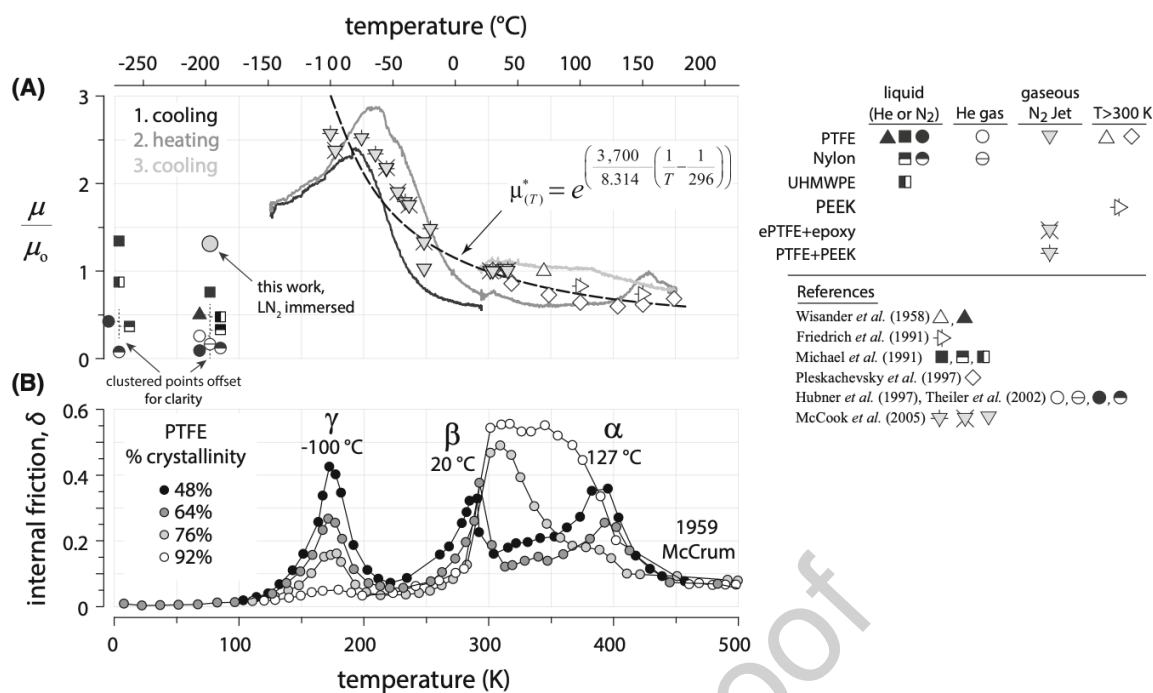


Fig. 30 : A) Normalized temperature-dependent friction of self-mated PTFE (including literature data of other polymers); B) Internal friction from torsional energy dissipation (reprinted with permission from Springer Nature [161]).

Dynamic mechanical analyses by Tan and Stephens [114] confirmed that the storage modulus (E') and loss factor ($\tan \delta$) vary systematically with both temperature and frequency. These rheological trends correlate directly with friction hysteresis, supporting the view that PTFE friction is a bulk-mediated phenomenon. In this framework, the apparent friction coefficient, μ , reflects the superposition of interfacial shear and viscoelastic damping.

Thermomechanical coupling also influences the steady-state friction. Indeed, when the frictional heat exceeds the dissipation capacity, limited by low thermal conductivity of PTFE ($0.25 \text{ W m}^{-1} \text{ K}^{-1}$), melting can propagate into the subsurface, leading to microcracking and sudden friction spikes.

Generally, viscoelastic dissipation and frictional heating strongly condition the formation and durability of the interfacial layer generated during the sliding. The chemical and mechanochemical processes governing this layer are discussed in the following section.

6.2. Tribochemistry and transfer film dynamics

6.2.1. Film formation and evolution

The tribological response of PTFE is fundamentally governed by the formation and evolution of its transfer film. The initial stages of transfer-film development are dominated by subsurface cracking and the release of fibrillar or platelet-like debris. Several studies indicate that such debris progressively compact and evolve under shear and frictional heating, yielding a transfer film whose interfacial region becomes enriched in degraded (partially defluorinated and carbon-enriched) fragments that adhere strongly to metals bearing native or tribo-oxidized surface layers (e.g., $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ on steel, Al_2O_3 on aluminum alloys, and TiO_2 on titanium alloys) [151,160,162].

Tribochemical interactions between defluorinated polymer fragments and the native oxides of the counterface further stabilize the film. Lu et al. [151] identified inorganic–organic complexes formed by such reactions that lower interfacial energy and promote film attachment. The morphology and cohesion of the resulting film depend sensitively on the interfacial chemistry and on the continuity of debris supply.

Environmental conditions also influence film stability. Johansson et al. [163] observed that humid and oxygen-rich atmospheres destabilize the transfer layer and increase the wear. In contrast, dry nitrogen favors thinner yet more cohesive films, underscoring the importance of tribo-oxidation in governing film integrity (Fig. 31).

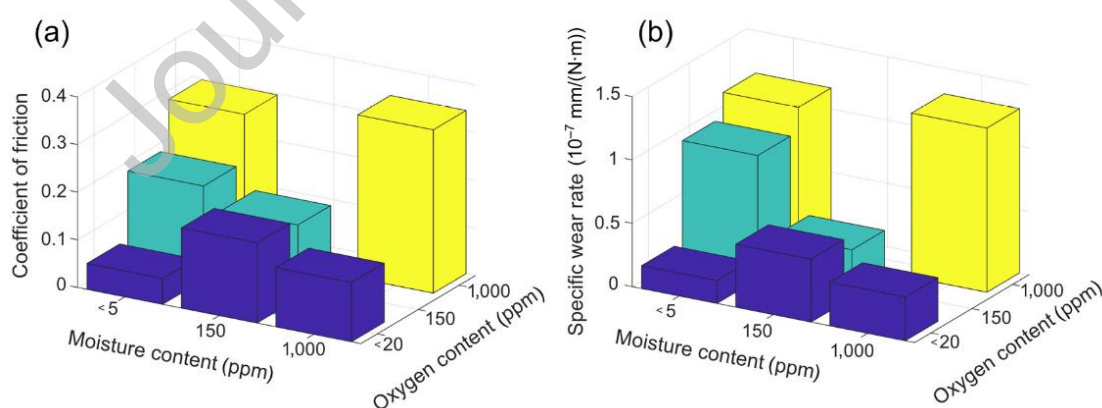


Fig. 31 : (a) Coefficient of friction and (b) specific wear rate of PTFE filled with carbon fibers in different environmental conditions (reprinted with permission from Springer Nature [163]).

Thermal effects further shape film evolution. Local heating at asperity contacts softens or partially melts the near-surface region of PTFE, promoting flow into the tribolayer and

facilitating compaction. However, excessive thermal accumulation accelerates chemical degradation. Liu et al. [164] reported that irradiated or heavily degraded PTFE forms dense carbonaceous residues that limit film mobility and may ultimately compromise lubrication.

6.2.2. *Tribochemical and mechanochemical interactions*

At the molecular scale, the tribochemical activity of PTFE is commonly attributed to shear-driven C–F bond scission. Although the exact stress required for bond cleavage is difficult to quantify experimentally, numerous studies support the homolytic formation of carbon-centered radicals during sliding [150,164]. These reactive species undergo secondary reactions with counterfacial oxides, atmospheric oxygen, and adjacent PTFE chains, yielding partially defluorinated and oxidized fragments.

Defluorination represents the key tribochemical pathway. Lu et al. [151] and other IR spectroscopic studies [162,163], reported the emergence of C–CF_x, C=O, and C–O–C functions after prolonged sliding under nominal ambient conditions (Fig. 32). However, the interfacial temperature cannot be assumed to remain at room temperature, and the observed chemistry is consistent with chain scission and mild oxidation enabled by frictional heating. Loss of fluorine increases the polarity and reactivity of degraded PTFE fragments, thereby enhancing adhesion to metallic substrates while also reducing the polymer's intrinsic chemical inertness. The balance between these competing effects is central to long-term interfacial stability.

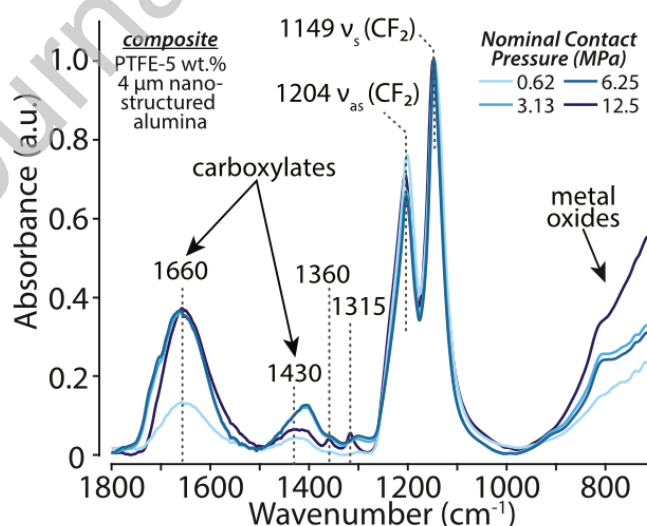


Fig. 32 : IR spectra of the wear surfaces of PTFE filled with 5 wt% 4 μ m nanostructured alumina tested at nominal contact pressures of 0.62, 3.13, 6.25, and 12.5 MPa. (reprinted with permission from ELSEVIER [162]).

As previously mentioned, the surrounding atmosphere and its moisture content also modulate tribochemical pathways [163]. This environmental sensitivity explains part of the variability among published wear rates for unfilled PTFE.

These tribochemical processes govern the adhesion, renewal, and durability of the transfer film and therefore provide the mechanistic basis for the use of fillers, irradiation, and surface engineering strategies discussed in the following sections.

6.3. Reinforced and modified PTFE systems

6.3.1. Fiber and particulate reinforcements

Reinforcement with fibers and ceramic particulates has long been the most effective strategy to overcome the inherently high wear rate of virgin PTFE. Since the early development of PTFE composites in the 1960s, systems incorporating glass fibers (GF), carbon fibers (CF), bronze, graphite, and a variety of ceramic fillers (such as alumina, silica, and titanium oxides, *vide-infra*) have been engineered to stabilize the soft polymer matrix, restrict cold flow, enhance load support, and promote the formation of more cohesive transfer films [165].

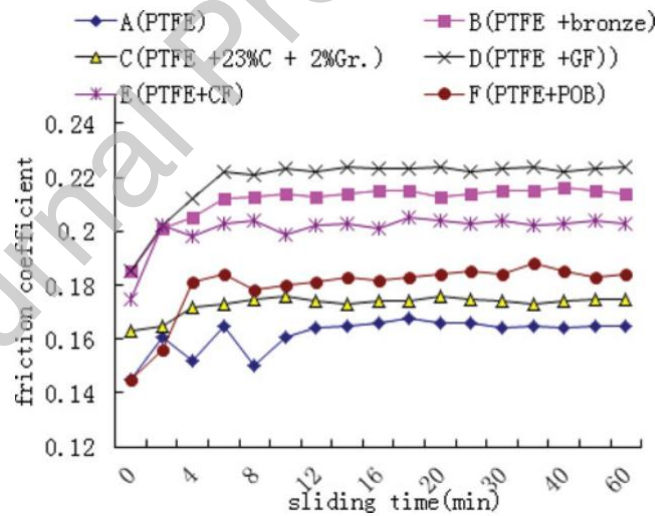


Fig. 33 : Frictional behavior of PTFE and PTFE composites under ambient conditions where C: carbon, Gr: graphite, CF: carbon fiber, GF: glass fiber, and POB: poly-p-oxybenzoyl (reprinted with permission from Taylor & Francis [166]).

Different studies describe how these fillers act through several complementary mechanisms [144,157,166]. Fibers increase stiffness and constrain plastic deformation, particulates enhance counterface conformity and abrasion resistance, and metallic or ceramic additives can anchor

degradation products within the tribofilm. Collectively, these mechanisms disrupt the continuous removal–reformation cycle characteristic of virgin PTFE and greatly extend wear life (Fig. 33).

Previous studies clearly show that the performance of reinforced PTFE depends strongly on filler type, morphology, and interfacial chemistry. Fibrous reinforcements generally provide the most significant improvement in load-bearing capacity, while lamellar or platelet-shaped fillers help to stabilize transfer films. Hybrid formulations that combine fibers with oxides or solid lubricants often induce synergistic effects, producing composites whose friction stability and wear resistance far exceed those of single-filler systems. Across all reinforced systems, improvements arise from a combination of subsurface mechanical stabilization, enhanced heat dissipation, and more cohesive anchoring of the transfer film. These trends and their quantitative outcomes are discussed in detail in the following subsections.

6.3.2. Glass and carbon fiber reinforcements

Glass fibers (GF) are among the earliest and the most widely implemented reinforcements for PTFE, valued for their ability to enhance dimensional stability and abrasion resistance while maintaining electrical insulation. Khedkar et al. [167] demonstrated that incorporating 20–25 wt.% GF reduces the specific wear rate of PTFE from 3×10^{-4} to $5 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, with only a modest increase in the friction coefficient value from $\mu = 0.08$ to 0.12. The performance improvement is due to increased load capacity and to the transfer film being more mechanically anchored, enabling it to resist delamination under shear. Mnif et al. [113] confirmed these effects for GF–MoS₂ hybrids.

Despite these advantages, the brittleness and relatively low thermal conductivity of GF (ca. $1 \text{ W m}^{-1} \text{ K}^{-1}$) can lead to localized heating and microcracking under heavy loads. Carbon fibers (CF) provide a more balanced reinforcement by combining higher stiffness with significantly better thermal conductivity (typically $10\text{--}20 \text{ W m}^{-1} \text{ K}^{-1}$). Their incorporation at 15–25 wt.% generally decreases both friction and wear by enhancing heat dissipation and stabilizing the interfacial layer. Sujuan et al. [166] reported that CF-filled PTFE composites exhibit the lowest and most stable friction traces (μ ranging from 0.09 to 0.12) across a wide temperature range (from 23 to 180 °C) among fiber-reinforced systems. In contrast, GF- and bronze-filled systems display higher and more temperature-sensitive friction coefficients (μ ranging between 0.15–0.30).

Overall, GF- and CF-reinforced PTFE composites typically exhibit friction coefficients in the 0.08–0.15 range and specific wear rates of 10^{-7} to 10^{-9} $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$, representing several orders of magnitude improvement over virgin PTFE [144]. Achieving optimal performance requires balancing the reinforcement fraction, interfacial bonding, and matrix ductility to maintain PTFE's self-lubricating behavior while maximizing wear resistance.

6.3.3. Particulate and ceramic fillers

Particulate fillers provide an alternative pathway to enhance the mechanical stability and tribochemical robustness of PTFE. Aderikha et al. [168] observed that adding as little as 1 wt.% SiO_2 nanoparticles, decreases the specific wear rate of PTFE by approximately two orders of magnitude, while preserving a low friction coefficient (μ about 0.10) (Fig. 34). At higher loadings (5 wt.%), wear increases again because particle agglomeration disrupts film continuity and promotes local stress concentrations. These observations highlight the importance of achieving a well-dispersed particulate phase. In other words, such improvements critically depend on particle dispersion and interfacial compatibility.

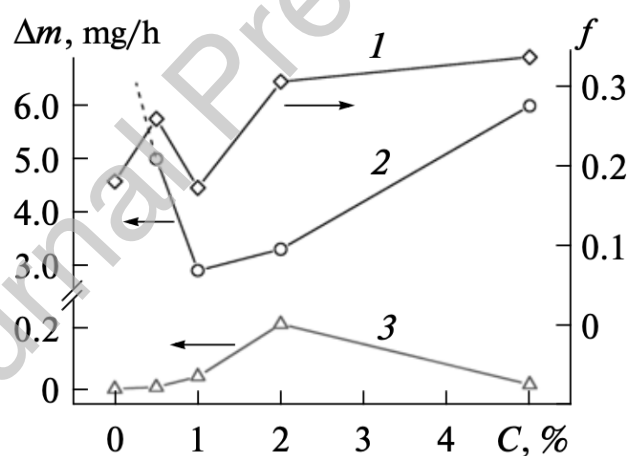


Fig. 34 : Dependences of friction coefficient (1) and wear rates of PTFE–silica composites (2) and steel counterbody (3) on filling degree. The wear rate of the original PTFE is ≈ 630 mg/h (reprinted with permission from Springer Nature [168]).

MoS_2 and graphite fillers function primarily through solid-lubricant mechanisms. Mnif et al. [113] reported that PTFE/ MoS_2 composites maintain friction coefficient values in the range 0.10–0.15 over prolonged cycling, with wear reduced by a factor of 3–5 relative to that of virgin PTFE. Graphite provides comparable friction levels but may exhibit less stable behavior under humid or high-temperature conditions, consistent with its known susceptibility to oxidative degradation.

Ceramic-filled systems also influence transfer-film morphology. Lu et al. [151] demonstrated that oxide surfaces promote the formation of adherent tribofilms enriched in degraded PTFE fragments and iron–oxygen–fluorine species when sliding against steel. These chemically modified films improve interfacial adhesion and help prevent subsurface delamination, a failure mode typically observed in unfilled PTFE.

Hybrid formulations that combine fibers with ceramic or lamellar fillers often display enhanced performance through complementary mechanisms: fibers provide load support and thermal stabilization, whereas particulates improve abrasion resistance and help maintain tribofilm continuity. Although the exact synergy depends on the composite architecture, such systems typically lead to lower friction and more stable wear behavior than their single-filler counterparts.

Quantitatively, particulate-reinforced PTFE composites generally exhibit friction coefficients in the 0.10–0.18 range and specific wear rates between 10^{-7} to 10^{-9} mm³ N⁻¹ m⁻¹. Wear reductions are most pronounced when ceramic particles are well-dispersed and chemically compatible with the matrix, confirming the critical role of microstructural control in achieving durable tribological performance [113,151,168].

6.3.4. Hybrid, irradiated, and lubricated systems

The inherent duality of PTFE, characterized by low friction and high wear, has motivated numerous attempts to design materials that combine the polymer's outstanding self-lubrication with enhanced cohesion and thermal stability. Beyond simple fiber or ceramic fillers, recent developments have focused on hybrid composites, radiation-modified PTFE, and lubricated or coating-based systems. Each strategy aims to i) stabilize the tribofilm, ii) improve interfacial bonding, or iii) regulate the energy-dissipation pathways that govern friction and wear.

6.3.5. Hybrid and multiscale composites

Beyond single-filler systems, hybrid PTFE materials exploit synergistic effects between fibrous, particulate, and lamellar fillers to combine mechanical reinforcement, enhanced thermal transport, and boundary lubrication within a single multiphase architecture. The goal is to integrate complementary functionalities that individually improve only one aspect of PTFE performance but, together, stabilize friction and suppress wear.

Mnif et al. [113] found that combining GF (15 wt.%) with MoS₂ (5 wt.%) results in significantly lower wear and more stable friction than either constituent alone. The fibers provide structural reinforcement and restrict cold flow, while MoS₂ contributes to additional shear planes that facilitate sliding at asperity contacts. Under dry sliding at 0.1 m s⁻¹ and 20 °C, the friction coefficient remained within the 0.18-0.22 range, while wear decreased by approximately a factor of 3 relative to that of virgin PTFE (Fig. 35).

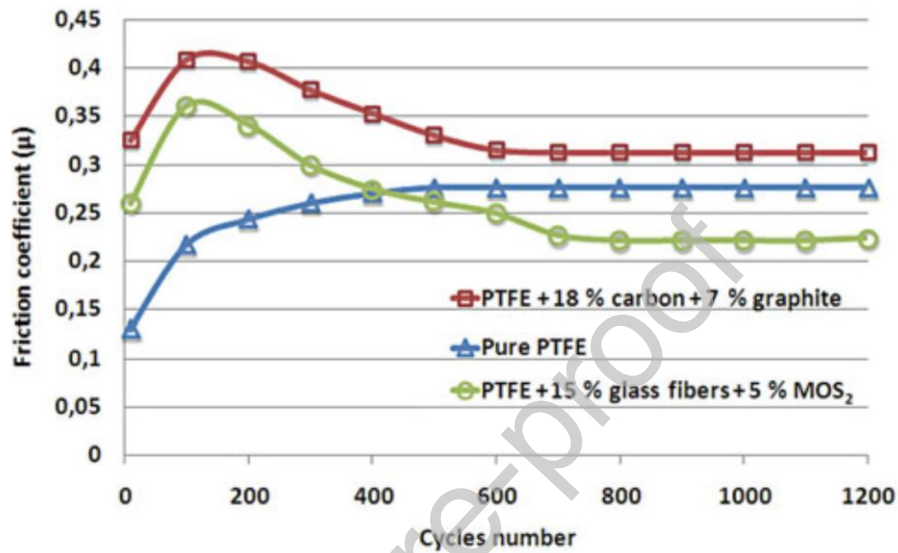


Fig. 35 : Variation of friction coefficient with cycle number for pure PTFE and PTFE composites (reprinted with permission from Taylor & Francis [113]).

Vasilev et al. [169] extended this concept to multiscale systems incorporating carbon fibers, basalt microfibers, and ultrafine PTFE powders. These composites achieved friction coefficients of 0.08-0.10 and exhibited wear rates up to one order of magnitude lower than those of conventional PTFE-CF materials. The improved performance was attributed to the formation of a hierarchical tribofilm in which the large fibers act as a mechanical scaffold. At the same time, the ultrafine PTFE phase fills interstitial gaps, promoting more uniform load transfer. Similar synergistic effects have been reported for other fiber/lamellar combinations [144,166,170].

Hybridization further enables tailoring of thermal behavior. The combination of conductive fillers such as CF, graphite, or bronze with harder ceramic particles (e.g., SiO₂, Al₂O₃) can help to distribute frictional heat more uniformly and reduce localized softening or melting in the near-surface region. Such thermal stabilization has been associated with smoother friction traces and extended steady state sliding regimes in several composite systems [170] (Fig. 36).

In summary, hybrid and multiscale composites illustrate the versatility of PTFE-based systems: by integrating reinforcement, lubrication, and thermal management within a single microstructure, these formulations achieve tribological stability levels unattainable with single-filler materials.

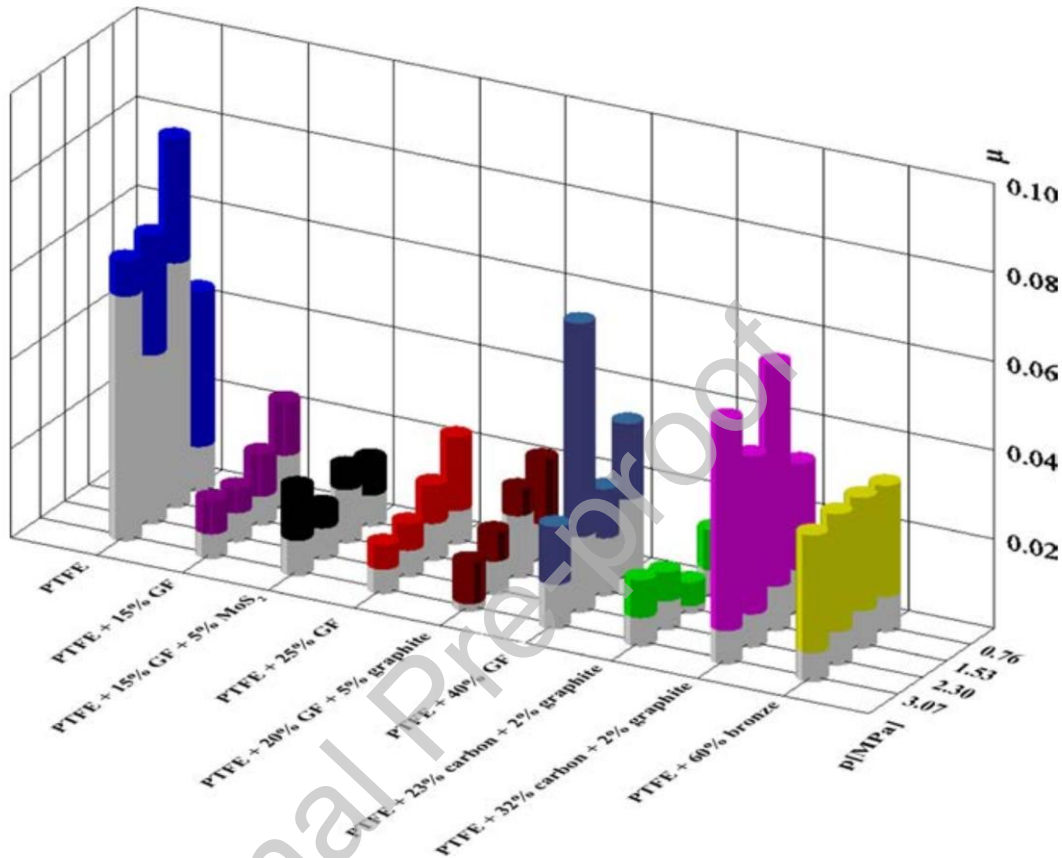


Fig. 36 : Friction coefficient under water lubrication for pure PTFE and various PTFE composites (reprinted with permission from Emerald Publishing [170]).

6.3.6. Radiation-modified and self-reinforced PTFE

An alternative strategy, independent of fillers, is based on radiation processing, including γ -rays, electron beams, and proton irradiation. Irradiation offers a molecular-level strategy to enhance PTFE's tribological behavior without altering its intrinsic low-shear surface chemistry. Controlled irradiation generates radicals, induces local crosslinking, and modifies lamellar organization, thereby improving the cohesion of the transfer film and the resistance of near-surface regions to shear-induced damage [117,171,172].

Tang et al. [173] demonstrated that γ -irradiation leads to partial crosslinking and densification of the PTFE microstructure. Under dry sliding, moderately irradiated samples exhibited a substantial reduction in wear, accompanied by a small increase in friction. However, at high doses, excessive crosslinking and chain scission led to embrittlement and microcracking, underscoring the need to fine-tune irradiation levels to avoid over-modification (Fig. 37).

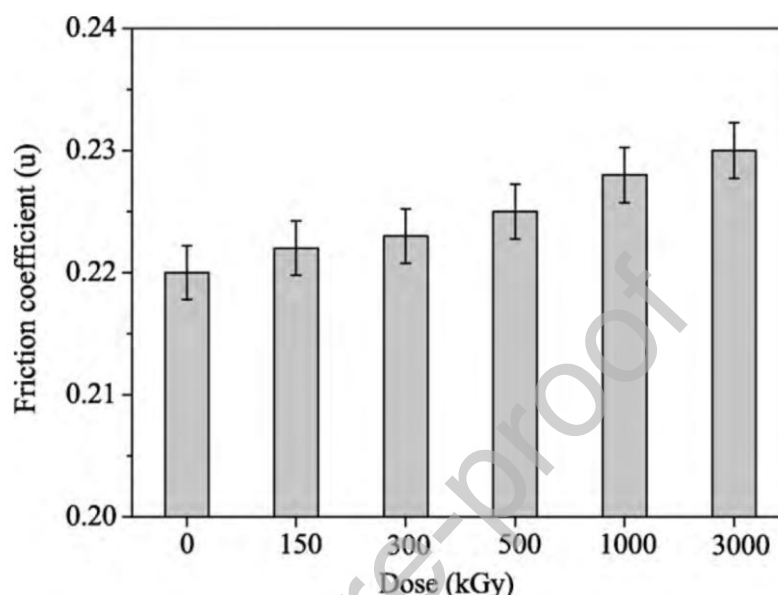


Fig. 37 : Effect of electron beam irradiation dose on average friction coefficient of PTFE samples (reprinted with permission from ELSEVIER [173]).

Chai et al. [171] refined this understanding by identifying an optimal γ -dose near 20 kGy. At this intermediate level, the friction coefficient remained low (about 0.08), while the specific wear rate decreased by approximately a factor of five relative to the pristine polymer. XPS and Raman analyses revealed the formation of CF_2 and CF-CF_x fragments, indicating mild defluorination but no extensive degradation of the helical backbone. These authors attributed the improved tribological stability to the development of a nano-crosslinked lamellar network that resists delamination during cyclic shear.

Proton irradiation induces a different modification pathway. Liu et al. [164] reported that proton-treated PTFE develops a carbon-enriched, partially graphitized surface layer, which increases hardness and reduces susceptibility to subsurface plastic flow. This densified interfacial zone improves wear resistance while maintaining friction below 0.1. Spectroscopic evidence confirmed both a decrease in fluorine content and the formation of carbon-rich domains, consistent with the enhanced compaction and mechanical robustness (Fig. 38).

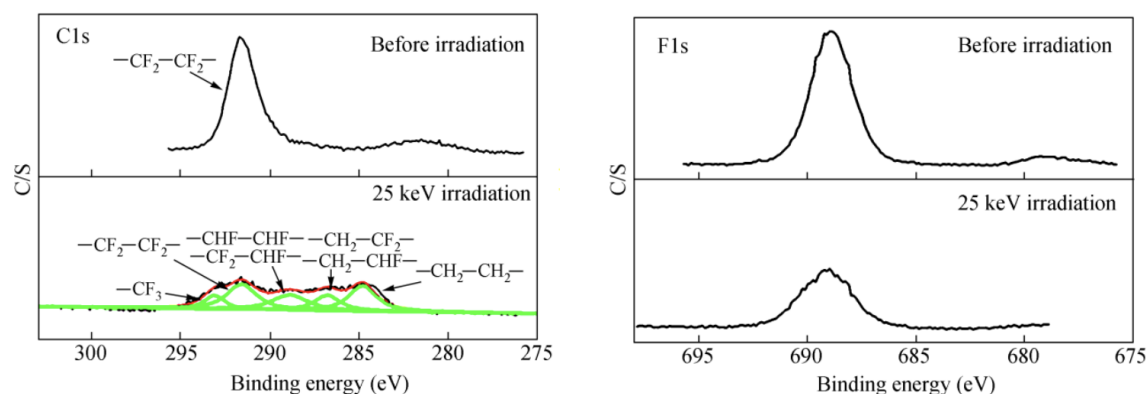


Fig. 38 : C1s and F1s XPS spectra of PTFE before and after proton irradiation (reprinted with permission from Springer Nature [164]).

A complementary approach to molecular modification was proposed by Wang et al. [174], who developed self-reinforced PTFE (SR-PTFE) by incorporating a small fraction (<8 wt.%) of pre-irradiated γ -ray-treated PTFE powders into the blend. The irradiated particles possessed residual radicals and partially crosslinked lamellae, enabling interdiffusion and chemical bonding with the virgin matrix during sliding. At an optimal loading of 4 wt.%, the composite exhibited a 43% reduction in wear and a 9% decrease in the friction coefficient compared with unmodified PTFE. SEM and XPS analyses revealed a dense and cohesive tribofilm enriched in compacted PTFE nanofragments and mixed Fe–O–F species when sliding on steel. At higher loadings (>8 wt.%), particle agglomeration led to embrittlement and reduced performance. This self-reinforcing strategy offers a unique route to enhance PTFE durability while maintaining chemical homogeneity, effectively bridging the gap between classical filler reinforcement and intrinsic molecular modification.

Together, these studies demonstrate that radiation-modified PTFE—whether *via* direct irradiation or self-reinforcing architectures—enhances tribological performance by improving the cohesion, chemical stability, and load-bearing capacity of the transfer film. By tuning the radical density, lamellar crosslinking, and interfacial chemistry, radiation-based approaches broaden the design space for PTFE tribomaterials beyond what is achievable with traditional fillers alone [117,164,171,172].

6.3.7. Coating-based and hybrid film systems

A fundamentally different approach uses coating-based designs to extend the benefits of PTFE lubrication to metallic or ceramic substrates. Such a method involves embedding the fluoropolymer in polymeric binders or hybrid organic–inorganic matrices. Unlike bulk

composites, where load support arises from the filler–matrix architecture, coating systems rely on controlled interfacial bonding, film integrity, and the progressive release of PTFE-rich debris to sustain a low-shear interface during sliding.

McCook et al. [175] demonstrated that incorporating expanded PTFE (ePTFE) into epoxy films produces a self-lubricating coating in which fibrillated PTFE acts as a reservoir of low-shear material. The improved performance results from enhanced crack resistance, improved film compaction, and PTFE debris' ability to maintain a continuous tribofilm on the counterface.

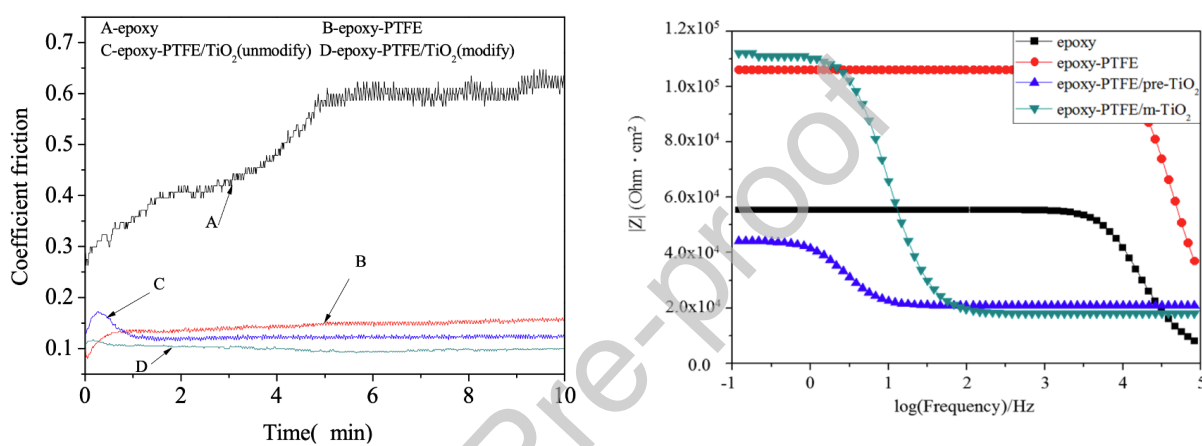


Fig. 39 : Friction coefficients and electrochemical impedance of the coatings in a Bode diagram (reprinted with permission from MDPI [176]).

Ying et al. (2020) [176] reported similar improvements in epoxy–PTFE composite coatings reinforced with silane-modified TiO₂ nanoparticles. The combined presence of PTFE and well-dispersed TiO₂ reduced the friction coefficient from $\mu \approx 0.22$ to 0.10 and significantly enhanced wear resistance, while also improving corrosion protection through coating densification and enhanced interfacial compatibility (Fig. 39).

For harder substrates such as cemented carbides, PTFE-based coatings provide an effective route to suppress direct hard–hard contact. Wang et al. [177] deposited PTFE coatings on YT15 cemented carbide using a PAI binder and spray processing, followed by thermal curing, and reported a marked reduction and stabilization of the friction coefficient under dry sliding against WC/Co balls: the uncoated carbide typically exhibited COF values around 0.35-0.45, whereas the PTFE-coated specimens remained around ca. 0.09-0.15 depending on load and speed. The improvement was attributed to the presence of a low-shear PTFE-rich surface layer and reduced

adhesive wear and plowing on the substrate. However, coating delamination/flaking remained the dominant wear mode at higher loads.

Together, these coating strategies illustrate how the intrinsic lubricity of PTFE can be integrated into rigid or conductive environments through appropriate binder selection and filler design. Composite PTFE-based films thus broaden the polymer's relevance for wear-resistant, corrosion-protective, and multifunctional surface-engineering applications.

6.3.8. Lubricated and superlubricated systems

Liquid lubrication and ionic-liquid-assisted interfaces provide an alternative pathway to reduce interfacial shear stresses in PTFE-based systems drastically. When combined with appropriate protic ionic liquids (PILs), PTFE composites can reach superlubricity—commonly defined as a friction coefficient below 0.01—by forming ordered, low-shear interfacial films that cannot be achieved under dry conditions. Zheng et al. [178] demonstrated robust macroscale superlubricity in a PTFE/steel tribopair lubricated with green protic ILs, achieving friction coefficients below 0.008 under specific laboratory conditions and strongly suppressed PTFE wear compared with conventional oils (e.g., polyalphaolefin PAO and polyethylene glycol PEG). Surface analyses supported the formation of a low-shear interfacial structure combining (i) an IL-derived interfacial layer (often rationalized as a dense Stern layer) and (ii) a tribochemical film on the steel counterface, consistent with a lubrication regime dominated by boundary film stability rather than solid transfer (Fig. 40).

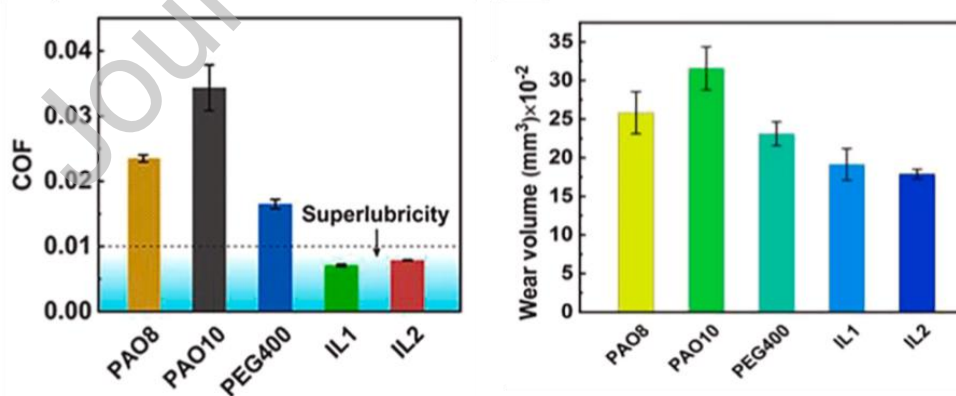


Fig. 40 : Left: Average friction coefficients of PTFE/stainless steel tribo-pair under lubrication of different lubricating oils (PAO8, PAO10, PEG4000) compared with ionic liquids (IL1 and IL2) under 5 N, 5 Hz. Right: Corresponding wear volumes vs these lubricating oils (reprinted with permission from ELSEVIER [178]).

Then, IL lubrication reveals that even trace amounts of reactive molecular species can reorganize the PTFE/metal interface, achieving friction levels several orders of magnitude

lower than those attainable with dry sliding. These findings open promising routes for engineering adaptive, low-shear, liquid-mediated interfaces in PTFE-based tribosystems.

6.3.9. Summary of performance ranges

Taken together, these strategies illustrate how mechanical reinforcement, chemical modification, and interfacial engineering can be combined to stabilize PTFE tribosystems. Their relative effectiveness and limitations are compared in the following section.

6.3.10. Comparative analysis and design guidelines

Across the wide range of PTFE-based systems described above, tribological performance can be rationalized in terms of three coupled mechanisms: (i) mechanical stabilization of the near-surface region, (ii) tribochemical anchoring and regeneration of the transfer film, and (iii) control of interfacial energy dissipation, either through viscoelastic damping or fluid-mediated lubrication. The best-performing materials are therefore not those with the lowest intrinsic friction, but those that maintain a cohesive, low-shear transfer layer over long sliding distances and under varying operating conditions. Because each stabilization mechanism becomes active at different length and time scales, PTFE systems tend to improve in a stepwise manner as additional reinforcement, chemical functionality, or lubrication pathways are introduced. Materials that resist transfer-film rupture, either by reinforcing the bulk, enhancing interfacial chemistry, or adding a fluid boundary layer, exhibit the most stable steady-state friction traces and the lowest wear rates [157,162,167,170].

6.3.11. Performance hierarchy

A comparison of the different approaches reveals a consistent performance hierarchy:

- *Virgin PTFE*: It exhibits excellent intrinsic lubricity ($\mu \approx 0.04\text{--}0.10$) but severe wear ($k \approx 10^{-4}\text{--}10^{-3} \text{ mm}^3\cdot\text{N}^{-1}\cdot\text{m}^{-1}$), reflecting the instability of its mechanically weak transfer film [152,159,179,180].
- *Fiber- and particulate-filled materials*: Adding glass or carbon fibers, bronze, or micro-sized ceramics reduces wear by one to two orders of magnitude, with a slightly higher friction coefficient (0.10–0.20) [156,157,167].

Table 6 : Representative friction and wear ranges and dominant stabilization mechanisms of PTFE-based systems

System type	Typical composition	Typical friction coefficient μ	Typical specific wear rate k ($\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$)	Dominant stabilizing mechanism	Key refs
Virgin PTFE	Neat polymer	0.04–0.10	10^{-4} – 10^{-3}	Low shear strength but weak cohesion; unstable transfer film	[150,151,156,157]
Fiber-filled PTFE	PTFE + GF or CF (≈ 15 – 25 wt%)	0.10–0.20	10^{-5} – 10^{-7}	Load sharing + subsurface stabilization; improved film compaction	[144,156,166,167]
Particulate / ceramic-filled PTFE	PTFE + Al_2O_3 / SiO_2 / TiO_2 (≈ 1 – 20 wt%)	0.10–0.18	10^{-7} – 10^{-9*}	Restricted plastic flow + tribochemical anchoring (metal fluorides)	[144,159,160,162,168]
Hybrid composites	GF + MoS_2 ; CF + Al_2O_3 / graphite	0.08–0.15	10^{-7} – 10^{-9}	Mechanical skeleton + boundary lubrication + film stabilization	[113,144,169,170]
Radiation-modified PTFE	γ /e-beam/proton irradiated PTFE	0.07–0.12	10^{-6} – 10^{-8}	Crosslinking/graphitization; improved cohesion of debris and film	[164,171,173]
Self-reinforced PTFE	PTFE + modified PTFE microphase (≈ 2 – 8 wt%)	≈ 0.08 – 0.11	10^{-6} – 10^{-7}	Cohesive “self” tribofilm via PTFE/PTFE interphase strengthening	[174]
Coating-based systems	Epoxy-PTFE, PTFE/ceramic coatings	0.12–0.18	10^{-7} – 10^{-9} (system-dependent)**	PTFE reservoirs + cohesive binder; added corrosion protection	[175–177]
Lubricated / IL-assisted contacts	PTFE composite + protic IL	0.006– 0.02	“below detection” / extremely low	Dual boundary layer + tribochemical fluid film	[178]

where GF, CF, PAI, and IL stand for glass fiber, carbon fiber, polyamide-imide, and ionic liquid, respectively.

* 10^{-7} – 10^{-9} is achievable in optimized nanofilled systems but remains strongly dependent on dispersion and operating conditions.

** For coatings, “specific wear rate” sometimes refers to wear depth per unit distance or per unit mass loss; comparisons must be made with caution.

- *Nanofilled and hybrid bulk composites:* Combining fibers, nanoparticles (SiO_2 , Al_2O_3), or lamellar solid lubricants (MoS_2 , graphite) yields low wear rates with μ comprised between 0.08 and 0.12 [144,168,169]. These systems derive their performance from synergistic mechanical and tribochemical stabilization of the transfer film.
- *Radiation-modified and self-reinforced PTFE:* γ -irradiation, electron-beam irradiation, or proton irradiation can emulate the performance of hybrid composites by creating crosslinked or graphitized surface layers. For optimized doses (i.e. tens to a few hundred kGy), wear can decrease by two to three orders of magnitude with minimal change in friction [164,171,173,174]. The advantages are the chemical homogeneity and the reduced filler/matrix mismatch.
- *Coating-based systems:* PTFE dispersed in epoxy or ceramic-rich matrices are characterized by μ values ranging from 0.12 to 0.18, while wear and corrosion resistance are improved.
- *Lubricated and ionic-liquid-mediated sliding:* With suitable protic ionic liquids, PTFE composites can enter the superlubricity regime with negligible wear, supported by the formation of a self-organized bilayer tribofilm [178]. But, system lifetime is then governed by lubricant stability rather than by the polymer.

Putting these classes together, a practical performance ranking for bulk materials can be constructed as follows: virgin PTFE < conventional fiber/microfilled composites < nanofilled and hybrid composites < radiation-modified or self-reinforced materials.

Coating-based and lubricated systems can surpass bulk materials in specific environments, but only when adhesion and lubricant chemistry are strictly controlled. The hierarchy thus reflects not only intrinsic material properties but also the robustness of the complete tribosystem.

Table 6 summarizes representative ranges of friction and wear, along with the dominant stabilization mechanisms for each class of PTFE-based system.

6.3.12. Dominant mechanistic factors

Across all PTFE-based systems (filled, hybrid, irradiated, coated, or lubricated), three mechanistic pillars consistently govern tribological performance. These principles repeatedly emerge from the literature and represent the common foundation underlying durable, low-friction, low-wear behavior.

- *Stabilization of subsurface deformation:* Durable PTFE systems consistently suppress subsurface shear localization, which otherwise triggers fibrillation, crack initiation, and transfer-film rupture. Mechanical stabilization can arise from fiber skeletons [156,157,167], ceramic inclusions that restrict plastic flow [162,168], or irradiation-induced crosslinking that reinforces lamellar cohesion [164,171,173]. Despite their different origins, these mechanisms converge toward the same outcome: creation of a coherent near-surface zone that limits cold-flow wear and maintains transfer-film attachment.
- *Control of interfacial thermal fields:* Transfer-film stability requires that flash temperatures remain within a limited operational window. High-conductivity fillers, such as CFs, graphite, or bronze [144,166,170], help to distribute frictional heat, preventing localized melting and thermal softening of the PTFE matrix. In contrast, systems dominated by insulating phases (glass fibers, SiO₂) exhibit greater sensitivity to thermal instabilities unless hybridized with conductive phases [169]. The most stable composites are those that homogenize the interfacial temperature field, thereby avoiding the oscillatory friction and episodic film rupture commonly observed in unfilled PTFE [157].
- *Regulation of tribochemical reactions:* Long-term wear resistance correlates strongly with the ability to balance interfacial reactivity. Beneficial tribochemical processes, such as the formation of metal fluorides (AlF₃, FeF₂) or oxide-enriched boundary layers, anchor the film and promote its renewal [151,162]. However, excessive reactivity can lead to embrittlement or oxidative depletion of the film. This balance can be tuned through the catalytic surfaces (e.g., alumina, titania), irradiation [171,173], or fluid-mediated boundary layers such as protic ILs [178], all of which improve transfer-film adhesion and continuity. The best-performing systems tend to exhibit self-regulated tribochemistry, neither too inert nor overly degradative.

Together, these comparative trends highlight that durable PTFE tribosystems are not defined by a single material parameter but by the coordinated tuning of mechanical stability, thermal

management, and interfacial chemistry. These insights provide the basis for the unified discussion presented in the following section.

6.4. General discussion and concluding remarks

The tribological response of PTFE emerges from a delicate interplay between molecular mobility, tribochemical activation, and mechanically driven film renewal. Across all PTFE-based systems, virgin, reinforced, irradiated, or hybrid, the persistence of a cohesive, low-shear transfer film is the central determinant of long-term friction and wear performance.

6.4.1. Unified mechanism

PTFE tribology can be rationalized as a self-regulating cycle in which mechanical shear generates debris. Then, tribochemical reactions anchor this debris to the counterface, and the resulting film protects the underlying polymer from further degradation.

6.4.2. Dominant parameters

Three main groups of parameters consistently govern the performance:

- Microstructure and mechanics.
- Thermal and tribochemical factors.
- Environmental.

Ultimately, long-term tribological stability in PTFE systems is achieved when interfacial renewal, mechanical integrity, and thermal dissipation evolve in a mutually compatible manner under sliding.

7. Surface, wettability, and adhesion

Objects manufactured from pure PTFE exhibit inherent hydrophobicity and low surface adhesiveness [181]. Hydrophobic polymers are generally identified by static water contact angles exceeding 90°. For PTFE, static contact angles measured on smooth, clean, sintered surfaces are typically in the 108-114° range [182], and values approaching ca. 118-120° have also been reported for unmodified PTFE [183]. Interestingly, according to Zhang et al. [183], stretching PTFE can drive the material surface into the superhydrophobic regime, with apparent contact angles up to ca. 165°, consistent with roughness-amplified wetting (Cassie–Baxter-type behavior). Hydrophobicity can also be enhanced through ion-plating treatments applied to PTFE coatings [184]. The origin of PTFE's hydrophobic behavior lies in the minimal

polarizability of its chains and the resulting low surface energy, which prevents strong specific interactions (e.g., hydrogen bonds) with water. This is consistent with the critical surface tension of PTFE, experimentally determined to be among the lowest reported for any solid polymer, in the range of ca. 18-20 mN/m [185]. However, PTFE wettability can be markedly altered in the presence of surfactants, which reduce the liquid–vapor surface tension and can adsorb at the solid–liquid interface, thereby lowering the effective interfacial tension. Various classes of surfactants –nonionic (e.g., Triton X100, Triton X165), cationic (cetyltrimethylammonium bromide, pinacyanol bromide), anionic (sodium dodecyl sulfate), and zwitterionic– have been studied, encompassing both hydrocarbon- and fluorocarbon-based molecules. The extent to which surfactant-containing aqueous solutions wet PTFE depends strongly on surfactant chemistry [186].

Because PTFE engages only weakly in van der Waals interactions, organisms such as ants and geckos, whose climbing abilities rely on these forces, exhibit limited adhesion on PTFE surfaces [187,188]. This same lack of intermolecular attraction also explains why conventional adhesives fail to bond to PTFE. Surface modification is possible, however, either by incorporating small quantities of comonomers or by applying various post-treatments to the material, including electron-beam irradiation [117,189], UV photon-exposure [190], glow-discharge processes [191,192], jet-plasma treatments [193], wet-chemical methods [194], and grafting techniques [195]. PTFE's surface properties are often reported to depend more strongly on surface conditions (cleanliness, roughness, oxidation/defluorination, and processing defects) than on molar mass or as-polymerized microstructure. In practice, surface-property measurements are almost always performed on sintered sheets or films, where defects introduced during shaping can dominate the results. Nevertheless, potential links between powder morphology (e.g., rod-like vs. spherical particles), dispersity, and the resulting surface/topography remain insufficiently studied, constituting a clear gap in the literature.

Although PTFE is often taken as the benchmark, its contact angle should be interpreted in the broader context of fluorinated polymers (FPs) to identify underlying structure–surface property relationships. Fig. 41 illustrates the wetting behavior of polar protic liquids on FP surfaces [196]. For fully FPs, the measured contact angles lie within experimental uncertainty ($\pm 2^\circ$), rendering them essentially indistinguishable. This convergence reflects the dominance of a CF_2 -rich surface layer with extremely low polarizability and negligible specific interaction capability.

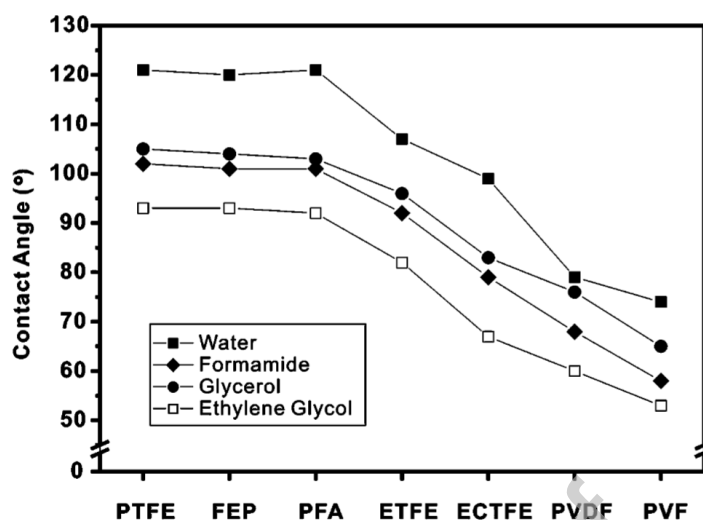


Fig. 41 : Advancing contact angles of various liquids on the surfaces of fluoropolymers. Polar protic liquids: water (filled squares), formamide (filled diamonds), glycerol (filled circles), and ethylene glycol (open squares) (reprinted with permission from ACS [196]).

In contrast, partially FPs exhibit progressively higher wettability as the surface chemistry departs from a fully fluorinated environment. Poly(vinylidene fluoride) (PVDF) and poly(vinyl fluoride) (PVF) exhibit the highest wettability within this class due to the presence of surface dipoles associated with C–H and C–F bond asymmetry, as well as acidic hydrogen atoms. These features enable multiple modes of interaction with contacting liquids, including dipole-dipole, dipole-induced dipole, and acid-base interactions (notably hydrogen bonding). Poly(ethylene-co-chlorotrifluoroethylene copolymer (ECTFE), which contains a substantial density of weak dipoles, displays intermediate wettability: higher than that of ETFE, whose dipoles are fewer and weaker, yet lower than those of PVDF and PVF [196].

Calleja et al. [197] further examined the evolution of ETFE surface properties upon fluorination. Hydrophobicity and lipophobicity were characterized using dynamic contact angle measurements with water and diiodomethane via advancing–receding protocols (Table 7). Fluorinated ETFE samples, particularly ETFE-f150 (fluorinated at 150 °C), and to a lesser extent ETFE-f95 (fluorinated at 95 °C), exhibited higher advancing and receding angles. This trend indicates a reduction in surface free energy due to enrichment of fluorinated groups at the outermost surface. The simultaneous increase in apparent contact angle hysteresis is consistent with nanoscale roughness amplification effects, where fluorination modifies both chemistry and topography.

Table 7 : Water and Diiodomethane Dynamic Contact Angle Values for ETFE (virgin), ETFE-f95 (fluorinated), ETFE-f150 (fluorinated), and PTFE (reprinted with permission from WILEY [197]).

	Water			ICH ₂ I		
	θ_a	θ_r	H	θ_a	θ_r	H
ETFE-f95	99.2 ± 4.0	68.3 ± 4.2	31.0	73.3 ± 10.7	54.5 ± 6.9	18.8
ETFE-f150	111.5 ± 8.9	90.8 ± 3.2	20.7	92.8 ± 5.0	79.0 ± 6.1	13.7
ETFE	96.8 ± 8.0	60.3 ± 8.3	36.5	66.7 ± 2.5	52.2 ± 11.2	14.6
PTFE	81.4 ± 3.3	50.5 ± 3.3	30.9	69.4 ± 7.0	53.7 ± 6.4	15.7

A more comprehensive understanding of PTFE surface-liquid interactions can be obtained by complementing contact angle data with an analysis based on Hansen Solubility Parameters (HSP) [198]. HSP describes intermolecular interactions through three contributions: dispersive (δ_D), polar (δ_P), and hydrogen-bonding (δ_H), which together define a three-dimensional Hansen space. While initially developed to rationalize bulk solubility behavior, HSP can also provide a practical semi-quantitative framework for interpreting trends in interfacial affinity. HSP values are typically obtained experimentally from solubility or swelling tests, or estimated using group-contribution methods [199]. Fig. 42 positions PTFE within Hansen space alongside reference liquids, where higher contact angles indicate lower affinity. This Figure combines a pseudo-3D representation with a projected color map, in which contact angles are color-coded as low (gray to purple: 0-30°), intermediate (blue to green: 30-90°), and high (yellow to red: 90-120°). Because PTFE is not soluble in conventional solvents (section 2), its Hansen parameters are commonly inferred from swelling-based approaches rather than accurate dissolution tests. For PTFE (with $\delta_D=16.20$, $\delta_P=1.80$, and $\delta_H=3.40$ (J/cm³)^{1/2}, grade L80 CR) [199], the location in Hansen space is clearly separated from polar and hydrogen-bonding liquids such as water, formamide, and ethylene glycol, consistent with its chemical inertness and weak specific interactions.

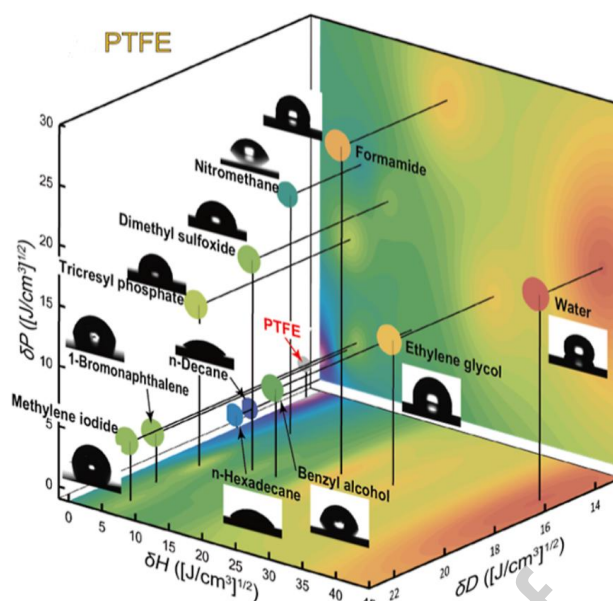


Fig. 42 : Pseudo 3D plot of probe liquids in HSP space with Cartesian coordinates (δ_D , δ_P , and δ_H axes), where contact angles on polymer substrate (images shown in insets) of PTFE are color-coded (wetttable: gray-purple, intermediate: blue-green, repelling: yellow-red). The projection of contact angles to the δ_H - δ_D and δ_H - δ_P planes is drawn in the same color as that in the pseudo 3D plots; the data-deficient region was interpolated using graphing software. The surface HSPs of polymers determined via linear regression using the least-squares method between experimental contact angles and estimated ones (for various δ_D , δ_P , and δ_H values) are plotted as those for ideally wettable liquids with a contact angle of 0° (in gray) (reprinted with permission from ACS [198]).

Experimental contact angles were measured using the sessile drop method on polymer films or plates corresponding to materials for which bulk HSP have been determined. It is essential to distinguish bulk HSP, which describe cohesive energy density within the material volume from effective surface HSP, which reflect only the outermost molecular layers probed in wetting experiments. Surface HSP values were obtained by fitting contact angle data using least-squares regression, adjusting the δ_D , δ_P , and δ_H values to define an “ideally wetting” condition (i.e., a contact angle of 0° as shown in gray) (Fig. 42). Although this approach involves approximations, it provides a practical route to map surface-affinity trends within the same Hansen framework used for bulk materials, thereby enabling a unified interpretation of PTFE’s low wettability in terms of both cohesive and interfacial energetics.

By correlating contact angle measurements of probe liquids on PTFE with their Hansen parameters, this representation provides a structured way to interpret PTFE’s surface affinity, within the same energetic framework used for bulk interactions. Rather than describing actual solubility behavior, the approach provides a relative scale of interfacial compatibility, highlighting PTFE’s position at the extreme low-polarity and low-hydrogen-bonding edge of Hansen space.

To extend this framework to interfacial phenomena, several formulations have been proposed to estimate liquid and solid surface energies, as well as their interfacial energy, from surface energy components. Among these, the geometric-mean approach of Owens and Wendt [200] proposed the surface free energy as the sum of dispersive and polar contributions and remains widely used due to its simplicity, while more recent treatments extend this logic to the three-component HSP framework described above. Contact angles predicted from such relations, using bulk HSPs derived from solubility or swelling data, have been compared with experimentally measured values obtained using sessile-drop methods. The generally good correlations observed across diverse polymer–liquid systems suggest that, despite the conceptual gap between bulk cohesive parameters and surface properties, HSP-based approaches can serve as a useful semi-empirical tool for rationalizing trends in wettability and interfacial energy. Nevertheless, these models do not explicitly account for surface reconstruction, chemical heterogeneity, or roughness effects, which can significantly influence contact-angle measurements. As such, HSP-based predictions should be regarded as a complementary interpretative framework rather than a substitute for direct surface characterization.

8. Electrical and dielectric properties of PTFE

8.1. Position of PTFE among polymer dielectrics

From an electrical standpoint, PTFE represents an extreme case among polymer dielectrics (Fig. 43). Unlike most organic polymers, whose dielectric behavior results from a combination of dipolar orientation, segmental mobility, and free-volume fluctuations, PTFE exhibits an almost purely electronic polarization mechanism. Its fully fluorinated $-\text{CF}_2-$ backbone suppresses permanent dipoles and rotational degrees of freedom, leading to a dielectric response that remains essentially invariant with frequency and temperature [201,202].

Consequently, PTFE exhibits a remarkably stable relative permittivity (ϵ_r) between 2.0 and 2.1 with extremely low dielectric losses ($\tan \delta < 10^{-4}$ over a broad frequency range). Its dielectric breakdown strength E_{bd} typically ranges from 40 to 60 $\text{kV}\cdot\text{mm}^{-1}$ for bulk specimens with thicknesses of 0.5–1 mm ([203,204]).

When normalized to permittivity, the normalized dielectric strength (E_{bd} / ϵ_r) reaches ca. 25 $\text{kV}\cdot\text{mm}^{-1}$ per unit ϵ_r , significantly higher than those of common insulating polymers such as PE

($\approx 12 \text{ kV}\cdot\text{mm}^{-1}$) or polyimide ($\approx 8 \text{ kV}\cdot\text{mm}^{-1}$). This combination of low polarizability and high breakdown strength places PTFE among the most efficient polymeric insulating materials.

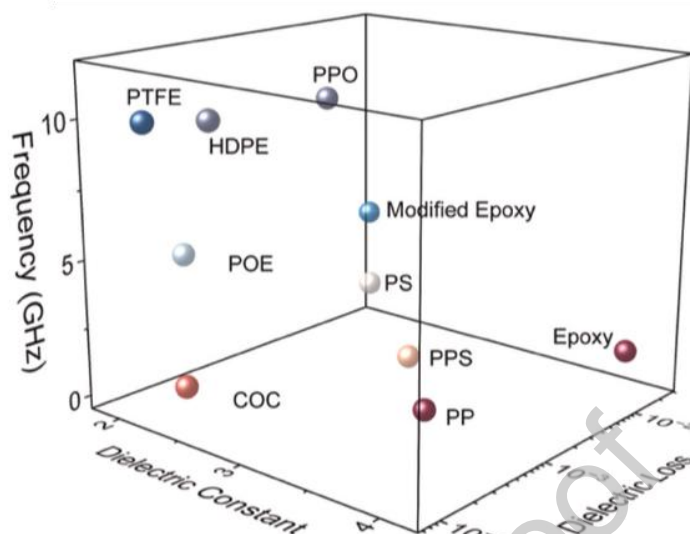


Fig. 43 : Comparative dielectric properties of different polymers (reprinted with permission from ELSEVIER [205]).

Compared with other polymer families, the contrast is pronounced. PE and polypropylene (PP) have slightly higher permittivity ($\epsilon_r \approx 2.3\text{--}2.4$) but stronger temperature dependence due to increased chain mobility above 80°C . Polymers containing polar functional groups, such as polyimides or polyetherimides (PEI), exhibit higher permittivity ($\epsilon_r \approx 3.2\text{--}3.5$) and significantly higher dielectric losses resulting from dipolar relaxation processes [202,205,206].

Among fluoropolymers, the dielectric behavior varies widely. PVDF exhibits ferroelectric polarization associated with its β phase, leading to ϵ_r values up to 12–13 and a pronounced frequency dispersion [207]. By contrast, melt-processable fluoropolymers such as FEP and PFA retain moderate permittivity values ($\epsilon_r \approx 2.1\text{--}2.3$) but generally show slightly higher dielectric losses due to reduced crystallinity and structural defects.

The molecular origin of the exceptional dielectric stability of PTFE lies in the highly symmetric helical conformation of its chain and the high bond energy of the C–F bond (ca. $485 \text{ kJ}\cdot\text{mol}^{-1}$), which suppresses orientational polarization and limits molecular mobility. Combined with its high crystallinity ($>90\%$) and density (ca. $2.2 \text{ g}\cdot\text{cm}^{-3}$), this structure yields a nearly ideal non-polar dielectric medium.

8.2. Intrinsic dielectric response of bulk PTFE

The dielectric response of bulk PTFE has been investigated for more than seven decades, with a remarkable consistency across studies despite variations in processing route, crystallinity, and molar mass [118,201,205,208].

Early measurements established a relative permittivity ϵ_r close to 2.05 and dielectric losses below 2×10^{-4} over the frequency range 50 Hz–3 MHz [201,209]. Later, broadband dielectric spectroscopy extending to gigahertz frequencies confirmed the absence of dipolar or space-charge relaxation within the accessible measurement window [210].

Minor variations reported in the literature (ϵ_r ranging from 2.00 to 2.15) are mainly attributed to microstructural heterogeneity, such as porosity or incomplete sintering. Samples containing residual voids may exhibit slightly higher apparent permittivities due to local electric-field distortions [210] (Fig. 44). Conversely, highly dense, crystalline PTFE consistently exhibits $\epsilon_r \approx 2.05$ [201,202].

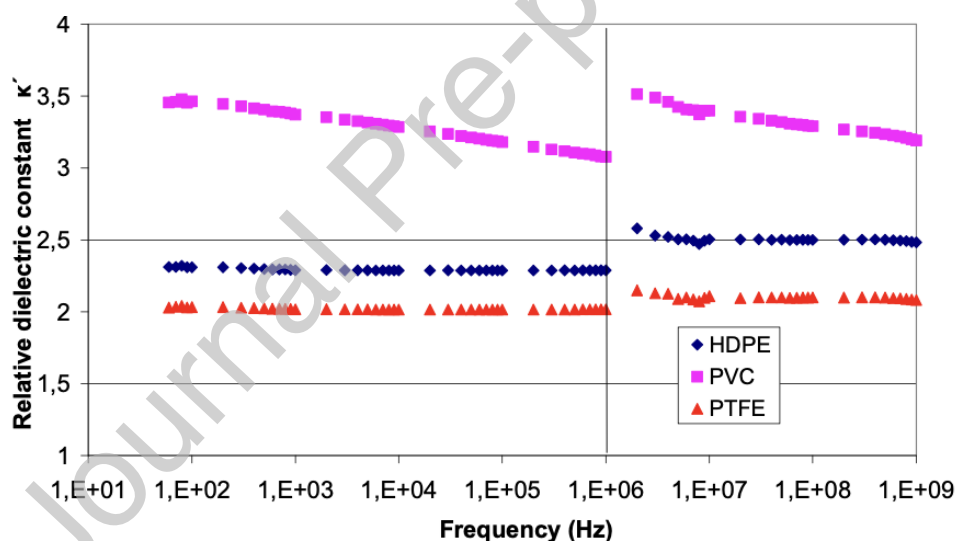


Fig. 44 : Relative dielectric constant results vs. frequency of PTFE and compared to HDPE and PVC. The vertical line at 1 MHz marks the boundary between the two measurement setups (reprinted with permission from IEEE [210]).

The absence of dielectric dispersion over a wide frequency range reflects the lack of orientational polarization. In PTFE, the only available polarization mechanisms are electronic ($\approx 10^{15}$ Hz) and vibrational ($\approx 10^{13}$ Hz), both occurring well beyond the frequency range typically explored in dielectric spectroscopy.

Temperature has only a minor influence on the dielectric response. Measurements between $-100\text{ }^{\circ}\text{C}$ and $+250\text{ }^{\circ}\text{C}$ show that ϵ_r varies by less than 2 %, while $\tan \delta$ remains below 10^{-4} until temperatures approaching the melting point [206,208].

This stability reflects the predominance of electronic polarization, described by:

$$P_e = \epsilon_0 (\epsilon_r - 1) E \quad (\text{eq 4})$$

where P_e is the electronic polarization density ($\text{C}\cdot\text{m}^{-2}$), ϵ_0 the permittivity of free space ($8.85 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$), ϵ_r the relative permittivity of the material, and E the applied electric field [202,206].

8.3. Breakdown strength and electrical aging

The dielectric breakdown strength, E_{bd} , of PTFE has been extensively investigated because it reflects both the intrinsic electronic stability of the polymer and the influence of microstructural defects. For dense bulk specimens (thickness $0.5\text{--}1.0\text{ mm}$), typical values range between 40 and $60\text{ kV}\cdot\text{mm}^{-1}$ [203,204]. However, reported values vary significantly across the literature, from about $20\text{ kV}\cdot\text{mm}^{-1}$ in porous or heterogeneous samples to more than $200\text{ kV}\cdot\text{mm}^{-1}$ in thin films ($<50\text{ }\mu\text{m}$) [118,211,212].

These variations highlight the composite nature of dielectric breakdown, which depends not only on the intrinsic electronic properties but also on the defect density, surface morphology, and testing conditions.

8.3.1. Thickness dependence and measurement dispersion.

Breakdown measurements performed according to IEC 60243 reveal a weak inverse dependence on sample thickness, approximately following a power-law dependence:

$$E_{bd} \propto t^{-0.15} \quad (\text{eq 5})$$

where t denotes the sample thickness [206].

This trend reflects the statistical probability of defect initiation rather than a fundamental material limit: thicker samples contain a higher density of structural heterogeneities, such as voids, inclusions, or surface defects, that can concentrate the electric field.

Consequently, direct comparison of breakdown values across studies without reporting sample thickness or measurement geometry often leads to misleading conclusions. Thin PTFE films

(20–50 μm) commonly reach 150–220 $\text{kV}\cdot\text{mm}^{-1}$, whereas sintered blocks of 1–2 mm thickness rarely exceed 50 $\text{kV}\cdot\text{mm}^{-1}$, even when produced from identical polymer grades [203,204,212] (Fig. 45).

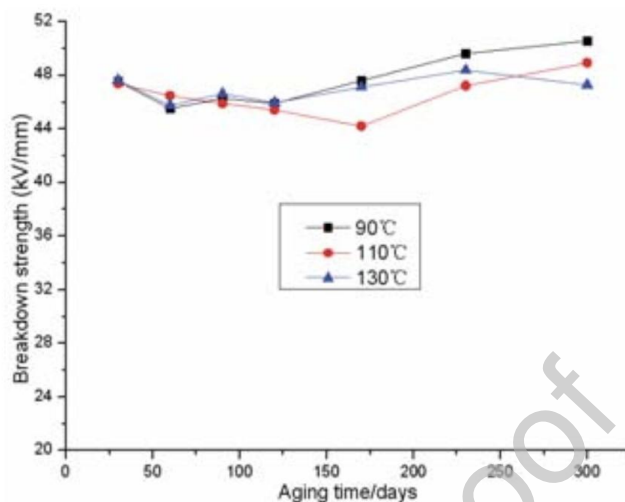


Fig. 45 : Breakdown field strength of PTFE films (thickness = 0.5 mm) versus aging time under three aging temperatures (reprinted from IEEE [204]).

Experimental conditions also influence the measured values. Flat electrodes generally produce lower breakdown fields than spherical electrodes due to edge effects, whereas air gaps at the electrode–polymer interface can initiate premature discharge. When measurements are performed in insulating oil or under vacuum, breakdown strengths may increase by 10–20%, illustrating the sensitivity of PTFE to local-field amplification [118].

8.3.2. *Electronic versus thermal breakdown mechanisms.*

Breakdown mechanisms in PTFE differ significantly from those observed in hydrocarbon polymers. Because of its large electronic band gap ($\approx 8\text{--}9$ eV) and low charge-carrier mobility, pure electronic avalanche breakdown is relatively unlikely under normal conditions. Instead, failure often follows a thermo-electronic mechanism, in which localized Joule heating at defect sites initiates partial bond scission within the polymer backbone [204,212].

Decomposition of C–F bonds produces volatile fluorocarbon fragments, such as CF_2 and CF_3 radicals, which facilitate the formation of a conductive channel. Post-mortem analyses typically reveal localized carbonization cones confined to regions of 10–50 μm around the discharge site, without an extensive macroscopic cracking [203].

The high crystallinity of PTFE (>90 %) further restricts electron transport. Charge carriers remain largely confined to amorphous interlamellar regions, where conduction processes are thermally activated rather than electronic in nature [118,202,206].

At extremely high electric fields ($>150 \text{ kV}\cdot\text{mm}^{-1}$), impact ionization can occur, leading to a rapid increase in current and thermal runaway within nanoseconds [118,206]. However, such conditions are rarely encountered in practical applications due to PTFE's low permittivity and moderate thermal conductivity (ca. $0.25 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), which limit the local energy density.

Generally, dielectric breakdown in PTFE should therefore be regarded not as a single intrinsic constant but as a statistically distributed property governed by defect population, microstructure, sample thickness, and testing protocol [118,203,212].

8.3.3. Aging mechanisms: corona and humidity effects

Long-term electrical endurance is one of the distinguishing features of PTFE relative to most engineering polymers. Under prolonged alternating current stress or corona discharge, degradation generally remains superficial. For example, Wei et al. [204] reported that after 300 days of exposure at 130°C under an electric field of $20 \text{ kV}\cdot\text{mm}^{-1}$, the breakdown strength decreased by less than 10 %. In comparison, epoxy insulation systems under identical conditions induced reductions exceeding 60 %.

Similarly, repetitive arc discharges produce only a thin carbonized surface layer, while the bulk polymer retains most of its insulating properties [212]. This behavior reflects PTFE's chemical inertness and low surface energy, which limit charge accumulation and inhibit the propagation of electrical treeing.

Moisture has a negligible influence on PTFE dielectric properties. Owing to its extremely low surface energy (ca. $18 \text{ mJ}\cdot\text{m}^{-2}$) and strong hydrophobicity (water contact angle $\approx 115\text{-}120^\circ$), water uptake remains below 0.01 wt.%. Consequently, dielectric losses remain largely unchanged even under high-humidity conditions, unlike in polar polymers such as polyimides or polyamides [231].

8.4. Temperature and radiation effects on dielectric stability

8.4.1. Thermal dependence and phase transitions.

The outstanding dielectric performance of PTFE is maintained over an exceptionally wide temperature range, from cryogenic conditions to temperatures near its melting point (ca. 327 °C). Unlike most organic polymers, whose dielectric properties are strongly influenced by dipolar relaxation or thermally activated conduction, PTFE exhibits only minor variations in permittivity and dielectric losses with temperature. Dielectric measurements performed between -200 °C and +300 °C show that the real permittivity, ϵ' , varies by less than 2 %, while the loss tangent remains below 10^{-4} over most of this range [201,206,208,209]. This remarkable stability arises from the absence of permanent dipoles and the predominance of electronic polarization in PTFE.

A weak dielectric anomaly is nevertheless observed near 19 °C, corresponding to the well-known crystalline phase transition from phase II to phase IV (see section 2). During this transition, the helical pitch of the $-\text{CF}_2-$ chain slightly changes, producing only a small increase in permittivity (<1 %) while dielectric losses remain essentially unaffected [120,201,208].

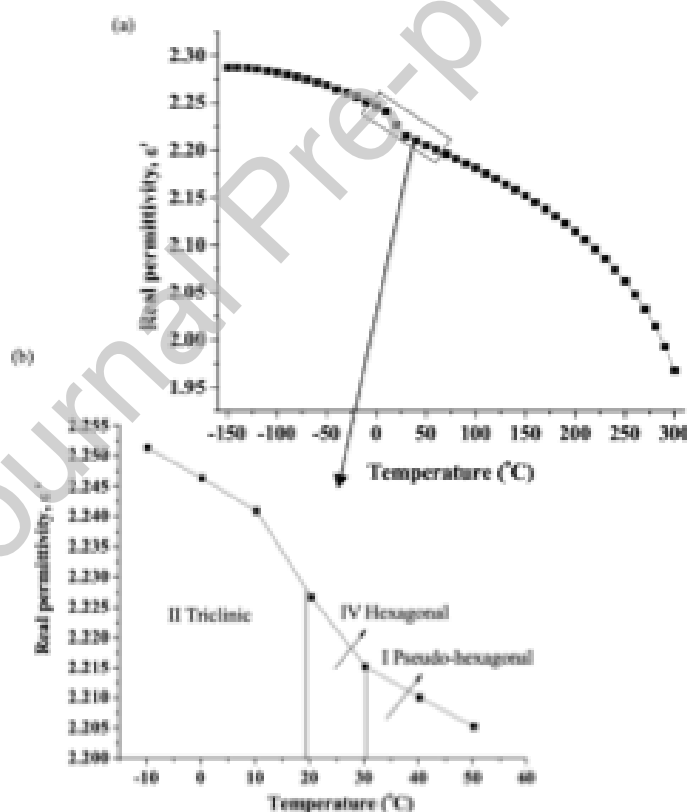


Fig. 46 : Real permittivity of PTFE as a function of temperature at 1.15 kHz. (a): -150 to 300 °C; (b): -10 to 50 °C (reprinted with permission from IEEE [208]).

At higher temperatures (100–250 °C), PTFE retains extremely low dielectric losses despite structural rearrangements such as lamellar thickening or limited chain mobility detected by

DSC and X-ray diffraction [101,110]. Only when temperatures approach the melting point does the electrical conduction begin to increase significantly, leading to a rapid rise in dielectric losses.

This thermal stability exceeds that of most polymer dielectrics. For example, PE and polyimide typically exhibit dielectric losses that increase by one to two orders of magnitude above 150–200 °C due to dipolar relaxation and thermally activated conduction processes.

8.4.2. Radiation-induced modifications.

The dielectric behavior of PTFE under ionizing radiation has been extensively studied in the context of nuclear and aerospace insulation [108,109,118]. Radiation exposure generates a combination of chain scission, crosslinking, and defluorination reactions that alter the polymer microstructure and local electronic density.

At moderate irradiation doses (10–100 kGy), chain scission predominates, particularly in amorphous regions [117]. The formation of radical species ($-\text{CF}_2\cdot$ and $-\text{CF}\cdot$) slightly increases permittivity and dielectric losses as localized polar groups or defects appear within the material. Under these conditions, ϵ_r typically increases from about 2.05 to approximately 2.15, while $\tan \delta$ may reach values close to 5×10^{-4} [108,109,118] (Fig. 47).

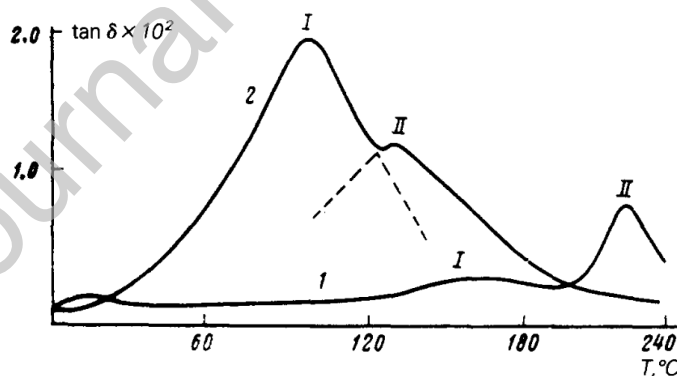


Fig. 47 : Plot of $\tan \delta$ vs temperature for irradiated PTFE at 300Hz. (1) γ -Irradiation in vacuum, dose 150 kGy; (2) γ -irradiation in air, dose 100 kGy (reprinted with permission from ELSEVIER [118]).

At higher doses (>500 kGy), crosslinking reactions compete with chain scission. Infrared and ESR analyses reveal the formation of $-\text{CF}_3$ end groups and carbon–carbon crosslinks, producing a denser but more defective crystalline texture [207,210] (Fig. 48). These structural changes generally lead to a moderate decrease in dielectric breakdown strength (20–30 %) due to the accumulation of defect sites that facilitate the charge injection.

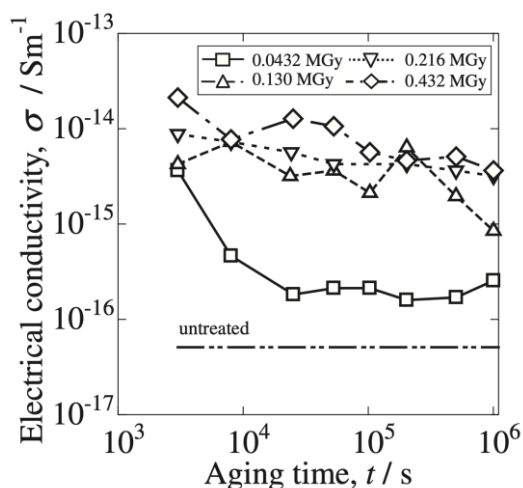


Fig. 48 : Effects of aging time on electrical conductivity of electron beam irradiated PTFE samples at various doses (reprinted with permission from the Japan Institute of Metals [207]).

Interestingly, part of the radiation-induced damage can be reversed by thermal annealing at temperatures above 300 °C. Under these conditions, volatile fluorocarbon fragments are removed, and recrystallization of partially degraded regions can occur, restoring part of the initial dielectric properties [118,204].

8.4.3. Coupled thermo-radiative degradation mechanisms

In environments such as nuclear reactors or space systems, PTFE may be exposed to simultaneous elevated temperatures and ionizing radiation. Under such combined conditions, radical mobility increases, and chain scission processes can accelerate. Studies report moderate increases in dielectric losses ($\tan \delta \approx 10^{-3}$) and permittivity values approaching $\epsilon_r \approx 2.3$ after very high radiation doses (ca. 10^6 Gy), although these values remain lower than those observed in most hydrocarbon polymers under similar conditions.

The dominant degradation pathway involves localized depolymerization of the PTFE chain. Polymer-bound $-\text{CF}_2\cdot$ radicals that undergo β -scission to form highly reactive difluorocarbene ($:\text{CF}_2$), which rapidly recombines to produce volatile TFE molecules, which diffuse out of the matrix [117].

Despite these structural modifications, PTFE generally retains its insulating character even under severe irradiation. The limited impact on dielectric properties reflects the fundamental electronic origin of polarization in PTFE, which is relatively insensitive to moderate changes in molecular topology.

8.5. Composite and filled PTFE systems

Although pristine PTFE is one of the most stable dielectric materials known, its relatively low permittivity ($\epsilon_r \approx 2.05$) and poor thermal conductivity (ca. $0.25 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) restrict its use in certain electronic and microwave devices. Consequently, numerous studies have led to the development of PTFE-based composites incorporating ceramic or carbon fillers in order to tailor their dielectric and thermal properties while maintaining their insulating performance. In such heterogeneous systems, the dielectric response is governed not only by the intrinsic permittivity of the filler or its loading fraction but also by the morphology of the composite and the quality of the filler-matrix interface.

Because PTFE is chemically inert and non-polar, untreated fillers generally interact weakly with the polymer matrix, which may lead to interfacial voids and local electric-field amplification. These heterogeneities promote interfacial charge accumulation, often described as Maxwell–Wagner–Sillars polarization, thereby increasing dielectric losses.

For this reason, the design of PTFE composites relies heavily on interface engineering. Surface functionalization of fillers using silane coupling agents, titanates, or bio-inspired coatings such as polydopamine has proven particularly effective in improving dispersion and interfacial adhesion [213–216]. When interfacial compatibility is improved, moderate increases in permittivity can be achieved while maintaining low dielectric losses.

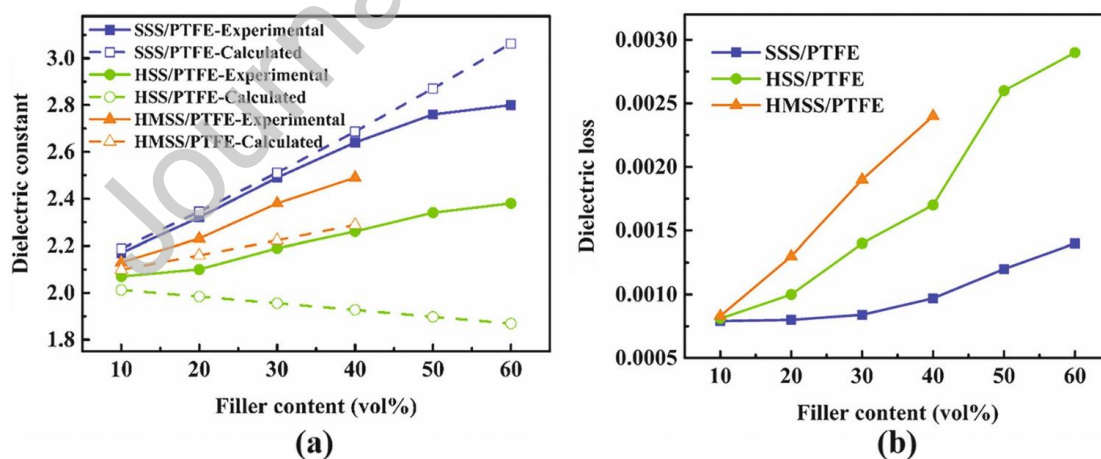


Fig. 49 : Dielectric properties variations of SiO₂/PTFE composites with different SiO₂-based filler contents: a) dielectric constants, b) dielectric losses, where HSS, HMSS, and SSS stand for hollow silica spheres, hollow mesoporous silica spheres, and solid silica spheres, respectively (reprinted with permission from Springer Nature [215]).

8.5.1. Oxide and silicate fillers

Silica-based composites are among the most extensively investigated PTFE dielectric systems because they offer a favorable compromise between permittivity enhancement and low dielectric losses. For example, Chen et al. [82] reported that PTFE–SiO₂ composites containing nanoscale silica increased ϵ_r from approximately 2.1 to about 2.35 while maintaining dielectric losses near 6×10^{-4} at microwave frequencies.

Surface functionalization of silica particles further improves composite performance by reducing interfacial porosity and promoting homogeneous dispersion. Various treatments using silane coupling agents or related modifiers have been reported to yield ϵ_r values of 2.5–2.6, with $\tan \delta$ typically below 10^{-3} (Fig. 49) [213,215,217,218].

More recently, fluorinated interfacial layers have been proposed to enhance compatibility between PTFE and oxide fillers. Jin et al. [219] demonstrated that surface fluorination of SiO₂ particles using pentafluorostyrene significantly reduces interfacial porosity and lowers dielectric losses to approximately 1.5×10^{-3} at 40 GHz while maintaining $\epsilon_r \approx 2.38$ (Fig. 50).

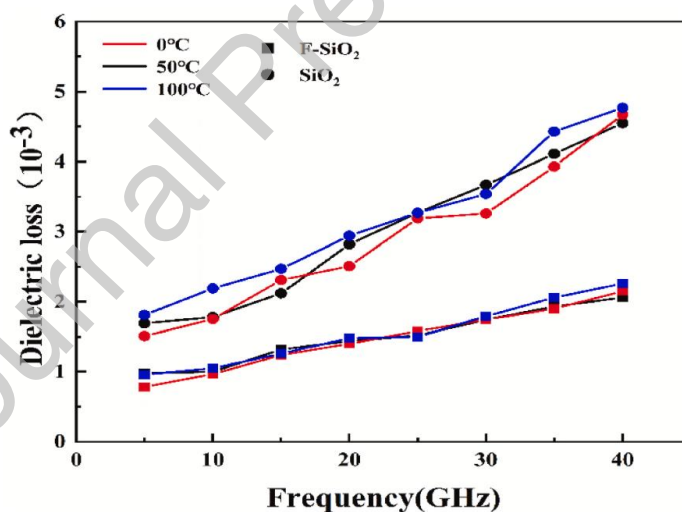


Fig. 50 : Dielectric properties of F–SiO₂/PTFE composite with 5 wt.% pentafluorostyrene (PFS) varying with temperature (reprinted with permission from ELSEVIER [219]).

8.5.2. Thermally conductive nitrides

In recent years, electrically insulating but thermally conductive fillers such as boron nitride (BN) and aluminum nitride (AlN) have attracted considerable attention [86]. These materials combine moderate dielectric constants ($\epsilon_r \approx 4$ –5) with very high thermal conductivity.

Hybrid PTFE composites containing BN and AlN can increase thermal conductivity up to $1.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, nearly six times higher than that of neat PTFE, while maintaining relatively low dielectric losses ($\tan \delta \approx 8 \times 10^{-4}$) and breakdown strengths above $40 \text{ kV}\cdot\text{mm}^{-1}$ [86,220].

The success of these systems lies in their ability to enhance phonon transport without introducing electrically conductive pathways.

8.5.3. *Conductive fillers*

Conductive nanofillers such as carbon nanotubes (CNTs), graphene, or metallic nanoparticles can significantly increase permittivity even at low loadings. However, these materials rapidly approach the percolation threshold.

For example, CNT contents above ca. 1 vol% typically produce dramatic increases in dielectric losses and a sharp decrease in breakdown strength due to the formation of conductive networks [221]. Surface-modified CNTs coated with silica or polydopamine can partially suppress this effect, allowing moderate permittivity enhancement ($\epsilon_r \approx 3.2$) while keeping $\tan \delta$ close to 10^{-3} [216].

Nevertheless, the trade-off between permittivity enhancement and dielectric stability remains a fundamental limitation of conductive fillers.

8.5.4. *Role of the interphase*

In PTFE composites, the interfacial region between filler and polymer matrix plays a decisive role in determining the dielectric behavior. Because PTFE lacks reactive functional groups, a strong interfacial bonding must be engineered through the surface treatments such as plasma activation, sodium–naphthalene etching, or coupling agents.

Experimental and modeling studies suggest that an interphase layer with a thickness of 5–20 nm and intermediate permittivity often occurs around the functionalized fillers [215,219]. This interphase acts as a dielectric buffer that reduces electric-field concentration and suppresses the charge trapping. For instance, Luo et al. [214] demonstrated that adding a titanate coupling agent to $\text{Li}_2\text{Mg}_3\text{TiO}_6$ (LMT)-filled PTFE improved ϵ_r uniformity (2.4–2.6) and reduced $\tan \delta$ by 50 % (Fig. 51).

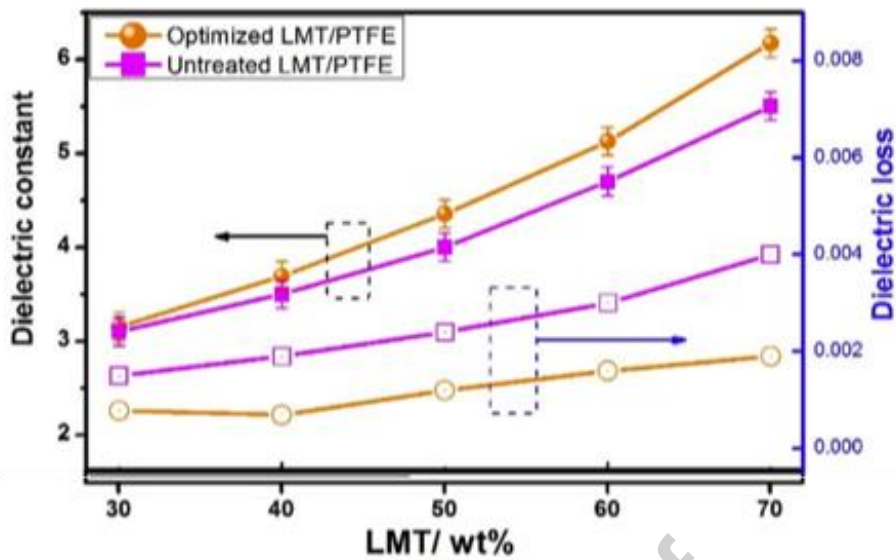


Fig. 51 : The variation of dielectric properties with LMT loading content for optimized and untreated LMT/PTFE composites (reprinted with permission from ELSEVIER [214].

As a result, the macroscopic dielectric properties of PTFE composites cannot be described solely by simple mixture rules but instead emerge from the complex interplay between filler morphology, interface structure, and microstructural continuity.

8.5.5. Comparative evaluation

When data are compiled, several quantitative tendencies emerge and can be summarized in Table 8.

These results clearly indicate that interface-controlled systems, such as $\text{SiO}_2/\text{PDA}/\text{PTFE}$ or BN/AlN hybrids, offer the optimal balance between permittivity enhancement and loss suppression. In contrast, high-k ceramics ($\epsilon_r > 20$) rarely yield practical advantages because interfacial mismatch introduces parasitic conduction and reduces the breakdown field.

8.6. Frequency and high-frequency behavior

8.6.1. Frequency dispersion in pristine PTFE

The dielectric response of PTFE remains remarkably stable over an exceptionally broad frequency range. From a few hertz up to several tens of gigahertz, PTFE preserves an almost constant permittivity ($\epsilon' \approx 2.04\text{--}2.06$) together with extremely low dielectric losses (i.e., $\tan \delta < 10^{-4}$) [201,202,208,222,223] (Fig. 52).

Table 8 : Non-exhaustive list of fillers in PTFE

Filler type	ϵ_r (10 GHz)	$\tan \delta$ ($\times 10^{-4}$)	E_{bd} ($kV \cdot mm^{-1}$)	Remarks	Ref
None (Neat PTFE)	2.05	< 1	50–60	Reference	[201–204,209,222]
SiO ₂ (20 vol %)	2.4–2.6	3–8	45–55	Low-loss, stable	[82,215]
Al ₂ O ₃ (20 vol %)	3.0–3.3	10–20	40–50	Increased loss	[224,225]
Mg ₂ SiO ₄ (40 vol %)	4.5–4.8	20	35–45	High ϵ_r , degraded Ebd	[143]
BN + AlN hybrid (30 vol %)	3.0	8	40–50	High thermal conductivity	[86,220]
CNT (0.5 vol %)	3.2	10–50	20–30	Onset of percolation	[216,221]
SiO ₂ /PDA (20 vol %)	2.6	5	55–60	Best compromise	[215,216,219]

where PDA stands for polydopamine.

This frequency independence reflects the absence of dipolar relaxation processes in PTFE. Because polarization arises almost exclusively from electronic displacement of electrons within the C–F bonds, the characteristic relaxation frequencies lie in the optical range and remain far beyond the frequency window typically explored in dielectric spectroscopy.

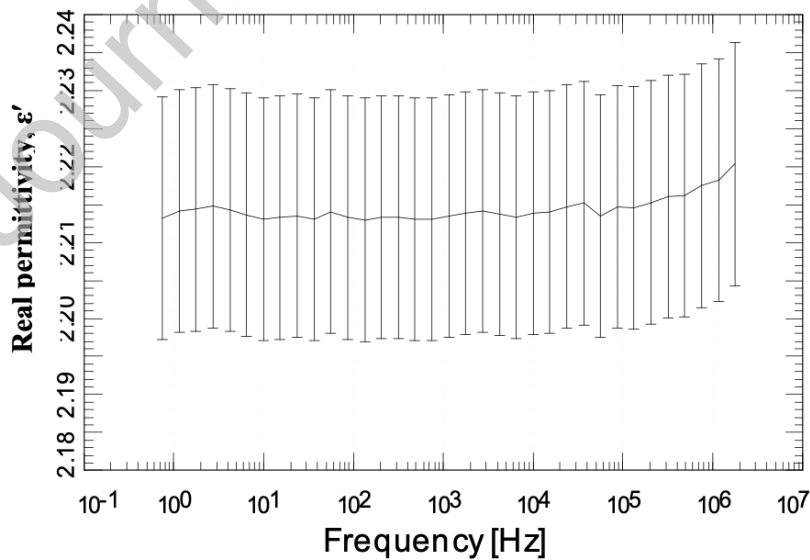


Fig. 52 : Real permittivity of PTFE as a function of frequency at room temperature (reprinted with permission from IEEE [208]).

Even at microwave frequencies approaching 100 GHz, only very small variations in permittivity are observed, generally below $\Delta\epsilon \approx 0.02$. These changes are associated with weak lattice-vibration contributions rather than with classical dielectric relaxation.

8.6.2. High-frequency performance of PTFE composites

The introduction of ceramic fillers slightly modifies the dielectric response of PTFE but generally preserves its remarkable frequency stability. In oxide- or nitride-filled systems, the relative permittivity typically increases from about 2.1 to 2.5-3.0 while remaining nearly frequency-independent across the microwave range [215,225].

Dielectric losses increase only moderately in these composites, with $\tan \delta$ values typically ranging from 4×10^{-4} to about 1.5×10^{-3} at 10 GHz. These values remain significantly lower than those observed in most engineering polymers containing polar functional groups, such as polyetherimide, polysulfone, polycarbonate, or polyetheretherketone (Fig. 43) [206,222]. By contrast, composites containing high-permittivity ceramic fillers often exhibit stronger dispersion and higher dielectric losses at microwave frequencies. For instance, BaTiO₃-based composites may exhibit decreases in ϵ' of several percent between 1 and 10 GHz, accompanied by increased losses due to interfacial polarization processes [143,224,226].

8.6.3. Millimeter-wave and emerging communication frequencies

Recent developments in high-frequency electronics, including 5G communication systems and radar technologies, have extended the characterization of PTFE composites to millimeter-wave frequencies above 60 GHz.

Recent laminate systems incorporating nano-Al₂O₃ or BN fillers exhibit permittivities of $\epsilon_r \approx 2.8$ and dielectric losses of 6×10^{-4} up to frequencies of about 110 GHz [225]. Such results confirm that moderate ceramic loading does not significantly degrade the intrinsic frequency stability of PTFE.

By comparison, conventional epoxy-glass or cyanate-ester laminates typically exhibit greater permittivity dispersion and significantly higher dielectric losses in the same frequency range [219,222,227,228].

Because signal propagation in microwave circuits depends directly on the square root of permittivity, the exceptional stability of PTFE ensures minimal phase distortion and group-delay dispersion across wide bandwidths, which explains its widespread use as a substrate material in high-speed communication systems.

8.7. Perspective and outlook

The PTFE dielectric behavior illustrates how a chemically simple polymer can achieve exceptional electrical stability through an unusual combination of molecular symmetry, high crystallinity, and minimal dipolar activity. Because polarization in PTFE is dominated by instantaneous electronic displacement, its dielectric response remains remarkably insensitive to temperature, frequency, and environmental perturbations. This intrinsic stability explains why PTFE has remained a benchmark dielectric material for more than seven decades.

However, modern electronic technologies increasingly require materials that simultaneously combine low dielectric losses, tunable permittivity, and enhanced thermal management. In this context, PTFE composites represent a particularly promising strategy. By incorporating carefully selected ceramic fillers and controlling the structure of the filler–polymer interphase, it is possible to increase permittivity while preserving the polymer's intrinsic low-loss character.

Future developments will likely focus on the precise control of interfacial polarization mechanisms, particularly in nanostructured composites designed for millimeter-wave and sub-, terahertz communication technologies. In such systems, the challenge is no longer merely to maximize permittivity but to maintain dielectric homogeneity at the nanometer scale to avoid local-field amplification and energy dissipation. PTFE-based materials, therefore, continue to offer a unique platform for exploring the interplay between polymer structure, interfacial physics, and high-frequency dielectric performance.

9. Applications

9.1. Introduction

PTFE is widely used across numerous technical sectors, from electrical and medical equipment to clothing and even pyrotechnics (Fig. 53). As the applications of PTFE have already been extensively discussed by Puts et al. [11] and Dhanumalayan et Joshi [16], this section focuses on highlighting emerging applications of PTFE, rather than reiterating an exhaustive overview

of its past and established uses. The aim is to emphasize its contemporary relevance and the evolution of its uses in the context of current science and technology.

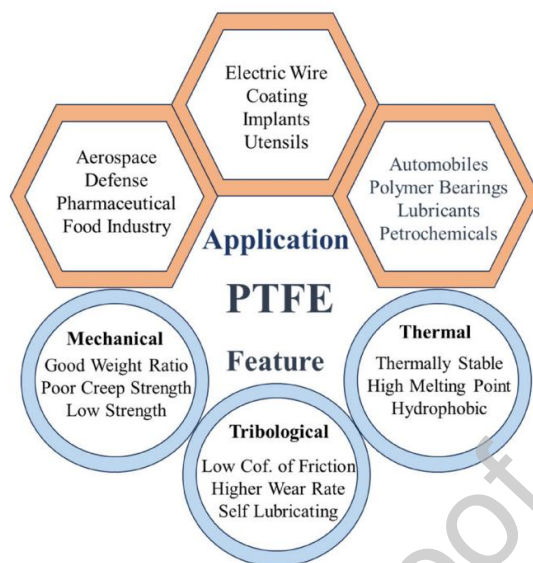


Fig. 53 : Brief overview of PTFE applications and features (reprinted with permission from WILEY [144]).

Thanks to its remarkable combination of chemical inertness, thermal stability, and low friction, this highly stable polymer has become indispensable in many industries. In recognition of its growing importance and status as the most widely produced and utilized fluoropolymer, global PTFE production reached 228,33 Kilotons in 2025 [229]. This was driven by increased demand from sectors such as chemical processing, surface coatings, specialty textiles, aerospace, automotive, medical devices, and advanced electronics (Fig. 53) [4,11,144,229].

9.2. PTFE in coating applications

PTFE is best known for its use as the non-stick coating on cookware and has long been used in the food industry for its chemical inertness, ease of cleaning, and non-stick properties. Its widespread adoption in consumer products, particularly non-stick cookware, stems from its excellent water- and fat-repellent properties that effectively prevent food from adhering during cooking [230]. The non-stick cookware sector alone accounted for 12,000 tons of PTFE consumption in 2023. When used under normal conditions, PTFE coatings are considered safe (section 10). However, overheating to temperatures above 380 °C for extended periods can lead to the formation and release of invisible gases (section 10).

PTFE is also used to coat textiles or fabrics to provide waterproofing [4,231]. In particular, expanded PTFE is used as a waterproof yet breathable membrane in clothing (commercially

known as Gore-Tex® (Fig. 54)). Additional applications of PTFE coatings include release coatings on molds, pipe liners, and vessel and thermocouple coatings in the pharmaceutical and chemical industries. These uses extend to pipe liners in acid plants, non-fouling coatings in heat exchangers, and anti-corrosion coatings for machinery housings [1,11]. It is common to find PTFE-coated magnetic stirring bars in virtually every chemistry laboratory. Besides, thanks to its essential tribological properties (section 6), PTFE also serves as a low-friction surface coating in various applications where reduced wear and smooth interaction are critical. For example, ultra-thin PTFE coatings have been applied to razor-blade cutting edges to reduce friction and provide a smoother shave [1,11].



Fig. 54 : Resistance of Gore-Tex® waterproof Shoes (photo taken by B. Ameduri).

Moreover, due to its exceptionally high limiting oxygen Index ($\text{LOI} > 95\%$), PTFE exhibits auto-extinguishing behavior, making it an outstanding material for cable coatings in aircraft applications, enhancing fire safety and reliability (e.g., electrical insulation in aerospace wiring systems) (Fig. 55) [226,232]. Furthermore, PTFE insulation is widely used in cable coatings within the oil and gas industry, particularly in deep-well environments, due to its excellent chemical resistance, low permeability, and broad thermal stability [233].

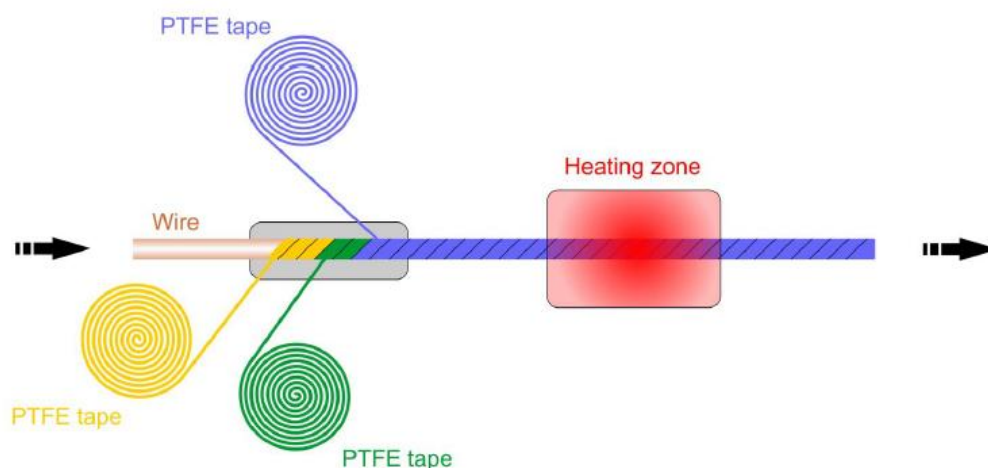


Fig. 55 : Cable insulated based on applying a PTFE three-layer coating around a wire to induce safety in airplanes, thanks to the excellent features of PTFE (reprinted with permission from M. Schlipf [232]).

The versatility of PTFE has led to its use in coatings and composites [234]. For example, Nickel-based coatings incorporating modified PTFE particles have been developed to enhance corrosion resistance. Polydopamine functionalization has been shown to facilitate the stable dispersion of PTFE particles in plating solutions, thereby enabling complexation with metal ions and enhancing adhesion and mechanical properties [235,236].

9.3. PTFE applications in the energy sector

The energy sector requires many fluoropolymers. Besides ionomers, copolymers of TFE with *co*-sulfonic acid perfluoroalkyl vinyl ether or perfluorosulfonic acid (PFSA) are used in PFSA membranes. At the same time, PTFE plays a pivotal role in proton exchange membrane fuel cells, serving as a membrane reinforcement and a gas diffusion layer coating that enhances both gas transport and mechanical stability [237,238]. Additionally, the presence of PTFE fibers in catalyst layers (especially at the cathode) facilitates oxygen transport, thereby supporting efficient electrochemical reactions [239] (Fig. 56).

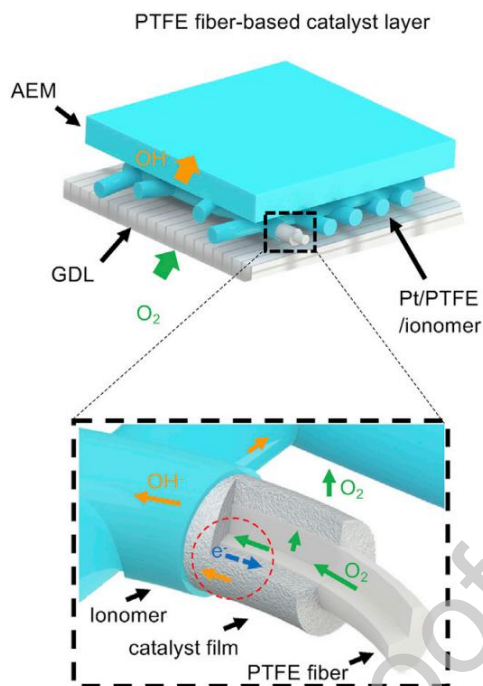


Fig. 56 : PTFE fiber-based catalyst layer for the oxygen reduction reaction (ORR) electrode in alkaline fuel cells. In the former case, gas (green), electron (blue), and hydroxide ion (orange) are transported by the gas pores, electronically conducting support, and ionomer, respectively. In the latter, the PTFE fibers provide an additional transport pathway for O_2 due to their high affinity for nonpolar gases. In both (A) and (B), the red circle denotes a site where electrochemical reactions can happen (reprinted with permission from CellPress [239]).

Additionally, Dong et al. [240] used expanded PTFE (e-PTFE) as a reinforcing framework for PFSA membranes, in which surface modification enhances interfacial compatibility, mechanical strength, and proton conductivity for hydrogen fuel cell applications. In this context, Guo et al. [241] summarized the strategies to control the membrane pore structure as well as the functionalization of PTFE porous membranes. These authors also reviewed the main issues linked to the practical applications of PTFE porous membranes. They suggested the appropriate PTFE membrane production technology to match the variety of well-designed applications.

Though most binders in lithium-ion battery (LIB) cathodes are made of PVDF [242], PTFE has also been shown to improve performance due to its chemical inertness and nonpolar nature [243]. PTFE has been employed as an alternative binder to enhance the electrochemical performance of LIB based on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes. However, owing to the highly nonpolar nature of PTFE, commonly used organic solvents are ineffective at separating cathode materials from PTFE-based lithium-ion batteries. Consequently, effective strategies for separating and recycling cathode materials from these batteries must be developed [244]. Moreover, PTFE has also been utilized as a source of fluorine for the surface fluorination of

reactive anode materials [245]. Upon thermal treatment, PTFE decomposes, generating fluorinated species that react with the anode surface to form a thin, stable fluorinated layer. This surface modification effectively suppresses undesirable side reactions with the electrolyte, enhancing interfacial stability and improving the electrochemical performance and cycling durability of battery anodes, both of which are key features for evaluating LIB efficiency. Thus, the use of PTFE demonstrates its potential beyond conventional binder applications, serving as a functional material for surface engineering in advanced battery systems [245].

It is important to note that PTFE is widely used in the nuclear sector. Thanks to its chemical inertness in HF, F₂, or KF, this exceptional polymer is used for seals, fluid circuits, tubing, elbows, cable insulation, and instrumentation, as well as for high-purity containers employed in nuclear fuel analysis [246].

9.4. Use of PTFE in electronics

In the field of electronics, thanks to a long-term electrical endurance (section 8.3.3), PTFE is a critical component in high-frequency cables, flexible printed circuits, and insulation in 5G (Fig. 57. a) and 6G devices due to its low dielectric loss, thermal stability, and chemical inertness [232,247,248]. Porous PTFE fibers have also been shown to resist and enable terahertz pulse transmission through low-loss channels [247,248] (Fig. 57. b). Furthermore, PTFE has also been involved in robotics and artificial intelligence supercomputers.

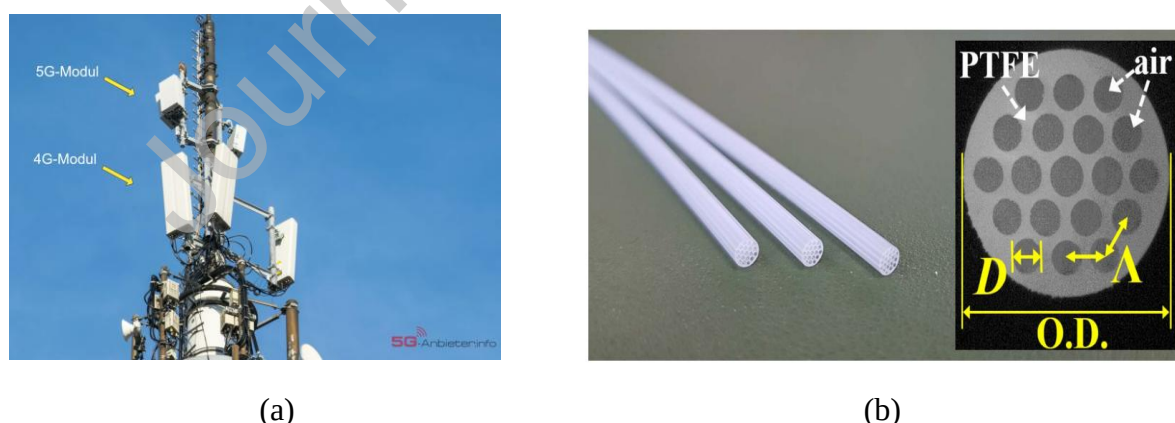


Fig. 57 : a) 5G antenna systems made from PTFE [232]. b) Photograph and cross-section of the porous core fiber made of PTFE. The porous fiber has 19 air holes arranged in a hexagonal lattice, with air-hole diameter (D), pitch (A), and outer diameter (O.D.). (reprinted with permission from IEEE [248]).

9.5. PTFE in Printing Technologies

Zhang et al. [249] extend PTFE's applications to advanced fabrication techniques, such as 3D micro-printing (μ -printing) (Fig. 58), which is based on digital ultraviolet (UV) lithography. In

this method, PTFE nanoparticles are dispersed in a photocurable polyethylene glycol diacrylate (PEGDA) solution and printed layer by layer into predefined microstructures. Subsequent sintering steps are then employed to remove the polymer matrix, leaving pure PTFE microstructures. The use of this approach has enabled the fabrication of 3D PTFE micro-scaffolds for applications such as droplet lasers and electrostatic-driven biomimetic water striders, thereby underscoring the potential of micro/nano-structured superhydrophobic PTFE surfaces and the versatility of 3D printing in microengineering [250]. Such a study by Nieswic et al. [250] demonstrated an innovative strategy for the 3D printing of PTFE vascular grafts using digital light processing (DLP) of PTFE latex particles. In this process, the PTFE nanoparticles are dispersed in a photocrosslinkable, dimethacrylated Pluronic resin (similar to PEGDA), enabling direct printing in an aqueous environment. Following thermal and chemical post-treatments, the composite structure was transformed into a fully sintered device. The printed materials present excellent mechanical properties, including a Young's modulus of approximately 18 MPa and an elongation at break of ca. 157 %, while maintaining impermeability up to 4 bar due to controlled internal porosity (ca. 27 %). In addition, fibroblast cytotoxicity assays confirmed biocompatibility in accordance with ISO 10993 standards. This two-step printing and conversion process provides a compelling route toward the rapid fabrication of patient-specific PTFE grafts with complex morphologies, overcoming the limitations of traditional paste extrusion and stretching methods [250].

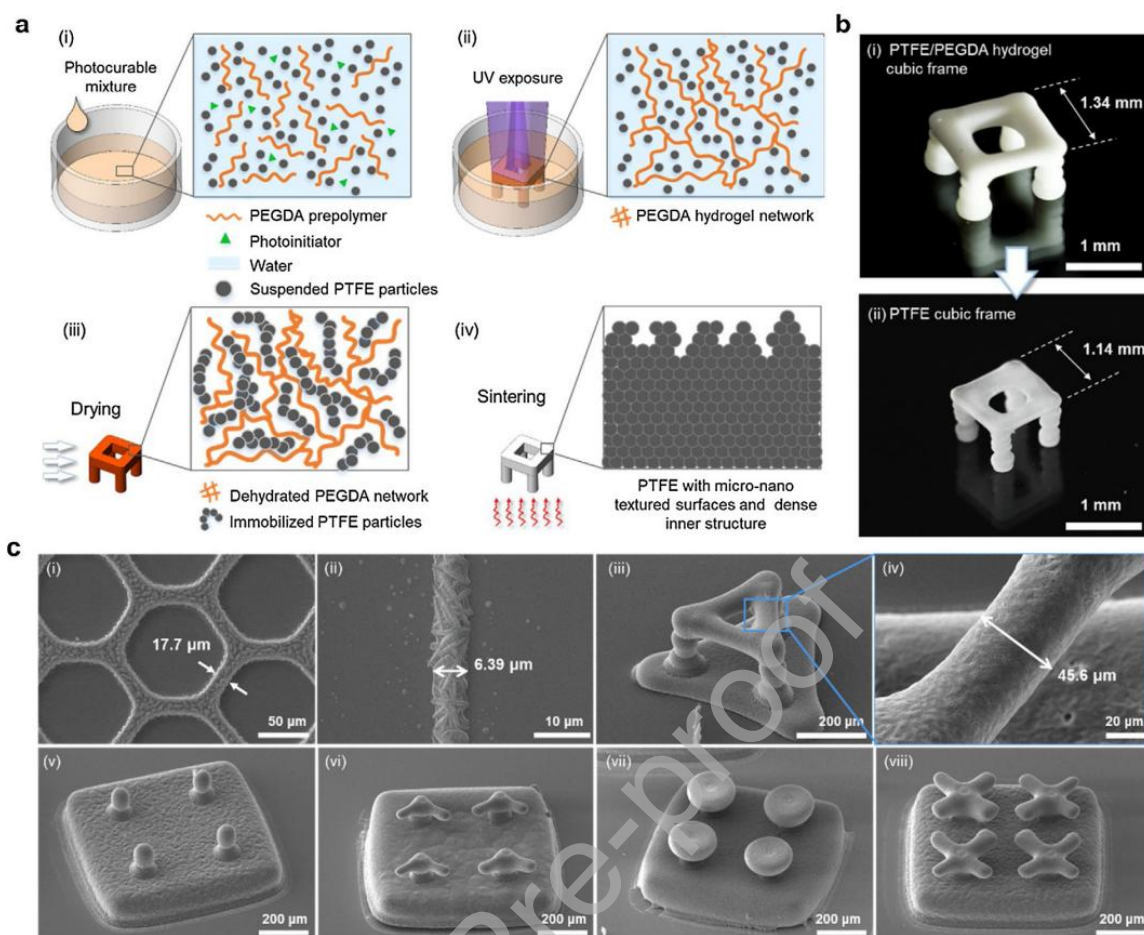


Fig. 58 : Schematic of the 3D μ -printing flowchart and images of the printed PTFE microstructures. (a) Printing flowchart: (i) Preparation of UV curable PTFE/PEGDA colloidal dispersion; (ii) Photocuring of the colloidal dispersion with a user-defined UV pattern; (iii) Drying of the printed microstructure to remove water; (iv) Sintering of the dried microstructure to remove PEGDA. Steps (i) & (ii) are repeated for 3D printing of microstructures. (b) Photographs of a printed cube-frame microstructure before and after sintering. (i) 3D printed and dried PTFE/PEGDA microstructure; (ii) 3D PTFE microstructure after sintering. (c) SEM images of 3D -printed PTFE microstructures: (i) micro-honeycomb structure; (ii) micro line; (iii) & (iv) 3D triangular-frame; (v) micro-ball array; (vi) zigzag micro-beam array; (vii) micro-mushroom array; (viii) suspended micro-cross array (reprinted with permission from ELSEVIER [249]).

More recently, Caldon's group [251] supplied a comprehensive review on fluoropolymers in additive manufacturing. Furthermore, Phillips et al. [252] reported that PTFE, as a non-polar polymer filler, also plays a key role in reducing terahertz (THz) absorption when incorporated into photopolymer resins (Vero White®, supplied by the Stratasys company). PTFE-filled composites manufactured by stereolithography (or DLP) with filler ratios ranging from 1:10 to 4:10 exhibited progressively enhanced THz transparency as the PTFE content increased. The highest PTFE loading (approximately 30 wt.%) resulted in an absorption coefficient of $15.3 \pm 0.3 \text{ cm}^{-1}$ at 1 THz, which is a 27.8 % reduction compared to that of the pure photopolymer. This

enhancement can be attributed to PTFE's inherently low dielectric loss at THz frequencies (section 8).

The unique combination of chemical stability, thermal resistance, low friction, and electrical insulation continues to drive PTFE's broad adoption across industries, including aerospace, automotive, medical devices, electronics, construction, energy technologies, and advanced microfabrication, confirming its indispensable role in modern materials Science.

9.6. PTFE in automotive and transportation applications

In the automotive industry [226], PTFE is a key high-performance polymer of choice for components exposed to extreme operating conditions, thanks to its exceptional chemical resistance, thermal stability, and low-friction properties. Its primary applications include sealing and fluid-transfer systems, encompassing components such as gaskets, O-rings, valve stem seals, and linings for fuel and transmission hoses. In addition, with the rapid shift toward electric vehicles, micronized and compounded PTFE are being integrated into ultra-thin thermal and high-voltage wiring insulation. In these systems, the material's exceptional properties enhance vehicle reliability and ensure long-term durability.

Moreover, one of its most significant applications is in fuel lines, where it provides excellent resistance to gasoline, diesel, and other fuels and can withstand high pressures and operating temperatures, both of which are particularly important for high-performance engines. PTFE coatings are also commonly applied to automotive components, such as brake calipers, piston rings, and engine parts, to reduce friction and enhance durability. PTFE is also used in air-conditioning hoses, power-steering systems, and other high-pressure hydraulic lines thanks to its resistance to heat, moisture, and aggressive chemicals.

As demand for high-performance, long-lasting automotive systems continues to grow, PTFE's importance in fluid handling and sealing applications is expected to increase.

9.7. PTFE in medical applications

The medical sector benefits greatly from PTFE's biocompatibility and chemical inertness (for more information (section 10.)), as evidenced by its 38,400 metric tons usage in 2023, with over 17,000 hospitals adopting PTFE-coated surgical tools and medical devices to ensure non-stick surfaces and long-term durability. PTFE is used in implantable devices, such as coatings for stents, grafts, catheters, hernia mesh, and surgical mesh, as well as in prosthetics, leads, and foil for magnetic resonance imaging (MRI), computed tomography (CT), and mammography

machines [253,254]. The use of ePTFE extends to surgical instruments and equipment, including shears, cutters, and staplers used in minimally invasive procedures. Its presence is also notable in blood collection bags, suction devices used in respiratory therapy and anesthesia, and intravenous solution bags [255,256].

A comprehensive review of clinical trials conducted on ePTFE devices [255] underscores its extensive application: a total of 61 studies were identified in the field of guided bone regeneration for maxillofacial diseases, 43 of which focused on stents, hemodialysis, and bypass grafts. In addition, 8 studies concentrated on hernia repair, 8 on heart repair, and 14 on other medical fields [255]. These findings provide evidence that fluoropolymers such as PTFE are generally safe for use in body prostheses and medical devices (for more information, see section 10) [256,257].

9.8. Summary

PTFE's unique properties, including exceptional chemical inertness, high thermal stability, low coefficient of friction, and pronounced hydrophobicity, position it among the most advanced and reliable high-performance polymers available today. This makes it an essential component in applications where long-term stability, durability, reliability, security, and performance under extreme physical and chemical conditions are paramount.

10. Health Context: Is PTFE Hazardous?

10.1. PTFE is regarded as a Polymer of low concern (PLC)

According to the Organization for Economic Cooperation and Development (OECD) definition [258,259], PTFE is considered a PFAS. However, that definition does not say anything about molar mass or dispersity. Indeed, while PFOA and PFOS have molar masses of 414 and 500 g.mol⁻¹, respectively, the molar mass of PTFE can reach several million g.mol⁻¹ [1,9,11,15,16,260]. This large difference influences several features, such as water solubility, thermal and aging resistance, and the penetration (or not) of fluorochemicals into the lipidic human membrane [28,260,261]. As a consequence of its high molar mass, PTFE is highly insoluble (*e.g.*, in water, octanol, and solvents) [262] and thus is not mobile, solid, and too large to migrate into the cell membrane, making it non-bioavailable and non-bioaccumulative. More recently, Henry and Timmer [260] demonstrated that PTFE-FA (high molar mass, fine powder, microparticulate PTFE meeting the ASTM D4895 specification) does not i) exhibit any

mobility, ii) undergo degradation, iii) adsorb to soil or sediment, iv) partition from water or organic matter into air (as a gas or vapor), and v) undergo a long-range transport in air, water, or soil, nor transform into or release non-polymeric PFAS. Actually, it fulfills 13 of the PLC-accepted criteria set by the OECD [263], which cover parameters such as oligomer content, molar mass, dispersity, particle size, thermal, chemical, aging, and UV stability, as well as surface charge.

Therefore, PTFE can be considered a PLC from human and environmental health standpoints [260]. Although PTFE's applications have traditionally been evaluated primarily from the perspective of consumer use, Sales et al. [264] highlighted that its advantages are even more evident in industrial contexts, where it supports decarbonization, circularity, safety, reliability, durability and exceptional overall performance.

10.2. Biotic and abiotic

The Carbone-Fluorine bond is extremely strong (with a dissociation energy of $485 \text{ kJ}\cdot\text{mol}^{-1}$) and difficult to substitute. Thus, PTFE differs from hydrocarbon polymers related to their outstanding physico-chemical, thermal, and oxidative properties [1,4,7,10,11,265]. It exhibits a high degree of environmental stability due to such a strong carbon-fluorine bond. Under abiotic conditions [260] (Fig. 59), PTFE is considered chemically inert and resistant to hydrolysis, photolysis, and thermal degradation in conditions that are environmentally relevant, and it does not readily dissolve, disperse, or transform in aquatic or terrestrial environments. In terms of biotic factors [260] (Fig. 59), PTFE is also regarded as biologically inert, with no evidence of enzymatic degradation by microorganisms, plants, or animals. Its high molar mass prevents bioavailability, uptake, and bioaccumulation, and PTFE particles are expected to remain largely unchanged when passing through biological systems. Consequently, environmental exposure to PTFE is primarily associated with the physical presence of particulate material rather than chemical toxicity, an important consideration in environmental risk assessment [260,266].

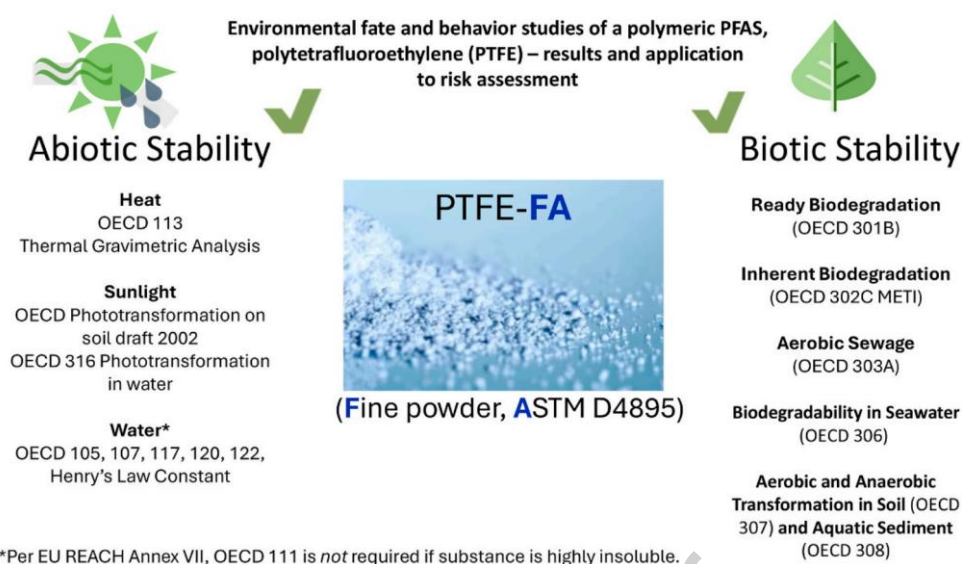


Fig. 59 : PTFE environmental fate: Persistence under abiotic and biotic conditions (reprinted with permission from ELSEVIER [260]).

However, its persistence has pushed authorities and regulatory agencies to consider it as a PFAS, but useful [260]. Recently, Health Canada [267] has redefined the PFAS context in their PFAS regulations, excluding fluoropolymers for risk management purposes, despite the chemical structure. Since fluoropolymers have been excluded from this family grouping, they are also excluded from this determination regarding the Persistence and Bioaccumulation Regulations of the Canadian Environmental Protection Act, 1999 (CEPA) [267]. Though the PTFE production is the highest among all fluoropolymers, and it accounts for approximately 70 % of the overall fluoropolymer market [268] (some sources state that PTFE production is around 200,000 tons per year [229]), it is thus much lower than that of all plastics (< 0.1 %) [253,267].

10.3. Biocompatible

The essential-use concept [254] distinguishes between applications in which, based on current knowledge, no alternative materials can match the performance of PFASs [269], and those in which lower performance levels are acceptable and achievable. It also distinguishes between cases in which the use of PFASs is unnecessary. If it is desired to preserve access to the unique, unmatched performance of PFASs, the importance of making selective, environmentally responsible use of them is all the greater.

It quickly became clear that identifying situations in which the use of PFAS is unnecessary, and alternatives are available, is crucial. The OECD's revised definition [270] emphasizes that the term "PFAS" does not indicate whether a substance is harmful; it simply denotes compounds containing a fully fluorinated methyl or methylene group. Distinguishing between essential and

non-essential uses is therefore a key strategy for managing substances of concern effectively [254]. According to Decision IV/25.19 of the Montreal Protocol, a use is considered “essential” only if it is necessary for health, safety, or the functioning of society, and if no technically and economically feasible alternatives exist.

In 2023, the FDA approved a semi-fluorinated alkane, perfluorohexyloctane ($C_6F_{13}C_8H_{17}$, marketed as Miebo® trademark by Bausch and Lomb), as a preservative-free, single-component eye drop to reduce tear evaporation in the treatment of dry eye disease [271]. It is important to note that the active ingredients in pharmaceuticals, biocides, and plant protection products are regulated by frameworks other than REACH and are granted unlimited derogations in the EU PFAS restriction proposal. Given the potential risks associated with emissions, especially for plant protection products, the proposal recommends that the EU address these risks in the relevant regulations to minimize PFAS use and environmental release.

As a polymer, PTFE is not required to be registered under the European REACH regulation. The absence of regulatory incentives limits the amount of company-generated safety data disseminated to the public. To date, the most comprehensive safety assessment published concerns its use in cosmetics, conducted by the US Cosmetic Ingredient Review (CIR) expert panel [272]. According to this report, data from the Food and Drug Administration (FDA)’s Voluntary Cosmetic Registration Program (VCRP) indicates maximum usage concentrations of 13 % for products that remain on the skin, while 2.4 % for products that are rinsed off. It is worth mentioning that PTFE was used in cosmetics as a bulking agent thanks to its ability to reduce friction [272]. The substance has been incorporated into a variety of cosmetic products, including foundations, mascara, and lipsticks, to enhance texture and prolong shelf life (Table 9) [272]. Furthermore, to assess skin irritation and sensitization, two patch tests, one with 7.6% PTFE and the other with 12%, were performed on 26 and 15 human subjects, respectively. After 48 and 24 hours, respectively, no signs of irritation were observed in these people [272]. A repeated-insult patch test with 9% PTFE in 206 subjects also revealed no sensitization [272].

Table 9 : Frequency and Concentration of Use According to Duration and Type of Exposure of PTFE. (reprinted with permission from Sage [272]).

	PTFE	
	# of Uses	Concentration (%)
Totals/Conc. Range	365	0.11-13
Duration of Use		
Leave -On	343	0.11-13
Rinse off	22	0.15-2.4
Dilute for (bath) Use	NR	NR

Exposure Type		
Eye Area	229	0.11-13
Incedental Ingestion	4	NR
Incedental Ingestion-Spray	15 ^a	NR
Incedental Inhalation-Powders	31	0.6-3.0
Dermal Contact	325	0.11-12
Deodorant (underarm)	NR	NR
Hair- Non-Coloring	NR	NR
Hair-Coloring	NR	2.4
Nail	NR	NR
Mucous membrane	4	NR
Baby products	NR	NR

NR = Not Reported; Totals = Rinse-off + Leave-on + Diluted for Bath Product Uses. Note: Because each ingredient may be used in cosmetics with multiple exposure types, the sum of all exposure type uses may not equal the sum total uses. ^a It is possible that these products may be sprays, but it is not specified whether the reported uses are sprays.

Along with that, in an acute oral toxicity study conducted on rats, administering low-molar-mass PTFE resin did not result in mortality or clinical signs of toxicity at doses up to 17 g/kg [272]. In addition, a 90-day dietary study in rats with 25% PTFE reported no microscopic tissue changes. However, unsintered PTFE increased liver size [272]. In a nine-day inhalation study, exposure to a 20% PTFE dispersion produced no pathological findings, and mild respiratory symptoms were attributed to the propellants and dispersing agent rather than to the PTFE itself [272,273]. However, after six months of exposure to an unspecified concentration of PTFE, mice developed skin lesions, fur loss, and significant weight loss. Moreover, topical application of 20 % low-molar-mass PTFE resin in CCl₂F–CClF₂ (F-113) caused no skin sensitization in guinea pigs [273]. That review also reports that when 20 % low-molar-mass PTFE resin in F-113 was applied to rabbits' eyes, mild conjunctival irritation resolved within 72 hours and transient corneal injury resolved within 24 hours. Actually, these effects were comparable to those produced by the F-113 alone [273].

Furthermore, PTFE is recognized as non-carcinogenic and approved as safe and currently irreplaceable by authorities, including the FDA and the European Food Safety Authority (EFSA) [255,256].

Moreover, based on current knowledge, ca. 90 % of the fluoropolymers used in medical devices are PTFE [274], ETFE, FEP, and PVDF [256,275]. Expanded polytetrafluoroethylene (ePTFE) is also commonly used [256,255,276] (Fig. 60). Currently, there are no viable non-PFAS alternatives to these materials, and developing a substitute from conception to market is estimated to take 10 to 15 years. Moreover, banning PFAS would be risky, and it could

jeopardize millions of medical devices [256,277]. Indeed, upcoming PFAS regulations could significantly limit the availability of certain medical devices, which in turn may pose risks to patient safety. Physicians have begun issuing warnings about potential patient harm if the ECHA's proposed ban is adopted [277]. Several factors contribute to these concerns. PFAS such as PTFE are essential for coating guidewires, allowing them to move smoothly through blood vessels. Without PTFE and similar PFAS, guidewires may adhere to vascular walls, causing patient discomfort and increasing the risk of mechanical stress and thrombosis [256]. A range of medical procedures could be affected, including minimally invasive, endovascular, and gastrointestinal laparoscopic interventions. If the devices required for these procedures become less available, clinicians may have to rely more on open surgery, assuming that the tools needed for open procedures also remain accessible once a broad ban takes effect [277]. Furthermore, over 300,000 pacemakers and defibrillators are implanted annually in the United States, so a total PFAS ban could jeopardize access to these vital cardiac devices.

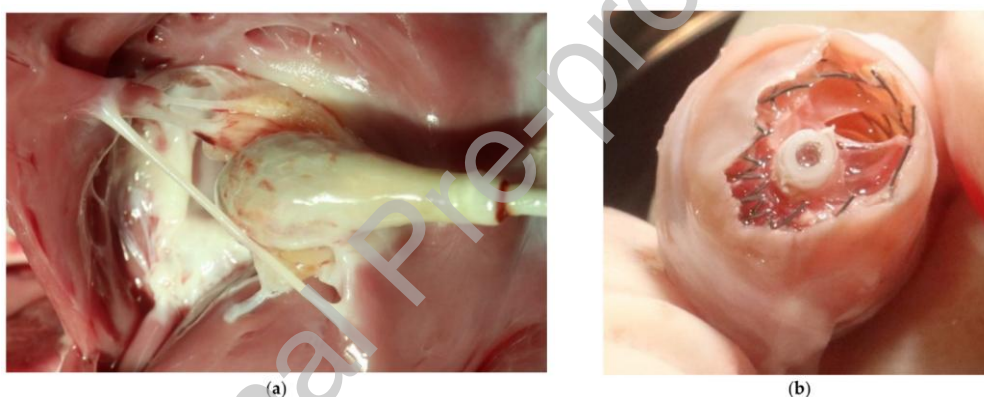


Fig. 60 : Gross estimation of the implanted spacer for Regurgitant Heart Valve Disease. **(a)** A smooth cell layer was formed over the ePTFE coating. The anterior leaflet, which has the most contact with the device, was slightly thicker than the other. **(b)** A seroma-like material was formed inside the self-expandable nitinol mesh (reprinted with permission from MDPI [276]).

In 2024, the American Cancer Society indicated that some PFASs are approved for use in the manufacture of non-stick cookware coatings. These coatings are made of PTFE and applied to the cookware through a heating process that tightly binds the polymer coating to the cookware, thus very little is capable of migrating into food, and no adverse health effects to be expected from cookware with PTFE non-stick coating according to the FDA [256]: “*The PFAS used in manufacturing of gaskets that come into contact with food do not pose a safety risk because they are also made of molecules that are polymerized*”. As recently as January 2025, the FDA stated that the use of non-stick coatings is approved [256,278]. According to EU law, food-contact materials, including cookware, must be manufactured so that, under normal foreseeable conditions of use, they do not release chemicals into food in quantities that may be hazardous

to human health. Additionally, according to EFSA [279], several studies indicate that fluoropolymer food-contact materials are unlikely to be a significant source of PFASs.

In a similar context, the German Agency for Risk Assessment (BfR) conducted a thorough analysis of current PTFE-coated cookware, ovenware, and frying pans on the market. Under normal usage conditions (no overheating), these products do not transfer fluorinated chemicals into food in quantities that pose a threat to human health. This consensus scientific view is shared by environmental advocacy groups, such as the Environmental Working Group (EWG) [280]: In February 2024, this Group stressed that PTFE is not a significant source of exposure and reports: *“But even though it is always been the poster child for PFAS exposure, this cookware is not anticipated to be a major source of exposure”* [1,11,280].

Moreover, a series of studies was conducted by researchers at Golden Collar to evaluate the toxicity of PTFE-coated surfaces. These studies encompass a range of assessments, including animal tests [281] and evaluations of cellular toxicity. The potential toxicity of the substance is evaluated using animal experiments, which are designed to observe the physiological and pathological effects resulting from animal exposure to the substance. The evaluation of cellular response to PTFE exposure is conducted through in vitro cell cultivation, followed by meticulous observation of cell growth, proliferation, and apoptosis. This study indicates that PTFE does not elicit any toxic effects in humans under normal conditions. However, this does not imply disregard for the potential risks associated with using these devices. In certain instances, the coating may exhibit heightened toxicity, particularly if it is used to produce additives or solvents deemed unsafe.

Along the same lines and in terms of genotoxicity and teratogenicity, antiohesive coating materials containing 60-73 % PTFE tested negative in both the Ames test (mutagenicity test) and micronucleus assay [272], and a more recent comprehensive study confirms these features [260].

In conclusion, PTFE is a unique specialty polymer that meets the 13 OECD criteria for polymers of low concern thanks to its exceptional properties. The essential use concept helps to distinguish between applications with no non-fluorinated alternatives, those with effective substitutes and convenience uses that are therefore non-essential. This framework can inform the phase-out of non-essential uses of PFAS. Regarding the toxicity, the environmental risk depends on the quantities released.

Since the 1970s, public health authorities around the world have taken a unanimous position on PTFE: it is inert, non-bioaccumulative, non-toxic, not water soluble, and therefore safe for consumers.

However, assessing the essentiality of PFASs is challenging due to the large number of substances involved and the limited publicly available information on their structures, performance, production volumes, environmental behavior, and toxicity. Strengthened collaboration and information exchange among industry, academia, regulatory agencies, research institutions, and civil society are required to address this challenge.

From another viewpoint, PTFE, widely used for its stability and resistance, was once thought to be inert. In addition, data submitted to ECHA in 2023 [282], in public comments on the EU's proposed universal PFAS restriction, indicate that large PTFE fragments remain stable under environmental conditions, indicating a low likelihood of microplastic formation [260]. Besides, as mentioned in section 10.2. Biotic and abiotic, Health Canada has excluded fluoropolymers from the PFAS family [267], while the UK follows such a trend.

11. Fate of PTFE at end of life

11.1. PTFE waste, microplastics, footprint, and End-of-Life

Once manufactured and placed into service, the environmental impact of PTFE shifts from its production phase to its interaction with the surrounding environment.

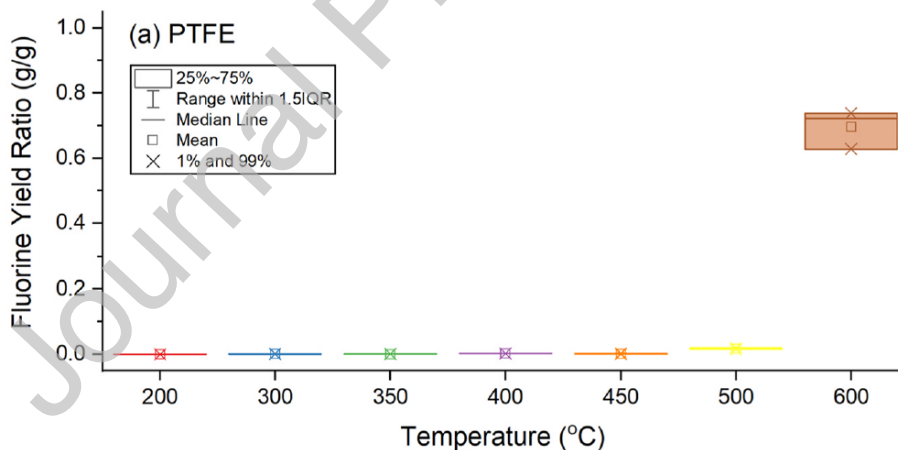
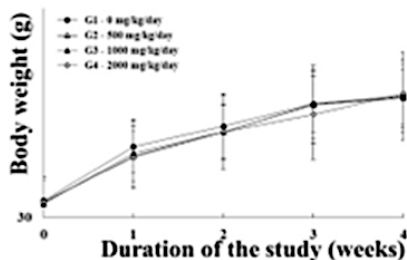


Fig. 61 : F yield (g/g_{fluoropolymer}) as a function of temperature for the thermal degradation of PTFE in air (reprinted with permission from ELSEVIER [283]).

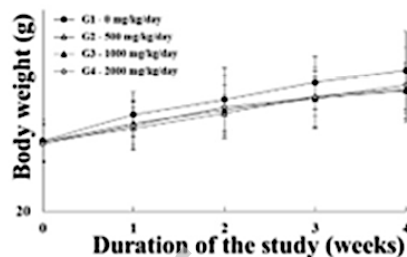
A significant benefit of PTFE is its remarkable resistance to chemical degradation, meaning it does not readily decompose or release harmful substances under typical operating conditions. This stability makes PTFE suitable for sensitive uses such as food processing (with specific grades) and medical devices (see section 10).

a approximately 5 μm , male

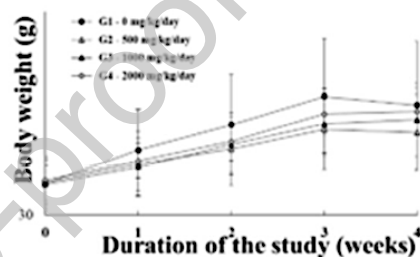
Dose \ Week	0	1	2	3	4
G1 - 0 mg/kg/day	31.2	35.1	36.5	38.1	38.7
G2 - 500 mg/kg/day	31.1	34.4	36.1	38.1	38.6
G3 - 1000 mg/kg/day	31.0	34.6	36.1	38.1	38.6
G4 - 2000 mg/kg/day	31.1	34.3	36.1	37.4	38.9

**b** approximately 5 μm , female

Dose \ Week	0	1	2	3	4
G1 - 0 mg/kg/day	25.3	27.2	28.3	29.6	30.5
G2 - 500 mg/kg/day	25.2	26.2	27.3	28.6	29.1
G3 - 1000 mg/kg/day	25.2	26.5	27.6	28.4	29.0
G4 - 2000 mg/kg/day	25.0	26.4	27.8	28.5	29.4

**c** 10–50 μm , male

Dose \ Week	0	1	2	3	4
G1 - 0 mg/kg/day	32.3	34.8	36.7	38.8	38.1
G2 - 500 mg/kg/day	32.4	33.8	34.9	36.4	36.1
G3 - 1000 mg/kg/day	32.3	33.6	35.2	36.7	37.1
G4 - 2000 mg/kg/day	32.6	34.0	35.4	37.5	37.7

**d** 10–50 μm , female

Dose \ Week	0	1	2	3	4
G1 - 0 mg/kg/day	25.4	26.5	28.5	30.5	29.7
G2 - 500 mg/kg/day	25.6	25.8	26.5	27.8	28.2
G3 - 1000 mg/kg/day	25.5	26.1	27.3	28.8	28.8
G4 - 2000 mg/kg/day	25.7	25.8	26.7	28.5	28.3

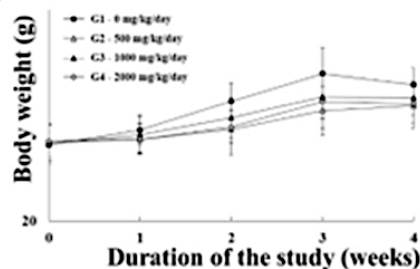


Fig. 62 : Male and female bodyweight changes after four weeks of repeated dosing with approximately 5 μm (a, b) and 10–50 μm (c, d) PTFE microplastics (reprinted with permission from MDPI [284]).

In addition, PTFE is generally biocompatible [256,260], does not support microbial growth, maintains reliable performance up to 260 $^{\circ}\text{C}$ in continuous service, and shows no significant degradation after 500 hours in laboratory aging tests [1,9,15,260]. Within this range, it remains stable without significant degradation or hazardous gas emissions [260]. According to other sources, PTFE remains essentially undegraded under moderate thermal conditions (≤ 500 $^{\circ}\text{C}$) (Fig. 61) [283]. Consequently, during its standard service life, PTFE is highly stable and poses a minimal direct environmental risk. While there is a small chance of microplastic formation [260], these microplastics do not lead to any hazardous issues [284–286].

Furthermore, given the low production of FPs (less than 0.1 % among all plastics) [253], the release of FP microplastics is quite low relatively insignificant compared to those from

commodity polymers [253,260]. The toxicity of PTFE microplastics (PTFE-MPs) has been investigated [260]. It indicates that PTFE-FA, even in microparticle form, neither increases PFAS levels in wastewater effluents nor inhibits microbial activity in sludge, in accordance with the ASTM D4895 specification [260]. Lee et al. [284] reported that after exposure to PTFE microplastics of 5-50 μm , no specific clinical sign was recorded during the 4-week observation period, and no significant differences were noted in body weight (Fig. 62), organ weight, or water and food consumption in the administration groups compared to the control group.

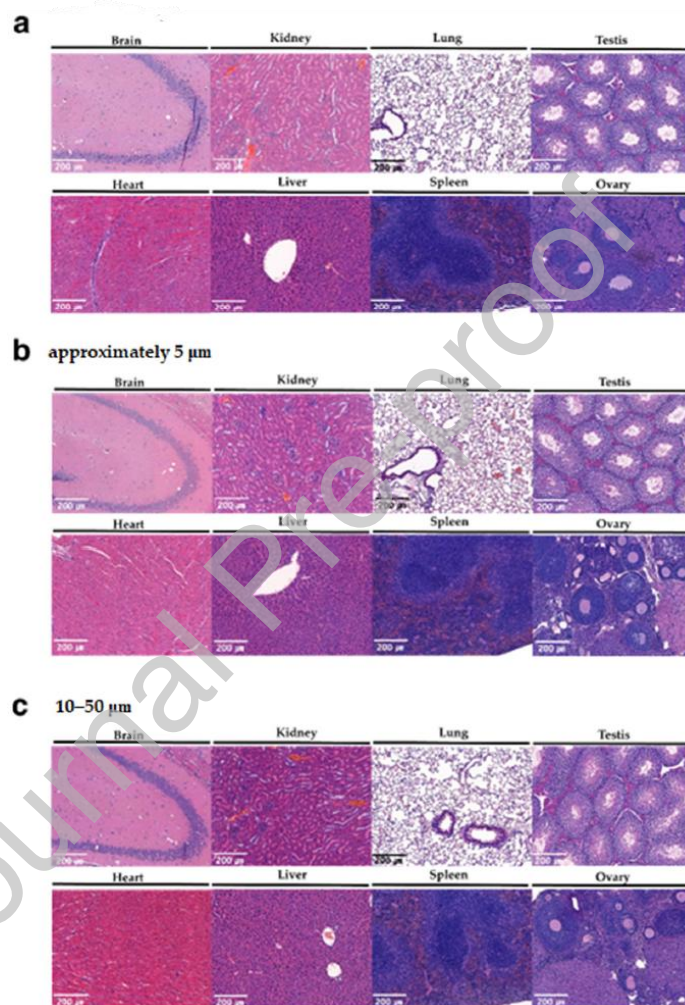


Fig. 63 : Histopathological evaluation of tissues from mice after four weeks of repeated dosing. Representative images of the brain (hippocampus), heart, kidney, liver, lung, spleen, testis, and ovary of the control mice (**a**), approximately 5 μm PTFE-treated mice (**b**), and 10–50 μm PTFE-treated mice (**c**). Scale bar = 200 μm (reprinted with permission from MDPI [284]).

Furthermore, no degenerative changes, such as inflammation, desquamation, or necrosis, were detected on histopathological evaluation (Fig. 63). Moreover, KC et al. [285] exposed six human cell lines representing tissues likely to come into contact with such particles to two sizes of irregularly shaped PTFE-MPs (6.0 and 31.7 μm). While no direct toxicity was observed, PTFE-MPs were found to affect different cell types. They appear to induce oxidative stress and

inflammation primarily through activation of the extracellular signal-regulated kinase (ERK) pathway, suggesting indirect, stress-mediated toxicity rather than direct cytotoxicity [285]. Alaraby et al.[286] also noted that the toxicity of PTFE particles depends on particle size and exposure conditions, with smaller particles and prolonged exposure increasing toxic effects. A comprehensive examination of the available literature on the subject reveals that toxicological investigations, incorporating both *in vitro* and *in vivo* studies, suggest that PTFE microplastics may potentially disrupt physiological homeostasis by inducing oxidative stress, inflammation, necrosis, and disruption of critical signaling pathways, including mitogen-activated protein kinase (MAPK) and protein kinase B/mammalian target of rapamycin (AKT/mTOR). Notwithstanding these findings, the comprehensive understanding of the full scope of PTFE risks remains limited [286]. A significant impediment is the lack of standardized, sensitive analytical techniques that reliably identify and quantify PTFE microplastics, particularly at the nanoscale, in complex environmental and biological matrices. This technical gap hinders accurate exposure assessments and comprehensive risk evaluations [286].

Overall, these findings demonstrate that the behavior of microplastics in the environment is not uniform and that their impact depends strongly on intrinsic properties such as molar mass, solubility, and bioavailability. This highlights the need for a more nuanced understanding to ensure that risk assessments and regulatory decisions accurately distinguish between particles that pose a high risk and those that have minimal environmental or biological relevance. Because of its unique characteristics, PTFE's high stability prevents its decomposition and raises questions about its release into microplastics.

As discussed above (sections 10.2 and 10.3), PTFE microplastics do not cause any problems. The primary concern is thermal decomposition at very high temperatures ($> 550\text{ }^{\circ}\text{C}$) [253,287]. Therefore, "secure landfilling" is recommended to prevent the material from fragmenting into smaller, more mobile particles in the environment.

In contrast to all plastics, FP consumption was estimated at 330,000 tons in 2021 [253] and 346,970 tons in 2023, although the exact figures vary by source. By 2028, the total market value of FPs in the Asia-Pacific region is expected to reach \$3.5 billion [253]. The relatively short life cycle of plastics also contributes to a sharp increase in the total amount of plastic waste. Currently, the global recycling rate for plastic waste is only 9% [253,288], while the recycling rate of fluoropolymers is merely 3.4% [253]. Similarly to all plastics [228,289], incineration is the main technique utilized for the elimination of FPs (it represented 83.5% in 2020, ca. 20.4 kt *versus* landfill, 13.1%, 3.1 kt and recycling, 3.4%, 0.8 kt), which is regarded as the destruction

of chemicals in the presence of heat and is mature technology used for various solid and liquid waste. Various reviews describe the incineration of PTFE [253].

It can be anticipated that, in the coming decades, many used polymers (including FPs) will accumulate, with their end-of-life management occurring via either incineration or landfill [253]. The incineration technique, generating hazardous hydrogen fluoride (HF) (and low molar mass PFAS), introduces potential risks to human health and the environment. In addition, landfilled plastic waste is exposed to a range of biochemical and enzymatic reactions and physical processes that may fragment it into microplastics [290,291], thereby raising health and environmental concerns [285,292,293]. The strong C–F bonds and stable helical conformation of PTFE (section 2) make it resistant to end-of-life degradation [16,294]. Recent studies have shown that PTFE microplastics can be detected and characterized using ICP-MS operated in single-particle mode [295,296]. This includes both SP-ICP-qMS approaches and F-selective SP-ICP-MS/MS techniques [295,296]. Thus, recycling processes, such as remanufacturing [253,297,298], degradation into valuable products, or, better yet, mineralization for possible circularity, would be of great interest.

Current technologies for disposing of discarded PTFE can be roughly divided into three categories: physical separation, chemical oxidation, and thermochemical conversion. Among them, thermochemical conversion technologies, i.e., pyrolysis, gasification, and combustion, outperform the former strategies by thoroughly destroying and mineralizing the large amounts of organic fluorine, providing an efficient, scalable, and widely available way to dispose of PTFE without producing PFAS-containing waste [299,300].

11.2. Recycling (chemical, thermal, mechanical, and using gamma irradiation)

Recycling PTFE has intensified and is challenging [253,268], although it exerts much pressure and poses potential hazards to the ecological environment. Various methods for recycling PTFE have been reported: gamma, electron beam, and proton radiation [57,303–307] have shown side products [308] but thermal depolymerization has been studied in most studies.

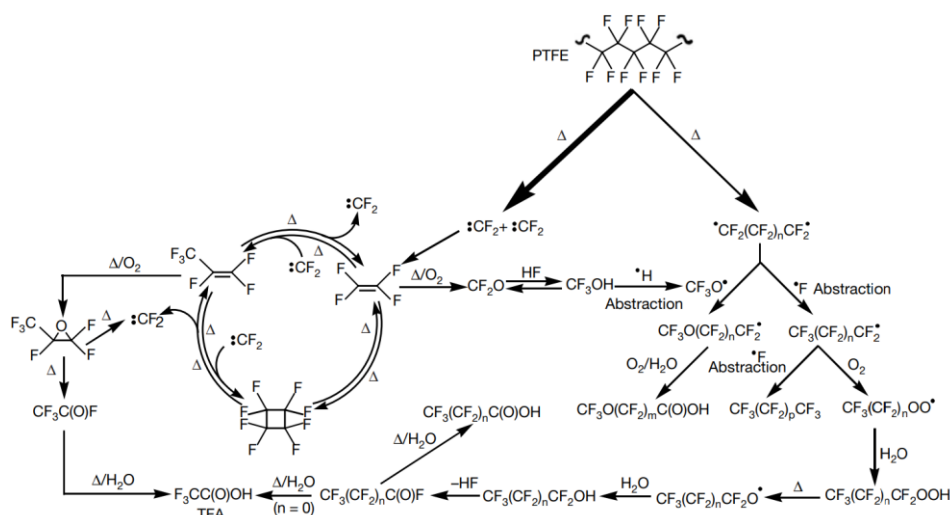


Fig. 64 : Proposed significant pathways in the thermal decomposition of PTFE, highlighting unexpected fluorochemicals. (reprinted with permission from Nature [309]).

The thermal “unzipping” or depolymerization of PTFE (from 550 °C), releasing TFE and other fluorochemicals, has been known since the 50s [287,309–313] and has also been industrialized in a pilot plant [313]. These unexpectedly generated chemicals and TFE were identified by various analytic tools (especially liquid chromatography mass spectroscopy, LC-MS...) [309,314,315] (Fig. 64 and Fig. 65).

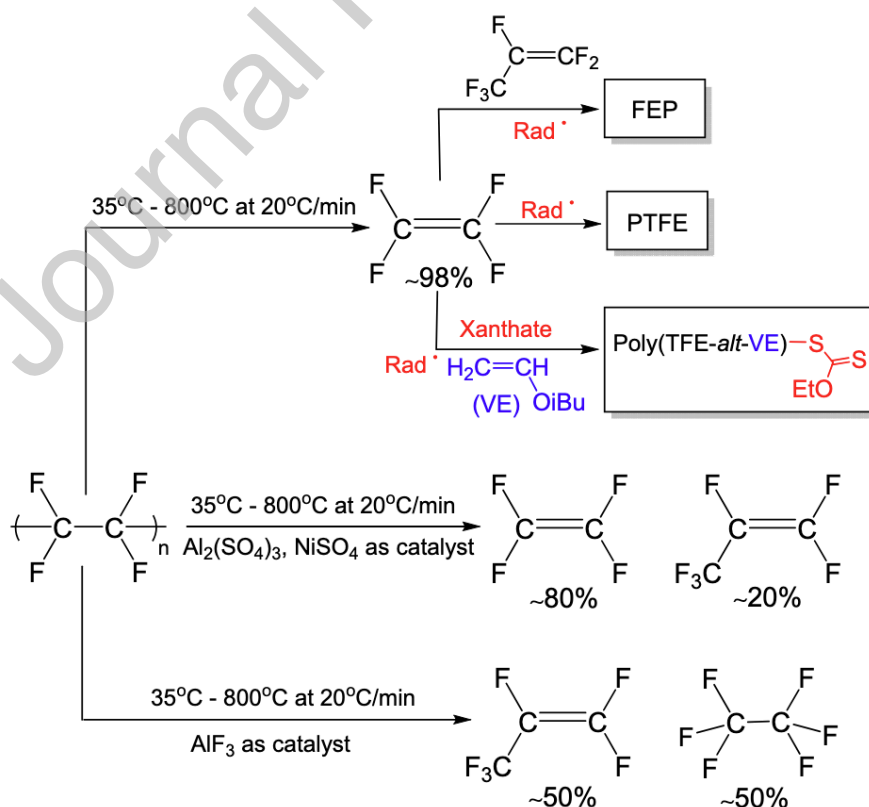


Fig. 65 : Thermal recycling of TFE from the thermolysis of PTFE with or without a catalyst and use for further (co)polymerization (readapted from MDPI [11,97,98,316]).

More recently, Yu et al. [268] reported a critical review on the current and global situation of PTFE (and its waste resources) recycling technologies, involving mechanical recycling and radiation cracking of PTFE, as well as recovering monomers from PTFE pyrolysis (though several references were missing) with anticipated development of environmentally sustainable and economically feasible chemical upgrading strategies [97,98,268], thus accelerating the process of industrializing the use of PTFE waste. A quite recent study by Lowe et al. [317] described a mechanochemical strategy for the reductive defluorination of PTFE, yielding an environmentally benign mixture of elemental carbon and sodium fluoride. The process employs inexpensive, commercially available chunks of sodium metal (though flammable; not specified) and proceeds rapidly at room temperature without any organic solvent. Remarkably, sodium fluoride (NaF) is obtained in 98 % yield (Fig. 66). Furthermore, the fluoride generated in the process can be directly upcycled *via in situ* mechanochemical fluorination reactions, delivering valuable sulfonyl fluoride and acyl fluoride products in excellent yields (Fig. 66).

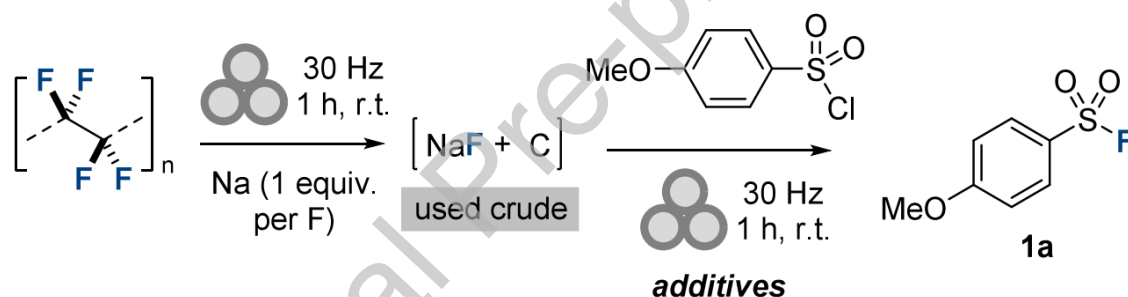


Fig. 66 : Mechanochemical Upcycling of Fluorine from PTFE to Sulfonyl Fluorides (reprinted with permission from ACS [317]).

Xiang and Tao [318] designed PTFE composites incorporating recycled PTFE waste powders, which were first compacted by compression molding at 40 MPa at room temperature in a cuboidal die and subsequently sintered at 380 °C for 2 h. Their results show that reprocessing PTFE debris can preserve mechanical integrity and enhance tribological properties, further illustrating the potential for a circular approach to PTFE. Moreover, Xi et al. [319] presented a mechanical recycling process for discarded PTFE/glass fiber laminates, in which the waste material is pulverized and recombined with new PTFE and glass layers to produce remanufactured composites that retain dielectric and structural properties comparable to those of the original material.

Chemical recycling of waste PTFE represents an advanced strategy [253,319] that transforms discarded plastics into high-value chemicals and fuels through processes such as thermal catalysis and other techniques [320].

Having demonstrated the recyclability of PTFE, the following section focuses on its degradation and mineralization.

11.3. Degradation-Mineralization

11.3.1. Thermal degradation of PTFE

Aleksandrov et al. [321] degraded TFE-based FPs waste (containing a mixture of FPs, Table 10) by means of a *BRENNkammer mit Dampfkessel* (Brenda) pilot plant. This enabled the authors to convert the mixture into inorganic fluorides, CO₂, and HF. Indeed, that efficient process requires high temperatures (850-1000 °C) to lead to no residual PFAS (< 1 ng/m³) in only 2 seconds. The same German team [322] revisited the incineration of FPs at their end of life and provided data supporting the mineralization of FP waste. They noted negligible PFAS release as products of incomplete combustion. These authors burned a mixed sample of FPs, representing 80% of commercially available FPs, under conditions representative of municipal and industrial waste incinerators operating in Europe. They used state-of-the-art emission sampling and Ultra-high Performance Liquid Chromatography coupled with tandem Mass Spectrometry (UPLC-MS/MS) and GC-MS to identify and quantify the released PFAS, for which standards were available and useful for this relevant work. Statistical analysis of the results confirmed the absence or insignificant amounts of PFAS, highlighting such efficient FP mineralization.

Chu et al. [323] investigated the microscopic thermal decomposition pathways of PTFE by combining plasma gasification experiments with multi-scale simulations. Molecular dynamics simulations identified two distinct degradation pathways: a pyrolysis-oxidation and chain-shortening-deep defluorination (POCD) route in oxygen, and a fluorine abstraction-hydrolysis-deep defluorination (FHD) route in steam. Density functional theory (DFT) calculations revealed the key roles of ¹O₂ and ¹H radicals in breaking the PTFE carbon backbone, supporting the proposed mechanisms. Experimental validation confirmed the simulation results, demonstrating that up to 80% of gaseous fluorine can be recovered within 5 minutes during plasma gasification, with optimal conditions determined *via* response surface methodology [323].

Table 10 : Mixture of various FPs in treatment of Brenda (where PFA and FKM stand for poly(TFE-co-perfluoroalkyl vinyl ether) and poly(VDF-co-HFP) copolymers or poly(VDF-*ter*-HFP-*ter*-TFE) terpolymer, respectively) [321].

Materials	Weight Fraction (wt.%)
PTFE tubes	63
PTFE tapes	7
PVDF	18
PFA	6
FKM Rubber	6

These researchers have begun to question the effectiveness of thermochemical conversion methods for PTFE mineralization, as well as the potential hazards posed by fluorinated byproducts. This creates an urgent need for more efficient, advanced PTFE mineralization technologies. To this end, a thorough examination of the intermediate and final products, thermal decomposition mechanisms, and effects of operating conditions during PTFE treatment is crucial. In addition, plasma-based techniques [117] have gained interest as a promising approach for FP degradation.

It is worth noting that Boucher et al. [324] and Koch [325] observed that the addition of nonvolatile basic compounds, such as calcium hydroxide Ca(OH)_2 and sodium hydroxide, can suppress the release of gaseous products (*e.g.*, atomic fluorine ($\text{F}_{(\text{g})}$)) during the thermal treatment of PTFE.

11.3.2. Mineralization via catalysts

A Japanese team [326] used molten alkaline metal hydroxide (NaOH, more efficient than KOH) to mineralize PTFE. The authors found that a simple, easy, and environmentally benign strategy based on a two-step procedure promotes the chemical recycling of PTFE to achieve effective mineralization. As a matter of fact, that route seems a bit surprising, since it is well known that

liquid sodium can react with PTFE. In the first step, PTFE was decomposed to soluble alkaline fluorides by degradation in molten hydroxides at elevated temperatures (500 °C). In a second step, CaF_2 , an essential starting mineral for all Organofluorine Chemistry, was obtained by treating the previous aqueous solution with CaCl_2 . PTFE was thus mineralized and, when heated with a large excess of NaOH at 500 °C for 3 h, 74 % yield of CaF_2 was obtained (Fig. 67). Actually, these temperatures are close to those enabling the unzipping depolymerization of PTFE [309].

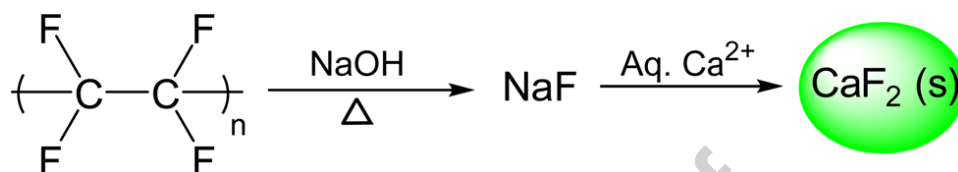


Fig. 67 : Suggested process of mineralization of PTFE by molten NaOH (reprinted with permission from RSC [326]).

These Japanese authors reported that (i) no decomposition was noted in the presence of molten NaOH below 400 °C, while ii) at 600 °C, the CaF_2 yields dropped to 46 % (from 67 % and 74 % at 450 °C and 500 °C, respectively, Fig. 68) [326].

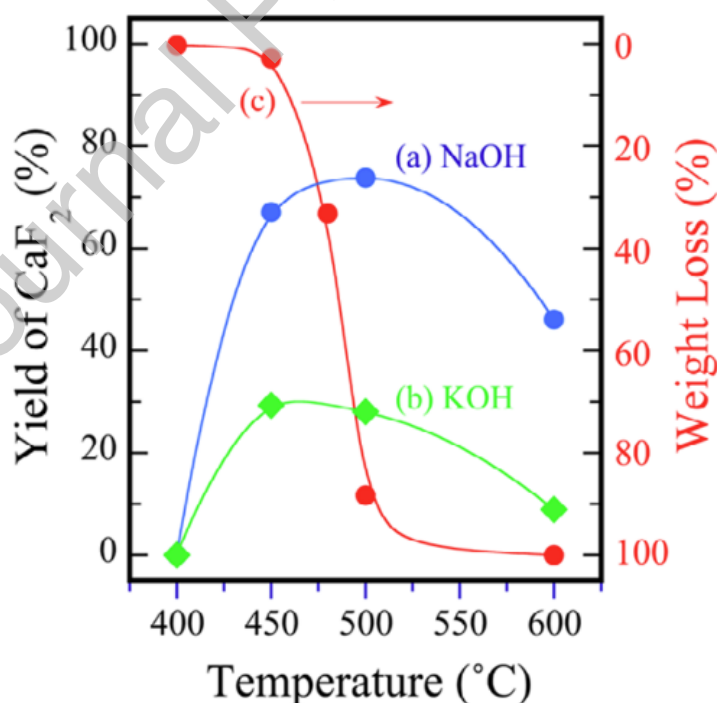


Fig. 68: Temperature dependence of PTFE degradation by molten alkaline hydroxides (curves a and b) and simple isothermal weight loss of PTFE (curve c). In each attempt, ca. 5 mmol of PTFE and an excess of MOH (M = Na, K) were used (reaction for 3 h at various temperatures under air) (reprinted with permission from RSC [326]).

For an increase of temperature up to ca. 450 °C, the macromolecular chains exhibit vigorous molecular motion, and chain scission occurs in the PTFE backbone. Subsequently, various small segments are generated from an unzipping mechanism [312]. The resulting fragments of the main chain underwent further scission to yield oligomers and/or low molar mass-derivatives. The obtained small molecules (*i.e.*, oligomers and monomers) then react with O^{2-} , which attacks the carbon atom according to a nucleophilic pathway to generate CO_2 and eliminate F^- .

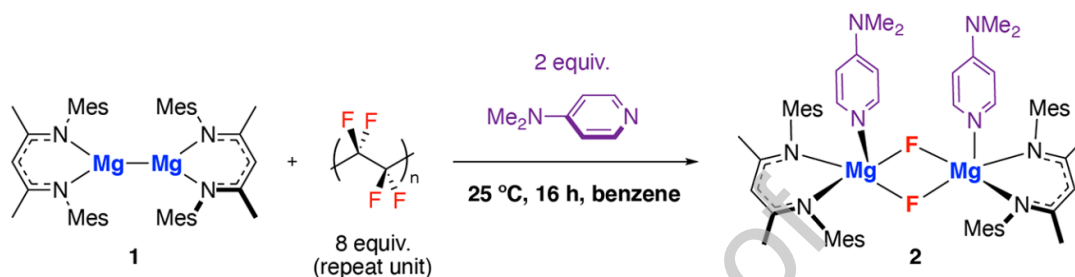


Fig. 69 : Room temperature reaction of magnesium complex **1** onto PTFE oligomers (reprinted with permission from ACS [327]).

Another approach involves a nucleophilic magnesium complex **1** (Fig. 69) that could react onto PTFE oligomers at room temperature, releasing a molecular magnesium fluoride, which was easily separated from the surface-modified PTFE [327]. The fluoride, in turn, could be utilized to transfer the fluorine atoms into a small array of compounds. This proof-of-concept study shows that the atomic fluorine content of PTFE can be harvested and reused in chemical synthesis.

11.3.3. Degradation by mechanochemistry

Mechanochemistry is a versatile room-temperature technique that supports green chemistry by enabling efficient, solvent-free or solvent-minimized reactions [328,329]. In this context, in addition to the above study on the valorization of PTFE [317], two recent mechanochemical investigations on the mineralization of PTFE have been reported. First, in 2025, the Gouverneur's team [330] proposed the total degradation of PTFE in the presence of phosphate activators at room temperature (Fig. 70), thereby returning to KF , which can serve as the fluorine source for further fluorination chemistry. At the same time, Shibata's group [331] used $KOtBu$ or other bases at 100 °C but reached a lower yield (42 %) on PTFE.

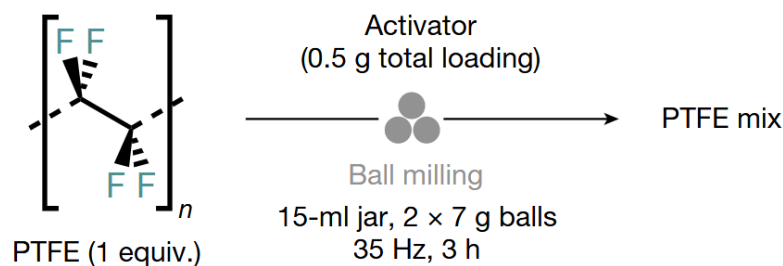


Fig. 70 : PTFE degradation induced by phosphate activators at room temperature (reprinted with permission from Spring Nature [330].

More recently, the British group [332] also used the same strategy to decompose PTFE in presence of silicate while Chen et al. [333] and Ackerman et al. [334] used metal nitride and KOtBu as activators, respectively in yields better than those reported by Shibata et al. [331]. Overall, Fig. 71 represents an interesting timeline, summarized by Lowe et al. [335].

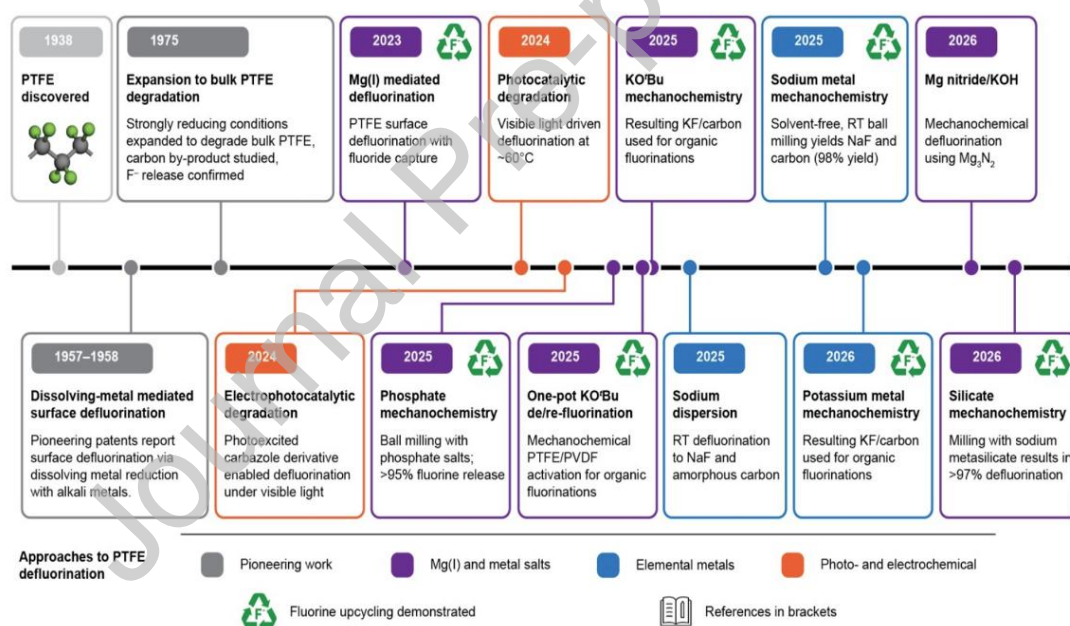


Fig. 71: Timeline, chronology and milestones for low temperature PTFE degradation and fluorine upcycling (reprinted with permission from the RSC [335].

11.3.4. Other methods of degradation of PTFE (chemical, tribochemical, and degradation by irradiation)

Park's research group [336] reported a chemical degradation approach for the e-PTFE support used in Proton Exchange Membrane Fuel Cell (PEMFCs), involving its reaction with radicals

and hydrogen peroxide during a Fenton reaction. After the Fenton reaction, the main chain of e-PTFE is cleaved, leading to significant changes in the support's chemical structure and morphology, thereby decreasing its tensile strength. However, the authors did not report a complete degradation of the e-PTFE [336]. Another simple and efficient method for the degradation of PTFE was reported by Nag et al. [337] in the presence of conventional metals such as gold, copper, zinc, silver, and iron (stainless steel) in an aqueous solution of carbohydrates like glucose and cyclodextrins, leading to the degradation of the polymer [337]. Nevertheless, the high cost of certain metals limits the industrial feasibility of this method. Fluoropolymers can also decompose when exposed to irradiation [117,268,303,338–341]. Dams and Hintzer [342] reported the degradation of high M_n fluoropolymers by electron beam radiation as a commercial process. However, this procedure leads to the formation of PFOA as a by-product at concentrations greater than 25 ppb. Nevertheless, the combination of irradiation and heat treatment in an oxygen-free atmosphere can reduce the formation of PFOA to less than 5 ppb [308].

11.4. Environmental Impact and Life-Cycle Assessment (LCA)

The recent study from Henry and Timmer [260] depicts a comprehensive analysis that PTFE does not induce any environmental issues due to its high thermal, aging and chemical resistance. LCA data on PTFE remain limited, yet available studies indicate a relatively high environmental footprint, particularly during production. The global warming potential (GWP) of CF_2ClH , the raw materials used for TFE synthesis, including upstream natural gas, chlorine for chloroform, fluorite (or Fluorspar), and sulfuric acid for hydrogen fluoride production, is estimated at 10.65 kg CO_2 -equivalent per kg TFE, based on cradle-to-gate data. For a PTFE-lined piping (2 in. diameter, 5 mm wall thickness), the carbon footprint was calculated to be 29.5 kg CO_2 -eq per meter of pipe, compared to 41.3 kg CO_2 -eq/meter for equivalent stainless-steel piping under similar operating conditions. Other industrial sources report that the production of 1 kg of PTFE generates between 7.06-7.8 kg of CO_2 [260] or ca. 13-18 kg of CO_2 [229]. Actually, when PTFE is used in wind turbine bearings, it can extend the turbine's operational life by up to 15 years. The reduced maintenance and replacement needs of these initial emissions are effectively "offset" within two to three years of operation. From another perspective, PTFE's environmental impacts are minimal during its use phase due to its durability, chemical inertness, and long service life [260].

12. Limits, challenges, prospects and outlooks

12.1. Irreplaceable polymer and possible alternatives to PTFE

As discussed in this review, PTFE has been used for many decades in a wide range of industrial and consumer applications due to its special and unique properties. However, following the European Union's restrictions on PFAS, which include PTFE, it has become essential to identify suitable substitutes. Actually, so far, no substitute of PTFE has been found.

To address this lack of PTFE alternatives, two recent AI-based studies have been reported. The first one examined more than 33,000 documents, including reviews, publications, patents, and scientific reports, to propose two interesting possible alternatives which failed when tested under conditions as aggressive as those tolerated by PTFE.

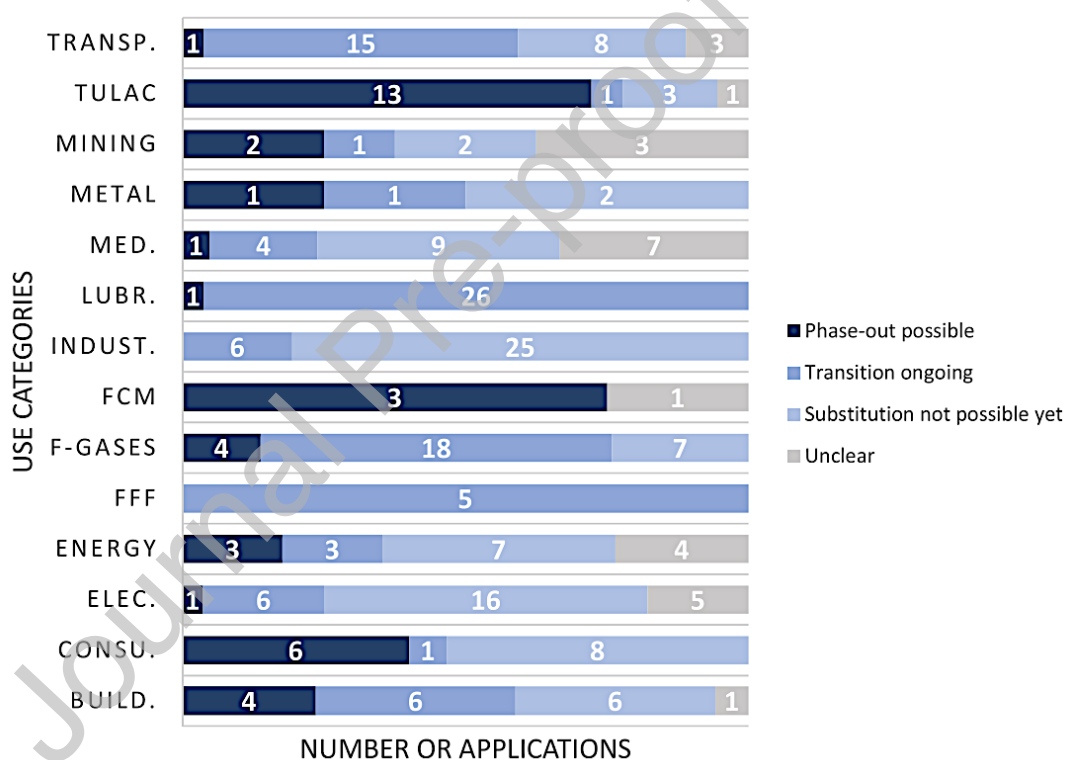


Fig. 72 : Substitution Potential of PFAS (reprinted with permission from ACS [343]).

The other study also identified various sectors and noted a total of 530 PFAS-free alternatives [343]. Based on a screening of potential concerns for the identified alternatives, their performance relative to PFAS, and their market availability, it is concluded that potentially suitable alternatives to PFAS are available for 40 applications. For 83 applications, no alternatives could be identified at the time of the study, and “*should be the focus of further research activities*”. Fig. 72 displays the potential for substituting PFAS in each use category. At last, for 93 applications, either no suitable alternatives have been identified at the time of the

analysis, or the suggested alternatives are still under development and not yet available on the market.

Moreover, from the Office of the Assistant Secretary of Defense for Energy, Installations, and Environment, no alternative has yet been identified to replace PTFE membranes, and it is estimated that from conception to market, a viable PFAS alternative would take 10 to 15 years.

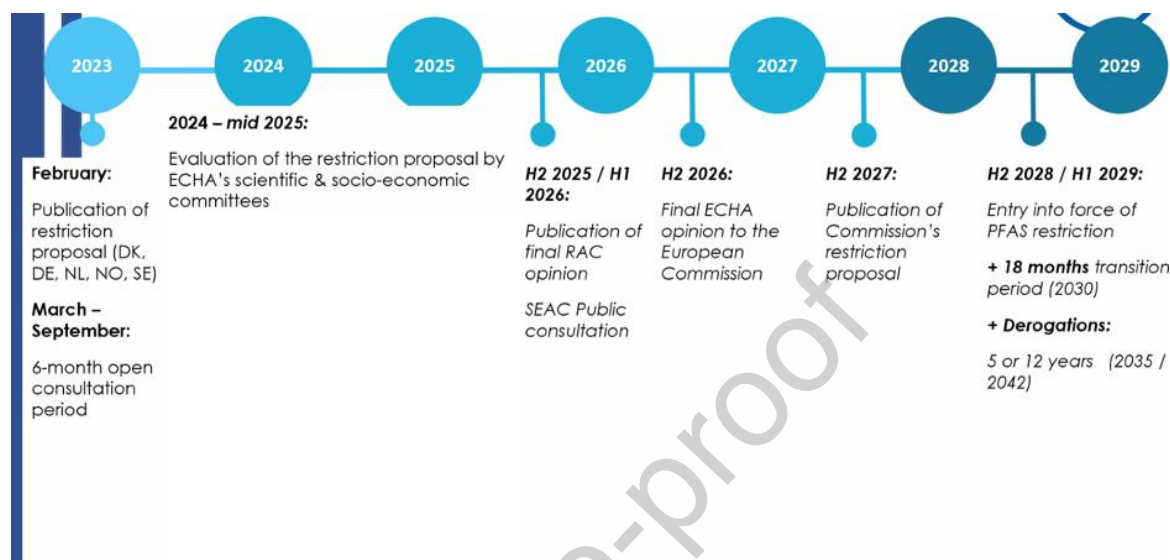


Fig. 73 : Timeline of the European Chemical Agency (ECHA) *versus* year (susceptible to be modified) [344].

Conclusions

PTFE is a safe material reaching quite high molar masses and is not currently subjected to regulatory restrictions. Thanks to its exceptional chemical, thermal, UV and aging resistance, waterproofness and moisture vapor permeability, PTFE is used in many advanced applications. As industries increasingly prioritize safety, operational efficiency and sustainability, PTFE's unique physicochemical properties, combined with continuous technological improvements, position this specialty polymer as a key material for next-generation of aerospace, electronics and medical technologies.

From the perspectives of decarbonization, circularity, risk prevention, reliability, durability and non-obsolescence, PTFE makes a substantial contribution to modern industrial systems. Its exceptional performance ensures its continued relevance, making it an irreplaceable material in many areas of daily life. PTFE components are incorporated into a wide range of products and devices, spanning diverse applications from industrial equipment to high-performance electronic systems and in medical apparatus.

Industrial sectors account for around 48 % of global PTFE consumption, while the electrical and electronic sectors represent approximately 22 %. PTFE market growth is particularly pronounced in the Asia-Pacific region, where PTFE-related industrial output increased by around 11% between 2022 and 2023, reflecting a strong demand driven by technological expansion and manufacturing growth. Thus, the global PTFE market size was valued at USD 3.63 billion in 2023 and is expected to reach USD 5.25 billion by 2030, growing at a Compound Annual Growing Rate (CAGR) of 5.5% from 2024 to 2030.

Although regarded as a PFAS under the OECD definition, PTFE meets the 13 PLC criteria. Following the first consultation on the PFAS dossier, which led to more than 5600 comments, a second public consultation on the PFAS restriction dossier is scheduled for spring 2026 was implemented and the consultation closed on May, 25th, 2026 (Fig. 73) [345]. 3511 comments from more than 250 individuals and 3200 organizations were submitted during the 60-day consultation on the draft opinion of ECHA's Committee for Socio-Economic Analysis (SEAC). Presently, SEAC is assessing the contributions and is expected to adopt its final opinion on the proposed restriction of PFAS by the end of 2026 [346]. Following this consultation Hence, numerous clarifications and regulatory decisions are expected that could significantly impact the future regulatory landscape for fluoropolymers.

Considering its exceptional properties, critical role in high-technology applications, and growing production, PTFE continues to maintain its high standard as a specialty polymer and remains an exceptional material. Many sectors, including medical technology, aerospace, car industries, optics and electronics, which require PTFE as a unique item, have begun to issue warnings if the ECHA's proposed ban is adopted, and it is expected that this material, like all FPs, will see more derogations.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. No conflict of interest exists in the submission of this manuscript, and the manuscript is approved by all authors for publication. The manuscript has not been submitted or considered for publication elsewhere.

Credit authorship contribution statement

Saly Hawila: writing – original draft, methodology, formal analysis. **Jean-Pierre Habas:** writing – original draft, methodology, formal analysis, conceptualization, supervision. **Bruno Améduri:** writing – original draft, methodology, formal analysis, conceptualization, supervision.

Data availability

Data will be made available on request.

Acknowledgment

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Graphical Abstract

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