

4 Introduction to Fluoropolymers

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4.1 Introduction

Fluoropolymer is usually olefinic polymer which consists of partially or fully fluorinated olefinic monomers such as vinylidene fluoride ($\text{CH}_2=\text{CF}_2$) and tetrafluoroethylene (TFE) ($\text{CF}_2=\text{CF}_2$). These polymers have been covered in great detail in a number of references (see General References). More specialty fluorinated polymers include perfluoroethers, fluoroacrylates, and fluorosilicones which are used in significantly smaller volume than olefinic fluoropolymers. These fluoropolymers and others are covered in detail elsewhere [1,2].

Commercial fluoropolymers include homopolymers and copolymers. Homopolymers contain 99% or more by weight one monomer and 1% or less by weight of another monomer according to the convention by American Society for Testing Materials (ASTM). Copolymers contain more than 1% or more by weight of one or more comonomers. The major commercial fluoropolymers are based on three monomers: TFE, vinylidene fluoride (VF_2), and to a lesser extent chlorotrifluoroethylene (CTFE). Examples of comonomers include perfluoromethyl vinyl ether (PMVE), perfluoroethyl vinyl ether (PEVE), perfluoropropyl vinyl ether (PPVE), hexafluoropropylene (HFP), CTFE, perfluorobutyl ethylene (PFBE), and exotic monomers such as 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole.

The fluoropolymers reviewed in this chapter include polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer (PFA), fluorinated ethylene-propylene polymer (FEP), ethylene-tetrafluoroethylene copolymer (ETFE), ethylene-chlorotrifluoroethylene copolymer (ECTFE), polychlorotrifluoroethylene (PCTFE), polyvinylidene fluoride (PVDF), and polyvinyl fluoride (PVF). Classification, preparation, properties, fabrication, safety considerations, and economics of fluoropolymers are reviewed. Monomer synthesis and properties have also been discussed.

A good rule of thumb to remember is that increasing the fluorine content of a polymer molecule increases its chemical and solvent resistance, flame resistance, and photostability; improves its electrical properties such as lower dielectric constant; lowers coefficient of friction; raises melting point; increases its thermal stability; and weakens its mechanical properties. Solubility of polymers in solvents usually decreases by increasing the fluorine content of the molecule.

4.2 Fluoropolymer Classification

The serendipitous discovery of PTFE in 1938 by Roy Plunkett of DuPont Company [3] began the era of fluoropolymers. PTFE has found thousands of applications because of its unique properties. Various fluoroplastics (Figure 4.1) have been developed since the discovery of PTFE. A number of companies produce these plastics around the world (Tables 4.1 and 4.2). Fluoropolymers are divided into two classes of perfluorinated and partially fluorinated polymers. Perfluorinated fluoropolymers are homopolymers and copolymers of TFE. Some of the comonomers may contain a small amount of elements other than C or F.

For example, PFA is a copolymer of TFE and perfluoroalkyl vinyl ether that contains oxygen. R_f is a perfluoroalkyl group of $\text{C}_1\text{--C}_4$.

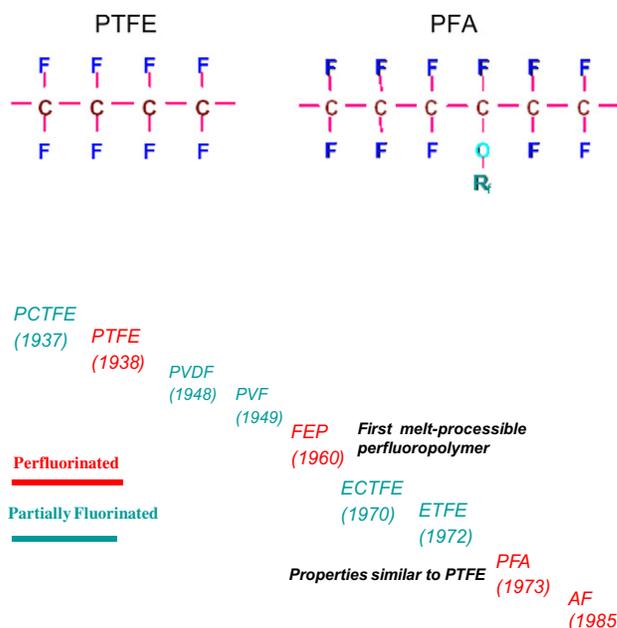


Figure 4.1 Evolution of fluoropolymer development over time. (PCTFE = polychlorotrifluoroethylene, PVDF = polyvinylidene fluoride, PVF = polyvinyl fluoride, FEP = fluorinated ethylene-propylene polymer, ECTFE = ethylene chlorotrifluoroethylene polymer, ETFE = ethylene-tetrafluoroethylene polymer, PFA = perfluoroalkoxy polymer, AF = amorphous fluoropolymers).

Table 4.1 Global producers of fluoropolymers

Company	Product
DuPont	PTFE, FEP, PFA, ETFE, PVF
Daikin	PTFE, FEP, PFA, ETFE, PVDF, PCTFE, E-FEP
Arkema	PVDF, PCTFE
Asahi Glass	PTFE, PFA, ETFE
Solvay Solexis	PTFE, PVDF, ECTFE, PFA/MFA
Dyneon	PTFE, FEP, PFA, THV, PVDF
Constructive Bureau Russia	PTFE, small amounts of other polymers
Tarnowie-Moscicach S.A. Poland	PTFE
Kureha	PVDF
Honeywell	PCTFE

Table 4.2 Global producers of fluoropolymers

Company	Product
Gujarat Fluorochemicals Ltd.	PTFE
Hindustan Fluoropolymer	PTFE
Shanghai 3F	PTFE, PVDF, FEP
Fuxin Hengtong	PTFE
Jiangsu Meilan	PTFE
Jinan 3F	PTFE, FEP
Zhejiang Jusheng	PTFE
Zhonghao Chenguang Res Inst.	PTFE, PVDF
Shandong Dongyue	PTFE

Partially fluorinated fluoropolymers contain hydrogen (H) or other atoms such as chlorine, in addition to fluorine and carbon. The most significant are homopolymers and copolymers of PVDF. There are also copolymers and homopolymers of chlorotrifluoroethylene (PCTFE), although some have elastomeric properties. Other significant fluoroplastics include ETFE, ECTFE, and PVF.

4.3 Polymer Development History

PTFE cannot be fabricated by melt-processing techniques because of its high viscosity (10^{10} – 10^{12} poise at 380 °C). Melt-processible fluoropolymers have been developed by copolymerization of TFE. FEP, a copolymer of TFE and HFP, has a lower maximum continuous use temperature than PTFE

(200 °C vs. 260 °C) because of the deterioration of mechanical properties. PFA, a copolymer of TFE with PPVE or PEVE, offers thermal stability, melt-processibility and maximum continuous use temperature—260 °C. Both FEP and PFA are considered perfluoropolymers.

Copolymers of ethylene with tetrafluoroethylene (ETFE) and chlorotrifluoroethylene (ECTFE) are mechanically stronger than perfluoropolymers, accompanied with trade-offs of reduction in their chemical resistance and continuous use temperature and an increase in the coefficient of friction.

Amorphous copolymers of TFE are soluble in special halogenated solvents and can be applied to surfaces as a polymer solution to form thin coatings. The dried coating is as resistant to almost as many chemicals as PTFE. [4]

4.4 Monomer Synthesis

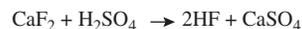
4.4.1 Synthesis of Tetrafluoroethylene

The first reliable and complete description of TFE synthesis was published in 1933 by Ruff and Bretschneider [5] in which they prepared TFE ($\text{CF}_2=\text{CF}_2$, CAS number 116-14-3) from decomposition of tetrafluoromethane in an electric arc. TFE was obtained by bromination and separation of the dibromide ($\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$) from the other reaction products. Dehalogenation with zinc was the next step for obtaining pure TFE. Commercially significant techniques for TFE preparation list fluorspar (CaF_2), hydrofluoric acid, and chloroform as the starting ingredients [6–13], as shown in the reaction sequence in Figure 4.2.

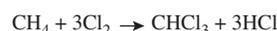
Among other compounds produced are HFP and a small amount of highly toxic perfluoroisobutylene.

Sherratt [14] and others [15] have provided complete descriptions of the preparation of TFE. The overall yield of TFE production depends on the pyrolysis reaction. The products of pyrolysis are cooled, scrubbed with a dilute basic solution to remove HCl, and dried. The resulting gas is

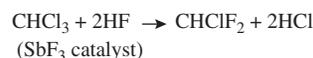
HF preparation:



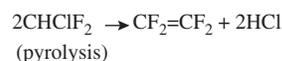
Chloroform preparation:



Chlorodifluoromethane preparation:



TFE synthesis:

**Figure 4.2** Synthesis reactions of tetrafluoroethylene.

compressed and distilled to recover the unreacted CHClF_2 and high purity TFE. Polymerization of TFE to high molecular weight requires extreme purity, thus ensuring the removal of all traces of telogenic hydrogen or chlorine-bearing impurities. TFE can autopolymerize if it is not inhibited by terpenes, such as α -pinene, terpene B, and d-limonene [16].

4.4.2 Synthesis of Hexafluoropropylene

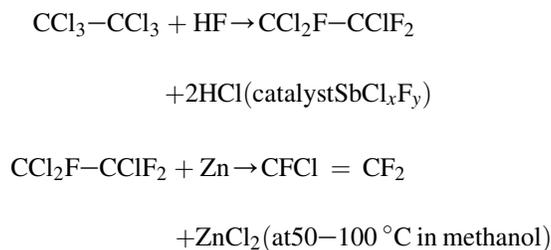
HFP ($\text{CF}_3\text{CF}=\text{CF}_2$, CAS number 116-15-4) was first prepared by Benning et al. [17] by pyrolysis. The full synthesis and identification of HFP was conducted by Henne [18]. A six step reaction scheme starting with the fluorination of 1,2,3-trichloropropane led to 1,2-dichloro-hexafluoropropane. The latter was dehalogenated with zinc in boiling ethanol to yield HFP. HFP is a co-product in the synthesis of TFE. HFP yield can be increased, in lieu of TFE production, by altering the reaction conditions such as reduction in the pyrolysis temperature and use of steam as diluent of the reactants [19,20].

4.4.3 Synthesis of Perfluoroalkyl Vinyl Ethers

Perfluoroalkyl vinyl ethers such as perfluoropropyl vinyl ether ($\text{CF}_2=\text{CF}-\text{O}-\text{C}_3\text{F}_7$, CAS number 1623-05-8) are synthesized according to the steps shown in Figure 4.3 as well as alternative techniques [21]. There are other processes including electrochemical methods for the production of perfluoro-2-alkoxy-propionyl fluoride [22].

4.4.4 Synthesis of Chlorotrifluoroethylene

This monomer is fairly simple to manufacture compared to the perfluorinated monomers [25–28]. The commercial process for the synthesis of CTFE ($\text{CF}_2=\text{CClF}$, CAS number 79-38-9) begins with 1,1,2-trichloro-1,2,2-trifluoroethane (TCTFE). It is dechlorinated by pyrolysis at 500–600 °C in vapor phase. An alternative method for preparation of TCTFE is catalytic dechlorination:

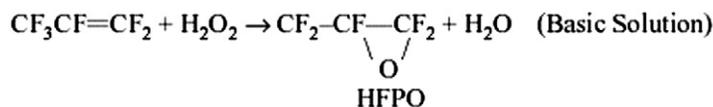


The reaction stream is put through a number of purification and distillation steps to remove the gaseous and liquid contaminants. CTFE is further purified by the removal of methyl chloride, dimethyl ether, and water by passing the gas stream through sulfuric acid. Water and hydrochloric acid are removed by passing the CTFE through an alumina column before condensing it into a liquid.

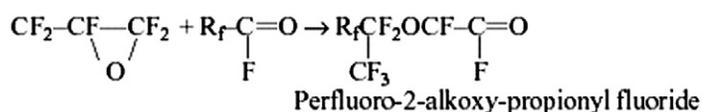
4.4.5 Synthesis of Vinylidene Fluoride

There are numerous ways to prepare vinylidene fluoride (VDF) ($\text{CF}_2=\text{CH}_2$, CAS number 75-38-7) [29,30]. Two

1. Hexafluoropropylene is converted hexafluoropropylene epoxy (HFPO) reacting HFP with oxygen under pressure in the presence of an inert diluent at 50–250 °C or with an oxidizer such as hydrogen peroxide in a basic solution:^{[43][44]}



2. HFPO is reacted with a perfluorinated acyl fluoride to produce perfluoro-2-alkoxy-propionyl fluoride:



3. Perfluoro-2-alkoxy-propionyl fluoride is reacted with the oxygen containing salt of an alkali or alkaline earth metal at an elevated temperature which depends on the type of salt. Examples of the salts include sodium carbonate, lithium carbonate, and sodium tetraborate:^[45]

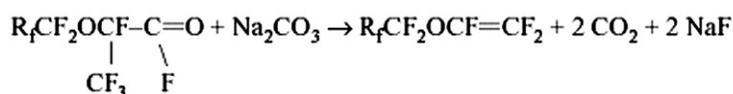


Figure 4.3 Synthesis of perfluoroalkyl vinyl ethers [23–24].

methods, including the popular commercial technique for VDF production, are described. Conversion of 1,1,1-trifluoroethane [31] begins by passing this gas through a platinum-lined Inconel tube, which is heated to 1200 °C. Contact time is about 0.01 seconds. The exit gases are passed through a sodium fluoride bed to remove the hydrofluoric acid and are then collected in a liquid nitrogen trap. VDF is separated by low temperature distillation. Unreacted trifluoroethane is removed at -47.5 °C and is recycled.

The commercial method begins with hydrofluorination of acetylene followed by chlorination [32], by hydrofluorination of trichloroethane [33], or by hydrofluorination of vinylidene chloride [34]. In each case the final product, 1-chloro-1,1-difluoroethane, is stripped of a molecule of hydrochloric acid to yield VDF.

4.4.6 Synthesis of Vinyl Fluoride

Vinyl fluoride (VF)($\text{CHF}=\text{CH}_2$, CAS number 75-02-5) [35–39] was first prepared by the reaction of 1,1-difluoro-2-bromoethane (CAS number 359-07-9) with zinc. Most approaches to VF synthesis have employed reactions of acetylene (CAS number 74-86-2) with hydrogen fluoride (HF) either directly or utilizing catalysts. Other routes have involved ethylene (CAS number 74-85-1) and HF, pyrolysis of 1,1-difluoroethane (CAS number 624-72-6) and fluorochloroethanes, reaction of 1,1-difluoroethane with acetylene, and halogen exchange of vinyl chloride (CAS number 75-01-4) with HF [40–42].

4.5 Monomer Properties

4.5.1 Properties of Tetrafluoroethylene

Tetrafluoroethylene **15, 44** is a colorless, odorless, tasteless, nontoxic gas which boils at -76.3 °C and melts at -142.5 °C. The critical temperature and pressure of TFE are 33.3 °C and 3.92 MPa. TFE is stored as a liquid; vapor pressure at -20 °C is 1 MPa. Its heat of formation is reported to be -151.9 kcal/mole. Polymerization of TFE is highly exothermic and generates 41.12 kcal/mole heat—the extent of which can be compared with the heats of polymerization of vinyl chloride and styrene, at 23–26 kcal/mole and 16.7 kcal/mole, respectively.

Safe storage of TFE requires its oxygen content to be less than 20 ppm. Temperature and pressure should be controlled during its storage. Increasing the temperature, particularly at high pressures, can initiate deflagration in the absence of air (TFE degrades into carbon tetrafluoride). In the presence of air or oxygen, TFE forms explosive mixtures in the molar percentage range of 14–43% [44]. Detonation of a mixture of TFE and oxygen can increase the maximum pressure to 100 times the initial pressure.

4.5.2 Properties of Hexafluoropropylene

Hexafluoropropylene is a colorless, odorless, tasteless, and relatively low toxicity gas, which boils at -29.4 °C and freezes at -156.2 °C. In a 4-hour exposure, a concentration of 3000 ppm corresponded to LC50 in rats [45,46]. Critical temperature and pressure of HFP are 85 °C and 3254 MPa. Unlike TFE, HFP is extremely stable with respect to auto-polymerization and may be stored in liquid state without the addition of telogen. HFP is thermally stable up to 400–500 °C. At about 600 °C under vacuum, it decomposes and produces octafluoro-2-butene ($\text{CF}_3\text{CF}=\text{CFCF}_3$) and octafluoroisobutylene [47].

4.5.3 Properties of Perfluoroalkyl Vinyl Ethers

Perfluoroalkyl vinyl ethers (PAVE) form [22] an important class of monomers in that they are comonomers of choice for the “modification” of the properties of homofluoropolymers in addition to broad use in the structure of copolymers of TFE. The advantage of PAVEs as modifiers over HFP is their remarkable thermal stability. A commercially significant example is perfluoropropyl vinyl ether (PPVE). PPVE is an odorless, colorless liquid at room temperature. It is extremely flammable and burns with a colorless flame. It is less toxic than HFP.

4.5.4 Properties of Chlorotrifluoroethylene

Chlorotrifluoroethylene is a colorless gas at room temperature and pressure. It is fairly toxic with an LC50 (rat) at 4-hour exposure and a concentration of 4000 ppm [49]. It has a critical temperature and pressure of 105.8 °C and 4.03 MPa. Oxygen and liquid CTFE react and form peroxides at fairly low temperatures. A number of oxygenated products, such as chlorodifluoroacetyl fluoride, are generated by oxidation of CTFE [48]. The same reaction can occur photochemically in the vapor phase. Chlorotrifluoroethylene oxide is a by-product of this reaction. The peroxides act as initiators for the polymerization of CTFE, which can occur violently.

4.5.5 Properties of Vinylidene Fluoride

Vinylidene fluoride, ($\text{CH}_2=\text{CF}_2$), is [49] flammable and is a gas at room temperature. It is colorless and almost odorless and boils at -84 °C. VDF can form explosive mixtures with air. Polymerization of this gas is highly exothermic and takes place above its critical temperature and pressure.

4.5.6 Properties of Vinyl Fluoride

Vinyl fluoride (75-02-5) (fluoroethene) is a colorless gas at ambient conditions [38]. It is flammable in air between the limits of 2.6 and 22% by volume. Minimum ignition

temperature for VF and air mixtures is 400 °C. Adding a trace amount (<0.2%) of terpenes is effective to prevent spontaneous polymerization of VF. Inhibited VF has been classified as a flammable gas by the U.S. Department of Transportation.

4.6 Polymerization and Finishing

4.6.1 Polytetrafluoroethylene, PTFE (CAS number 9002-84-0)

PTFE is produced [43,50] by free-radical polymerization mechanism in an aqueous media via addition polymerization of TFE in a batch process. The initiator for the polymerization is usually a water-soluble peroxide such as ammonium persulfate or disuccinic peroxide. A redox catalyst is used for low temperature polymerization. PTFE is produced by suspension (or slurry) polymerization without a surfactant to obtain granular resins or with a perfluorinated surfactant (emulsion polymerization) such as ammonium perfluorooctanoate to produce fine powder and dispersion products. Polymerization temperature and pressure usually range from 0 to 100 °C and 0.7 to 3.5 MPa. See Section 4.11 for information about ammonium perfluorooctanoate.

Granular PTFE is produced by polymerizing TFE alone or by using trace amounts of comonomers. A peroxide initiator, little or no surfactant, and other additives may be present in the aqueous polymerization medium that is vigorously stirred and sometimes buffered by an alkaline solution. Most of the polymer is formed in the gas phase in the shape of stringy and irregularly shaped particles. The particles are comminuted to different sizes, depending on the powder properties required by the fabrication process. For example, a smoother surface part requires smaller particle size while good flow is improved by larger particle size.

Fine powder PTFE is produced by polymerization of TFE in an aqueous medium in the presence of an initiator and surfactant. The polymerization does not follow a conventional emulsion mechanism but some of the principles, which apply. The stability of the dispersion during the polymerization, to avoid premature coagulation, is balanced against the need to break the emulsion to recover the PTFE. Low shear rate agitation is maintained during the polymerization using surfactant levels below the critical micelle concentration. The rate of polymerization and particle shape and size are affected by the concentration of the surfactant. Majority of the particles is generated in the early part of polymerization and grows as the cycle proceeds. Molecular weight and composition within the particle can be controlled using the polymerization ingredients and conditions.

The same polymerization process makes aqueous dispersions of PTFE as fine powder. The dispersion is concentrated

and stabilized using a variety of ionic and nonionic surfactants. Several concentration methods have been reported including electrodecentration, evaporation, and thermal concentration. Chemical additives to match them with the fabrication process or part property requirements can modify the final PTFE dispersion.

Filled compounds are produced from all three forms of PTFE using fillers such as glass fiber, graphite, metal powder, carbon fiber, and others [50].

4.6.2 Perfluoroalkoxy Polymer, PFA (CAS number 26655-00-5)

PFA is a copolymer of TFE and perfluoroalkyl vinyl ether such as PPVE. Copolymerization of perfluoroalkyl vinyl ethers with TFE can be done in a halogenated solvent [51,52] in an aqueous phase [53] sometimes containing some halogenated solvent, usually in the absence of a surfactant [54]. Terpolymers of this class contain other monomers such as HFP.

Commercially, PFA is polymerized by free-radical polymerization mechanism usually in an aqueous media via addition polymerization of TFE and PPVE. The initiator for the polymerization is usually water-soluble peroxide such as ammonium persulfate. Chain transfer agents such as methanol and acetone are used to control the molecular weight of the resin. Generally, the polymerization regime resembles that used to produce PTFE by emulsion polymerization. Polymerization temperature and pressure usually range from 15 to 95 °C and 0.5 to 3.5 MPa.

End groups are stabilized by treating the PFA with methanol, ammonia, amines, and elemental fluorine that produces CF₃ end groups [55–59]. The polymer is recovered, dried, and melt-extruded into cubes for melt fabrication processes. PFA is also available in bead (as polymerized), dispersion, and fine powder forms.

4.6.3 Perfluorinated Ethylene–Propylene Copolymer, FEP (CAS number 25067-11-2)

FEP is a random copolymer of TFE and HFP which can be polymerized, in an aqueous or a nonaqueous media [54,60]. Terpolymers of this class contain other monomers such as perfluoroalkyl vinyl ether (e.g., PPVE) to improve stress crack resistance.

Commercially, it is polymerized by free-radical polymerization mechanism usually in an aqueous (or nonaqueous) media via addition polymerization of TFE and HFP. The initiator for the polymerization is usually water-soluble peroxide such as potassium persulfate. Chain transfer agents could be used to control the molecular weight of the resin. In general, the polymerization regime and conditions

resemble those used to produce PTFE by emulsion polymerization. FEP is recovered, dried, and melt-extruded into cubes for melt fabrication processes. FEP is also available in dispersion form.

4.6.4 Ethylene—Co-tetrafluoroethylene Polymers, ETFE (CAS number 68258-85-5)

This plastic is a partially fluorinated straight-chain polymer with very high molecular weight [56]. It is produced by free-radical polymerization mechanism in a solvent or a hybrid (a solvent/aqueous mixture) media, using an organic peroxide initiator. Copolymerization of TFE and ethylene ($\text{CH}_2=\text{CH}_2$, molecular weight 28, CAS number 74-85-1) proceeds by an addition mechanism.

Copolymers of TFE and ethylene are highly crystalline and fragile at elevated temperatures and are modified by a third monomer. Production of ETFE terpolymers having improved high-temperature mechanical (especially tensile) properties has been demonstrated [63]. They comprise of 40–60 mole% ethylene, 40–60% TFE, and a small amount of a polymerizable vinyl termonomer such as perfluoroisobutylene, PPVE, and HFP.

4.6.5 Ethylene—Co-chlorotrifluoroethylene Polymers, ECTFE (CAS number 25101-45-5)

This polymer is formed by the polymerization of ethylene and CTFE [64] in aqueous and solvent mediums using organic peroxides and oxygen-activated triethylboron. Typical polymerization is done at 60–120 °C and a pressure of 5 MPa or higher. The polymerization reaction can also be initiated by radiation like gamma rays. The most effective catalyst is tri-*n*-butyl boron which produces an ECTFE with an alternating 1:1 ethylene to TFE ratio. To control the molecular weight of the resin, chain transfer agents such as chlorinated compounds, alcohols, and ketones are required.

4.6.6 Polychlorotrifluoroethylene, PCTFE (CAS number 9002-83-9)

CTFE is polymerized by bulk, suspension, and emulsion techniques [65]. Bulk polymerization takes place using halogenated acyl peroxide catalysts or UV and gamma rays. Suspension polymerization is carried out in aqueous medium using inorganic or organic peroxide catalysts. Emulsion polymerization yields a polymer with a normal molecular weight distribution and a molecular weight—melt viscosity relationship similar to bulk polymerized polymer. Inorganic peroxy catalysts initiate the reaction in the presence of halogenated alkyl acid salt surfactants. Emulsion polymerization produces the most thermally stable PCTFE.

4.6.7 Polyvinylidene Fluoride, PVDF (CAS number 24937-79-9)

The first successful aqueous polymerization of VDF was reported in 1948 [66] using a peroxide initiator in water at 50–150 °C and 30 MPa. No surfactants or suspending agents were present in the polymerization recipe. PVDF has been polymerized by a number of methods including emulsion, suspension, solution, and bulk. Later, copolymers of VDF with ethylene and halogenated ethylene monomers were also produced [67]. In 1960, a manufacturing process was developed and PVDF was first introduced to the market. Reaction temperature ranges from 10 to 150 °C at pressure of 1 MPa or higher. Similar to TFE, emulsion polymerization of VDF requires a stable fluorinated surfactant and an initiator such as peroxide or persulfate. Suspension polymerization is conducted in an aqueous medium sometimes in the presence of a colloidal dispersant such as a hydroxy cellulose. Solution polymerization of VDF in solvents using free radical initiators is another way of producing PVDF. PVDF is commercially produced by aqueous emulsion or suspension processes.

4.6.8 Polyvinyl Fluoride, PVF (CAS number 24981-14-4)

Vinyl fluoride undergoes free-radical polymerization [39,68]. The first polymerization involved heating a saturated-solution of VF in toluene at 67 °C under 600 MPa for 16 hours. A wide variety of initiators and polymerization conditions have been explored. Examples of bulk and solution polymerizations exist; however, aqueous suspension or emulsion methods are generally preferred. Copolymers of VF and a wide variety of other monomers have been prepared. More recently, interpolymers of VF have been reported with TFE and other highly fluorinated monomers such as HFP, perfluorobutylethylene, and perfluoroethyl vinyl ether.

4.7 Structure—Property Relationship

A way to understand the impact of fluorine is to explore the differences between linear polyethylene (PE) and PTFE [37] which is the ultimate fluoropolymer in terms of properties and characteristics. There are important differences between properties of PE and that of PTFE:

- PTFE is one of the lowest surface energy polymers
- PTFE is the most chemically resistant polymer
- PTFE is one of the most thermally stable polymers
- Melting point and specific gravity of PTFE are more than double those of polyethylene

PTFE and PE differences are attributable to the differences of C—F and C—H bonds. The differences in the

electronic properties and sizes of F and H lead to the following observations:

- F is the most electronegative of all elements (4 Paulings)
- F has unshared electron pairs
- F is more easily converted to F^-
- Bond strength of C–F is higher than C–H
- F is larger than H

The electronegativity of carbon at 2.5 Paulings is somewhat higher than that of hydrogen (2.1 Paulings) and lower than the electronegativity of fluorine. Consequently, the polarity of the C–F bond is opposite to that of the C–H bond, and the C–F bond is more highly polarized. In the C–F bond, the fluorine end of the bond is negatively charged compared to the C–H bond in which the carbon is negatively charged.

The difference in bond polarity of C–H and C–F affects the relative stability of the conformations of the two polymer chains. Crystallization of polyethylene takes place in a planar and trans conformation. PTFE can be forced into such a conformation at extremely high pressure [66]. PTFE, below 19 °C, crystallizes as a helix with 0.169 nm per repeat distance: it takes 13 C atoms for a 180° turn to be completed. Above 19 °C, the repeat distance increases to 0.195 nm which means that 15 carbon atoms are required for a 180° turn. At above 19 °C the chains are capable of angular displacement, which increases above 30 °C until reaching melting point (327 °C).

Substitution of F for H in the C–H bond substantially increases the bond strength from 99.5 kcal/mole for the C–H bond to 116 kcal/mole for the C–F bond. Consequently, thermal stability and chemical resistance of PTFE is higher than PE because more energy is required to break the C–F bond. The polarity and strength of the C–F bond render F atom abstraction mechanism for branching difficult. In contrast, highly branched polyethylene (>8 branches per 100 carbon atoms) can be synthesized. Branching mechanism

as a tool to adjust crystallinity is not practical for PTFE. Instead comonomers with pendent groups have to be polymerized with TFE.

Crystallinity of never-melted PTFE is in the range of 92–98% [28], consistent with an unbranched chain structure. FEP, a copolymer of TFE and HFP, has an as-polymerized crystallinity of 40–50%. In FEP, the pendent CF_3 group is bonded to a tertiary carbon that is less thermally stable than primary and secondary carbon atoms. Degradation curves (Figure 4.4) indicate degradation onset temperatures of 300 °C for FEP (0.02% weight loss) and 425 °C for PTFE (0.03% weight loss).

4.8 Polymer Properties of PTFE

4.8.1 PTFE Properties

PTFE has excellent properties such as chemical inertness, heat resistance (both high and low), electrical insulation properties, low coefficient of friction (static 0.08 and dynamic 0.01), and nonstick property over a wide temperature range (–260 to +260 °C). It has a density in the range of 2.1–2.3 g/cm³ and melt viscosity in the range of 1–10 GPa per second [44]. Molecular weight of PTFE cannot be measured by standard methods. Instead, an indirect approach is used to judge molecular weight. Standard specific gravity (SSG) is the specific gravity of a chip prepared according to a standardized procedure. The underlying principle is that lower molecular weight PTFE crystallizes more extensively, thus yielding higher SSG values [67].

PTFE that has not been previously melted has a crystallinity of 92–98%, indicating a linear and nonbranched molecular structure. Upon reaching 342 °C, it melts changing from a chalky white color into a transparent amorphous gel. The second melting point of PTFE is 327 °C because it never recrystallizes to the same extent as prior to its first melting.

First-order and second-order transitions have been reported for PTFE. The transitions that are close to room temperature are of practical interest because of impact on processing of the material. Below 19 °C the crystalline system of PTFE is a nearly perfect triclinic. Above 19 °C, the unit cell changes to hexagonal. In the range of 19–30 °C, the chain segments become increasing disorderly and the preferred crystallographic direction disappears, resulting in a large expansion in the specific volume of PTFE (1.8%) [68] which must be considered in measuring the dimensions of articles made from these plastics.

PTFE is by far the most chemically resistant polymer among thermoplastics. The exceptions include molten alkali metals, gaseous fluorine at high temperatures and pressures, and few organic halogenated compounds such as chlorine trifluoride (ClF_3) and oxygen difluoride (OF_2). A few other chemicals have been reported to attack PTFE at or near its upper service temperature. PTFE reacts with 80% sodium or

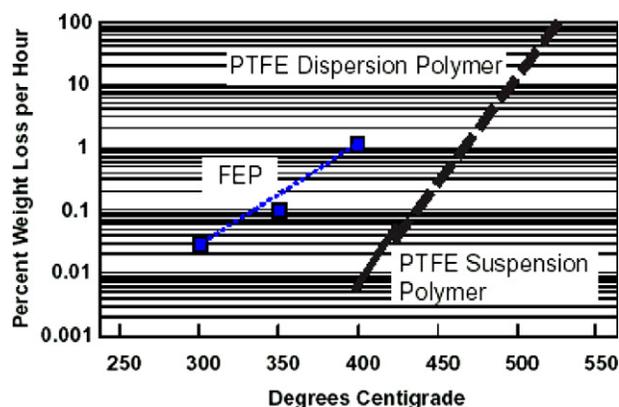


Figure 4.4 A comparison of thermal degradation of FEP and PTFE in air.

potassium hydroxide and some strong Lewis bases including metal hydrides.

Mechanical properties of PTFE are generally inferior to engineering plastics at the room temperature. Compounding with fillers has been the strategy to overcome this shortage. PTFE has useful mechanical properties in its use temperature range.

PTFE has excellent electrical properties such as high insulation resistance, low dielectric constant (2.1), and low dissipation factor. Dielectric constant and dissipation factor remain virtually unchanged in the range of -40 to -250 °C and 5 Hz to 10 GHz. Dielectric breakdown strength (short term) is 47 kV/mm for a 0.25-mm-thick film (ASTM D149). Dielectric breakdown strength is enhanced with decrease in voids in PTFE, which is affected by the fabrication process.

PTFE is attacked by radiation, and degradation in air begins at a dose of 0.02 Mrad.

4.8.2 PFA Properties

PFA polymers are fully fluorinated and melt-processible [52,69]. They have chemical resistance and thermal stability comparable to PTFE. Specific gravity of perfluoroalkoxy resins is in the range of 2.12–2.17. PFA has an upper continuous use temperature of 260 °C.

Crystallinity and specific gravity of PFA parts decrease when the cooling rate of the molten polymer is increased. The lowest crystallinity obtained by quenching molten PFA in ice was 48% (specific gravity 2.123).

Similar to PTFE, molecular weight of PFA cannot be measured by conventional techniques. An indirect factor called melt flow rate (MFR) also called melt flow index (MFI) is used which is the amount of polymer melt that would flow through a capillary rheometer at a given temperature under a defined load (usually in grams in 10 minutes). MFR is inversely proportional to viscosity; viscosity is directly proportional to molecular weight of the polymer.

PFA exhibits one first-order transition at -5 °C in contrast to two temperatures for PTFE at 19 and 30 °C. It has three second-order transitions at -100 , -30 and 90 °C [54].

PFA has excellent electrical properties such as high insulation resistance, low dielectric constant (2.1), and low dissipation factor. Dielectric constant and dissipation factor remain virtually unchanged in the range of -40 to -250 °C and 10^2 Hz to 2.4×10^{10} Hz. Dielectric breakdown strength (short term) is 80 kV/mm for a 0.25-mm-thick film (ASTM D149).

Chemical properties of PFA are similar to those of PTFE.

PFA is attacked by radiation, and degradation in air begins at a somewhat higher dose than that of PTFE which starts to degrade at 0.02 Mrad.

4.8.3 FEP Properties

Fluorinated ethylene-propylene copolymers are fully fluorinated and melt-processible [60,70]. They have excellent

chemical resistance and thermal stability. Specific gravity of FEP resins is in the range of 2.13–2.15. FEP has an upper continuous use temperature of 200 °C.

Similar to PTFE, molecular weight of FEP cannot be measured by conventional techniques. Like PFA, MFR is used to characterize molecular weight of FEP. MFR and the molecular weight are inversely related.

Molecular weight distribution is determined by measuring the dynamic module of the polymer melt using rheological analyses. Crystallinity of virgin (unmelted) FEP is 65–75%.

FEP exhibits a single first-order transition that is its melting point. Relaxation temperature of FEP increases with HFP content of the copolymer. FEP has a dielectric transition at -150 °C which is unaffected by the monomer composition or crystallinity (specific gravity).

Chemical properties of FEP are similar to those of PTFE and PFA.

FEP is attacked by radiation, and its degradation in air begins at a dose of 0.2 Mrad (10 times higher than that of PTFE).

4.8.4 PCTFE Properties

PCTFE is a semicrystalline polymer [62] with a helical polymer chain and a pseudo-hexagonal crystal. Crystal growth is spherulitic and consists of folded chains. Large size of chlorine constrains recrystallization after melting during processing. This resin has good properties at cryogenic temperatures relative to plastics in general, although they are inferior to other fluoropolymers except PVDF.

PCTFE has exceptional barrier properties and superb chemical resistance. It is attacked by a number of organic solvents.

PCTFE has low thermal stability and degrades upon reaching its melting point, requiring special care during processing.

4.8.5 ETFE Properties

PVDF and equimolar ETFE are isomers but the latter has a higher melting point and a lower dielectric loss than the former. ETFE crystallizes into unit cells believed to be orthorhombic or monoclinic [71]. The molecular conformation of ETFE is an extended zigzag. This polymer is dissolved in some boiling esters at above 230 °C, thus allowing determination of molecular weight (weight-average) by light scattering. ETFE has several transitions, alpha relaxation at 110 °C (shifts to 135 °C at higher crystallinity), beta at -25 °C, and gamma relaxation at -120 °C.

ETFE terpolymers have good mechanical properties including tensile and cut-through resistance and lower creep than perfluoropolymers. ETFE is more resistant to radiation than perfluoropolymers (modestly affected up to 20 Mrad) and can be crosslinked by radiation such as electron beam. Crosslinking is used to strengthen cut-through resistance of ETFE wire insulation.

ETFE has a dielectric constant of 2.6–3.4 and dissipation factor of 0.0006–0.010 as frequency increases from 10^2 to 10^{10} Hz.

ETFE terpolymers are resistant to stress cracking and chemical attack by most compounds. Strong oxidizing acids, concentrated boiling sulfonic acids, and organic bases (amines) attack ETFE and any chemical that affects PTFE, PFA, and FEP.

4.8.6 ECTFE Properties

ECTFE is semicrystalline (50–60%) and melts at 240 °C (commercial grade). It has an alpha relaxation at 140 °C, a beta at 90 °C, and gamma relaxation at –65 °C. Conformation of ECTFE is an extended zigzag in which ethylene and CTFE alternate. The unit cell of ECTFE's crystal is hexagonal.

Similar to ETFE, ECTFE terpolymers (same monomers) have better mechanical and abrasion and radiation resistance than PTFE and other perfluoropolymers.

Dielectric constant of ECTFE is 2.5–2.6, and independent of temperature and frequency. Dissipation factor is 0.02 and much larger than ETFE's.

ECTFE is resistant to most chemicals except hot polar and chlorinated solvents. It does not stress crack dissolve in any solvents. ECTFE has better barrier properties to SO₂, Cl₂, HCl, and water than FEP and PVDF.

4.8.7 PVDF Properties

Polyvinylidene fluoride is a semicrystalline polymer (35–70% crystallinity) with an extended zigzag chain [49]. Head-to-tail addition of VDF dominates but there are head-to-head or tail-to-tail defects that affect crystallinity and properties of PVDF.

PVDF has a number of transitions and its density alters for each polymorph state. There are four known proposed states, named as α , β , γ , and δ . The most common phase is α -PVDF which exhibits transitions at –70 °C (γ), –38 °C (β), 50 °C (α''), and 100 °C (α').

PVDF resists most organic and inorganic chemicals including chlorinated solvents. Strong bases, amines, esters, and ketones attack this resin. The impact ranges from swelling to complete dissolution in these solvents depending on the conditions. PVDF exhibits compatibility with a number of polymers. Commercially useful blends with acrylics and methacrylics have been developed.

PVDF, just as ETFE, readily crosslinks as a result of exposure to radiation. Radiation (gamma rays) has modest effect on the mechanical properties of PVDF.

4.8.8 PVF Properties

Poly(vinyl fluoride) is a semicrystalline polymer with a planar, zigzag conformation [23,24]. The degree of crystallinity can vary significantly from 20 to 60% and is a function of defect structures. Commercial PVF is

atactic, contains approximately 12% head-to-head linkages, and displays a peak melting point of about 190 °C [39,40].

PVF displays several transitions below the melting temperature. Lower T_g occurs at –15 to –20 °C and upper T_g is in the 40–50 °C range. Two other transitions at –80 °C and 150 °C have been reported.

PVF has low solubility in all solvents below about 100 °C. Polymers with greater solubility have been prepared using 0.1% 2-propanol polymerization modifier and were characterized in *N,N*-dimethylformamide solution containing 0.1 N LiBr. M_n ranged from 76,000 to 234,000 (osmometry), and M_s from 143,000 to 654,000 (sedimentation velocity).

High molecular weight PVF is reported to degrade in an inert atmosphere, with concurrent HF loss and backbone cleavage occurring at about 450 °C. In air, HF loss occurs at about 350 °C, followed by backbone cleavage around 450 °C.

PVF is transparent to radiation in the UV, visible, and near-infrared regions, transmitting 90% of the radiation from 350 to 2500 nm. PVF becomes embrittled upon exposure to electron-beam radiation of 1000 Mrad but resists breakdown at lower doses. It retains its strength at 32 Mrad while PTFE is degraded at 0.2 Mrad.

The self-ignition temperature of PVF film is 390 °C. The limiting oxygen index (LOI) for PVF is 22.6%. HF and a mixture of aromatic and aliphatic hydrocarbons are generated from the thermal degradation of PVF.

4.9 Fabrication Techniques

With the exception of two fluoropolymers, PVF and PTFE, the rest of the resins described in this chapter can be processed by standard melt-processing techniques such as injection, transfer and blow molding, extrusion and rotational molding. Process equipment for fluoropolymers must be made from corrosion-resistant alloys because of the corrosive compound that may be produced when fluoropolymers are heated above their melting points. Higher melt viscosity of these resins may require more powder and higher pressure rating equipment.

PTFE is processed using metal powder-processing techniques in which a preform is molded and “sintered.” Compression molding may also be used to fabricate PTFE parts. PTFE dispersions are applied by similar techniques to other coatings. Paste extrusion in which PTFE is blended with a hydrocarbon, prior to molding a preform, is used to continuously fabricate PTFE into tubes, tapes, and wire insulation. The hydrocarbon is vaporized before the part is sintered.

PVF is dispersed in a polar latent solvent such as dimethyl acetamide and is melt-extruded as a plastisol, followed by solvent removal by drying.

4.10 Applications

Properties of fluoropolymers that have led to applications include chemical resistance, thermal stability, cryogenic properties, low coefficient of friction, low surface energy, low dielectric constant, high volume and surface resistivity, and flame resistance. Fluoropolymers are used as liners (process surface) because of their resistance to chemical attack. They provide durable, low maintenance, and economical alternatives to exotic metals for use at high temperatures without introducing impurities. Electrical properties make fluoropolymers highly valuable in electronic and electrical applications as insulators, e.g., FEP in data communications.

In automotive and office equipment, mechanical properties of fluoropolymers are beneficial in low-friction bearings and seals that resist attack by hydrocarbons and other fluids. In food processing, the Food and Drug Administration approved fluoropolymer grades are fabrication material for equipment due to their resistance to oil and cleaning materials, and their anti-stick and low friction properties. In houseware, fluoropolymers are applied as nonstick coatings for cookware and appliance surfaces. Medical articles such as surgical patches and cardiovascular grafts rely on the long-term stability of fluoropolymers as well as their low surface energy and chemical resistance.

For airports, stadiums, and other structures, glass fiber fabric coated with PTFE is fabricated into roofing and enclosures. PTFE provides excellent resistance to weathering, including exposure to UV rays in sunlight, flame resistance for safety, and low surface energy for soil resistance, and easy cleaning.

4.11 Safety

Fluoropolymers are chemically stable and inert or relatively unreactive. Reactivity, generally, decreases as fluorine content of the polymer increases. Fluorine induces more stability than chlorine. Fluoropolymers can produce toxic products if overheated. Precautions should be taken to exhaust any degradation fragments produced during the processing and fabrication of parts from fluoropolymers [72]. This family of plastics has low toxicity and almost no toxicological activity. No fluoropolymers have been known to cause skin sensitivity and irritation in humans.

4.11.1 Ammonium Perfluoro Octanoate (APFO, also C8)

APFO is an essential processing aid in the manufacture of fluoropolymers. It is a polymerization aid that plays a critical role in the polymerization of TFE and fluorinated comonomers used to produce PTFE, PFA (MFA), and FEP. It acts as an intermediate for the majority of fluoropolymers and is eliminated during the finishing steps. Solid phase

fluoropolymers contain extremely small amounts of C8 of the order of a few parts per million. In the case of aqueous dispersion products a fraction of percent of APFO would normally be present in the dispersion products.

APFO has been found to be persistent in the environment. Consequently, since mid-2000's fluoropolymer manufacturers have taken steps to abate environmental emissions and reduce and eliminate the C8 from dispersion products. The industry has reduced the presence of C8 in its products by 95% as of 2010. Fluoropolymer manufacturers have committed to US Environmental Protection Agency (www.EPA.gov) to eliminate the use of C8 completely by finding alternative polymerization aids by 2015. For more information readers are encouraged to contact *Fluoropolymers Division* of the Society of Plastics Industry, Inc. (www.Fluoropolymers.org) or fluoropolymer manufacturers directly.

4.12 Economy

Fluoropolymers are more costly to produce than polyolefins and many other plastics due to capital costs and the cost of fluorine. Polymerization and finishing of these resins require processing of highly flammable hazardous materials, thus mandating the use of expensive construction material and elaborate equipment. In 2008, the cost ranged from less than US \$9 per kg for mechanical grade PTFE [73] to \$70 per kg for specialty grade PFA. Soluble perfluoropolymers cost \$10–20 per gram and are only used in high value applications.

4.13 Summary

Commercial fluoropolymers are based on TFE, VDF, and to a lesser extent CTFE. Examples of comonomers include PMVE, PEVE, PPVE, HFP, CTFE, and PFBE. The general consequences of substitution of fluorine for hydrogen in a polymer include increased chemical and solvent resistance, enhanced electrical properties such as lower dielectric constant, lower coefficient of friction, higher melting point, increased photostability and thermal stability, improved flame resistance, and weakened mechanical properties. The ultimate properties are achieved when a polymer is entirely fluorinated.

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