Fluoropolymers

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INTRODUCTION

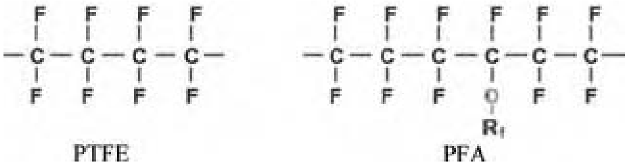
In this entry, fluoropolymer means a polymer that consists of partially or fully fluorinated olefinic monomers, such as vinylidene fluoride ($CH_2{=}CF_2$) and tetrafluoroethylene ($CF_2{=}CF_2$). Commercial fluoropolymers include homopolymers and copolymers. Homopolymers contain 99 wt.% or more one monomer and 1 wt.% or less of another monomer according to the convention by American Society for Testing Materials. Copolymers contain 1 wt.% or more of one or more comonomers. The major commercial fluoropolymers are based on tetrafluoroethylene, vinylidene fluoride, and to a lesser extent chlorotrifluoroethylene. Examples of comonomers include perfluoromethyl vinyl ether (PMVE), perfluoroethyl vinyl ether (PEVE), perfluoropropyl vinyl ether (PPVE), hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE), and perfluorobutyl ethylene (PFBE).

Fluoropolymers discussed 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).

In this entry, the classification, preparation, properties, fabrication, safety considerations, and economics of fluoropolymers are discussed. Monomer synthesis and properties have also been discussed. Increasing the fluorine content of a polymer increases chemical and solvent resistance, flame resistance, and photostability, improves electrical properties, such as dielectric constant, lowers coefficient of friction, raises melting point, increases thermal stability, and weakens mechanical properties.

FLUOROPOLYMER CLASSIFICATION

The era of fluoropolymers began with the serendipitous discovery of PTFE by Roy Plunkett of DuPont Company[1] while conducting research to find new refrigerants. A number of fluoroplastics have been developed since the discovery of PTFE. They are divided into two classes of perfluorinated and partially fluorinated polymers. Perfluorinated fluoropolymers are homopolymers and copolymers of tetrafluoroethylene (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 C_1 to C_4.



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 vinylidene fluoride (VDF). There are also copolymers and homopolymers of CTFE, although some have elastomeric properties. Other significant fluoroplastics include ETFE and PVF.

POLYMER DEVELOPMENT

Because of its high viscosity (10^{10}–10^{12} poise at 380°C), PTFE cannot be fabricated by melt-processing techniques. Melt-processible fluoropolymers have been developed by copolymerization of TFE, and 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. Whereas, PFA, a copolymer of TFE with PPVE or PEVE, offers thermal stability, melt-processibility, and a maximum continuous use temperature of 260°C. Both FEP and PFA are considered perfluoropolymers.

Copolymers of ethylene with tetrafluoroethylene (ETFE) and chlorotrifluoroethylene (ECTFE) are mechanically stronger than perfluoropolymers, with some 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 is.[2]

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MONOMER SYNTHESIS

Synthesis of Tetrafluoroethylene

The first reliable and complete description of synthesis was published in 1933 by Ruff and Bretschneider[3] in which they demonstrated the preparation of TFE ($CF_2{=}CF_2$, CAS number *116-14-3*) from the decomposition of tetrafluoromethane in an electric arc. Then TFE was obtained by bromination and separation of the dibromide ($CF_2Br–CF_2Br$) 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,[4–11] as shown in the reaction sequence in Fig. 1.

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

Sherratt[12] has provided a description 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 compressed and distilled to recover the unreacted $CHClF_2$ and to recover high purity TFE. Polymerization of tetrafluoroethylene to a high molecular weight requires extreme purity, hence the removal of all traces of telogenic hydrogen or chlorine-bearing impurities. Tetrafluoroethylene can autopolymerize if it is not inhibited with terpenes, such as α-pinene, Terpene B, and D-limonene.[13]

HF preparation:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$$

Chloroform preparation:

$$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$$

Chlorodifluoromethane preparation:

$$CHC1_3 + 2HF \rightarrow CHClF_2 + 2HCl$$
(SbF_3 catalyst)

TFE synthesis:

$$2CHC1F_2 \rightarrow CF_2{=}CF_2 + 2HCl$$
(pyrolysis)

Fig. 1 Synthesis reactions of tetrafluoroethylene. (Courtesy of William Andrew Publishing, Inc.)

Synthesis of Hexafluoropropylene

Hexafluoropropylene ($CF_3CF{=}CF_2$, CAS number *116-15-4*) was first prepared by Downing et al.[14] by pyrolysis. The full synthesis and identification of HFP was conducted by Henne and Woalkes.[15] A six-step reaction scheme starting with the fluorination of 1,2,3-trichloropropane led to 1,2-dichlorohexafluoropropane, which was dehalogenated with zinc in boiling ethanol to yield hexafluoropropylene.

Synthesis of Perfluoroalkylvinylethers

Perfluoroalkylvinylethers, such as perfluoropropylvinylether ($CF_2{=}CF–O–C_3F_7$, CAS number *1623-05-8*) are synthesized according to the steps shown in Fig. 2. There are also electrochemical processes for the production of perfluoro-2-alkoxy-propionyl fluoride.[16]

Synthesis of Chlorotrifluoroethylene

This monomer is fairly simple to manufacture compared with the perfluorinated monomers.[17,18] The commercial process for the synthesis of CTFE ($CF_2{=}CClF$, 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 the preparation of TCTFE is catalytic dechlorination:

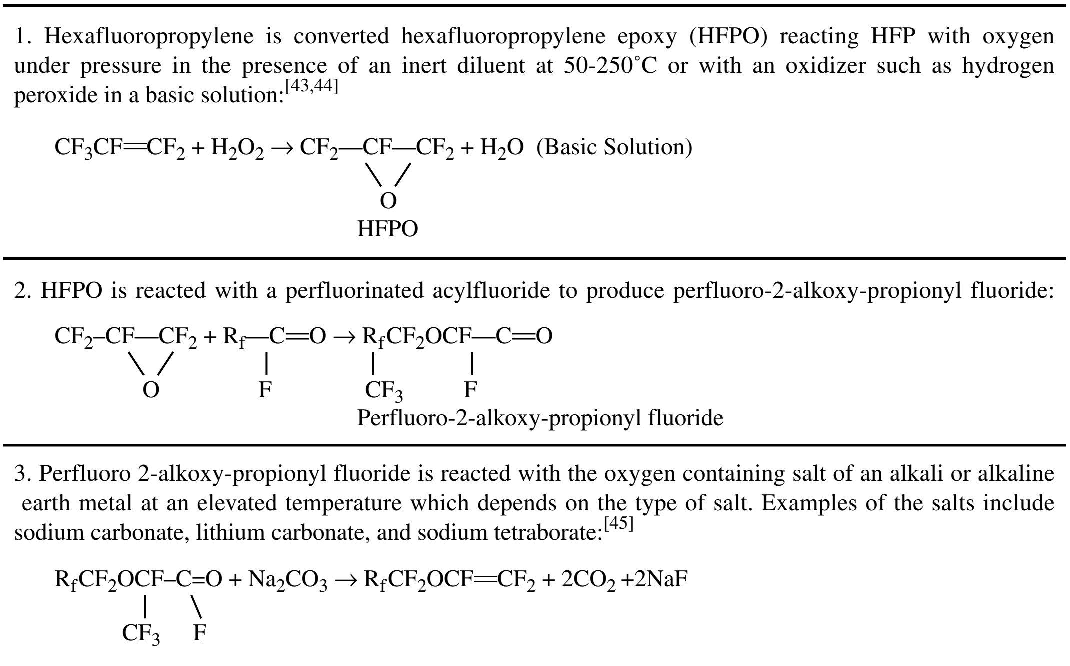
$$CCl_3-CCl_3 + HF \rightarrow CCl_2F-CClF_2 + 2HCl$$
(catalyst $SbCl_xF_y$)

$$CCl_2F-CClF_2 + Zn \rightarrow CFCl = CF_2 + ZnCl_2$$
(at 50 – 100°C in methanol)

The reaction products are put through a number of purification and distillation steps to remove the gaseous and liquid contaminants. Chlorotrifluoroethylene 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.

Synthesis of Vinylidene Fluoride

There are numerous ways to prepare VDF ($CF_2{=}CH_2$, CAS number *75-38-7*). Two methods, including the popular commercial technique for VDF production, are described. Conversion of 1,1,1-trifluoroethane[19] begins by passing this gas through a platinum-lined Inconel tube, which is heated to 1200°C. Contact time is about 0.01 sec. The exit gases are passed through a sodium fluoride bed to remove the hydrofluoric



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]

$$CF_3CF{=}CF_2 + H_2O_2 \rightarrow \underset{O}{CF_2{-}CF}{-}CF_2 + H_2O \text{ (Basic Solution)}$$

HFPO

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

$$\underset{O}{CF_2{-}CF}{-}CF_2 + R_f{-}\underset{F}{C}{=}O \rightarrow R_fCF_2O\underset{CF_3}{CF}{-}\underset{F}{C}{=}O$$

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]

$$R_fCF_2O\underset{CF_3}{CF}{-}\underset{F}{C}{=}O + Na_2CO_3 \rightarrow R_fCF_2OCF{=}CF_2 + 2CO_2 + 2NaF$$

Fig. 2 Synthesis of perfluoroalkylvinylethers. (From Ref.[16].)

acid and are then collected in a liquid nitrogen trap. Vinylidene fluoride 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,[20] by hydrofluorination of trichloroethane,[21] or by hydrofluorination of vinylidene chloride.[22] In each case, the final product, 1-chloro-1,1-difluoroethane, is stripped of a molecule of hydrochloric acid to yield vinylidene fluoride.

Synthesis of Vinyl Fluoride

Vinyl fluoride[23,24] was first prepared by the reaction of 1,1-difluoro-2-bromoethane [*359-07-9*] with zinc. Most approaches to vinyl fluoride synthesis involve reactions of acetylene [*74-86-2*] with hydrogen fluoride (HF) either directly or utilizing catalysts. Other routes involve ethylene [*74-85-1*] and HF, pyrolysis of 1,1-difluoroethane [*624-72-6*] and fluorochloroethanes, reaction of 1,1-difluoroethane with acetylene, and halogen exchange of vinyl chloride [*75-01-4*] with HF.[25–27]

MONOMER PROPERTIES

Properties of Tetrafluoropropylene

Tetrafluoroethylene is a colorless, odorless, tasteless, and nontoxic gas, which boils at −76.3°C and melts at −142.5°C. Critical temperature and pressure of tetrafluoroethylene are 33.3°C and 3.92 MPa. It is stored as a liquid; vapor pressure at −20°C is 1 MPa. Its heat of formation is reported to be −151.9 kcal/mol. Polymerization of tetrafluoroethylene is highly exothermic and generates 41.12 kcal/mol heat. The extent of which can be compared to the heats of polymerization of vinyl chloride and styrene, 23–26 and 16.7 kcal/mol, respectively.[28]

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%. Detonation of a mixture of tetrafluoroethylene and oxygen can increase the maximum pressure to 100 times the initial pressure.

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-hr exposure, a concentration of 3000 ppm corresponded to LC50 in rats.[29] Critical temperature and pressure of hexafluoropropylene are 85°C and 3254 MPa. Unlike tetrafluoroethylene, HFP is extremely stable with respect to autopolymerization and may be stored in liquid state without the addition of telogen.

Hexafluoropropylene is thermally stable up to 400–500°C. At about 600°C under vacuum, HFP decomposes and produces octafluoro-2-butene ($CF_3CF{=}CFCF_3$) and octafluoroisobutylene.[30]

Properties of Perfluoroalkylvinylethers

Perfluoroalkylvinylethers (PAVE) form an important class of monomers in that they are comonomers of choice for the ‘‘modification’’ of the properties of homofluoropolymers in addition to their broad use in the structure of copolymers of TFE. The advantage of PAVE as modifiers over hexafluoropropylene is their remarkable thermal stability. A commercially significant example is PPVE. It is an odorless and colorless liquid at room temperature. It is extremely flammable and burns with a colorless flame. It is less toxic than hexafluoropropylene.[16]

Properties of Chlorotrifluoroethylene

Chlorotrifluoroethylene is a colorless gas at room temperature and pressure. It is fairly toxic with an LC50 (rat), 4 hr of 4000 ppm.[31] 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 are generated by the oxidation of chlorotrifluoroethylene, such as chlorodifluoroacetyl fluoride.[32] 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.

Properties of Vinylidene Fluoride

Vinylidene fluoride (VDF), $CH_2{=}CF_2$, is flammable and is a gas at room temperature. It is colorless and almost odorless and boils at -84°C. Vinylidene fluoride can form explosive mixtures with air. Polymerization of this gas is highly exothermic and takes place above its critical temperature and pressure.[33]

Properties of Vinyl Fluoride

Vinyl fluoride (VF) [*75-02-5*] (fluoroethene) is a colorless gas at ambient conditions.[23] Vinyl fluoride is flammable in air between the limits of 2.6 and 22 vol.%. 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 vinyl fluoride. Inhibited vinyl fluoride has been classified as a flammable gas by the U.S. Department of Transportation.

POLYMERIZATION AND FINISHING

Polytetrafluoroethylene [*9002-84-0*]

PTFE is produced[28,34] by free-radical polymerization mechanism in an aqueous media via addition polymerization of tetrafluoroethylene 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*) 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.

Granular PTFE is produced by polymerizing tetrafluoroethylene 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 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 of 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 electrodecantation, 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 of PTFE are produced from all three forms of using fillers, such as glass fiber, graphite, metal powder, carbon fiber, and others.[34]

Perfluoroalkoxy Polymer [*26655-00-5*]

PFA is a copolymer of TFE and a perfluoroalkyl vinyl ether, such as perfluoropropyl vinyl ether PPVE. Copolymerization of perfluoroalkylvinyl ethers with tetrafluoroethylene can be done in a halogenated solvent,[35] in an aqueous phase[36] sometimes containing some halogenated solvent usually in the absence of a surfactant.[37] Terpolymers of this class contain other monomers like hexafluoropropylene HFP.

Commercially, PFA is polymerized by free-radical polymerization mechanism usually in an aqueous media via addition polymerization of TFE and perfluoropropyl vinyl ether. The initiator for the polymerization is usually water-soluble peroxide, such as ammonium persulfate. Chain transfer agents such methanol, acetone and others 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 CF_3 end groups.[38–42] The polymer is recovered, dried and melt-extruded into cubes for melt fabrications processes. PFA is also available in bead (as polymerized), dispersion and fine powders forms.

Fluorinated Ethylene–Propylene Copolymer [*25067-11-2*]

FEP is a random copolymer of TFE and HFP, which can be polymerized, in an aqueous or a nonaqueous media.[37] 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 hexafluoropropylene. 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. For melt fabrication processes, FEP is recovered, dried, and melt-extruded into cubes. It is also available in dispersion form.

Ethylene-co-tetrafluoroethylene Polymers [*68258-85-5*]

This plastic is a partially fluorinated straight-chain polymer with a very high molecular weight.[37] 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 tetrafluoroethylene and ethylene ($CH_2{=}CH_2$, molecular weight 28, CAS number *74-85-1*) proceeds by an addition mechanism.

Copolymers of tetrafluoroethylene 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.[43] They comprise of 40–60 mol% ethylene, 40–60 mol% tetrafluoroethylene, and a small amount of a polymerizable vinyl termonomer, such as perfluoroisobutylene, perfluoropropyl vinyl ether, and hexafluoropropylene.

Ethylene-co-chlorotrifluoroethylene Polymers [*25101-45-5*]

Ethylene and chlorotrifluoroethylene have been polymerized[18] in aqueous and solvent mediums using organic peroxides and oxygen-activated triethylboron. Typically, polymerization is done at 60–120°C and at a pressure of 5 MPa or higher. The polymerization reaction can also be initiated by radiation, such as by gamma rays. The most effective catalyst is tri-*n*-butylboron which produces an ECTFE with an alternating 1 : 1 ethylene : TFE ratio. To control the molecular weight of the resin, chain transfer agents, such as chlorinated compounds, alcohols, and ketones were required.

Polychlorotrifluoroethylene [*9002-83-9*]

Bulk, suspension, and emulsion techniques are used to polymerize CTFE .[44] 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 that of 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.

Polyvinylidene Fluoride [*24937-79-9*]

The first successful aqueous polymerization of vinylidene fluoride was reported in 1948[45], using a peroxide initiator in water at 50–150°C and 30 MPa. No surfactants or suspending agents were present in the polymerization recipe. Polyvinylidene fluoride has been polymerized by a number of methods including emulsion, suspension, solution, and bulk. Later, copolymers of vinylidene fluoride with ethylene and halogenated ethylene monomers were also produced.[46] In 1960, a manufacturing process was developed and PVDF was first introduced to the market. Reaction temperature ranges from 10 to 150°C at a pressure of 1 MPa or higher. Similar to that of TFE, emulsion polymerization of vinylidene fluoride 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 dipsersant like a hydroxy cellulose. Solution polymerization of VDF is conducted in solvents using free-radical initiators. PVDF is commercially produced by aqueous emulsion or suspension process.

Polyvinyl Fluoride [*24981-14-4*]

Vinyl fluoride undergoes free-radical polymerization.[23,24] The first polymerization involved heating a saturated solution of VF in toluene at 67°C under 600 MPa for 16 hr. A wide variety of initiators and polymerization conditions have been explored. Examples of bulk and solution polymerizations exist; however, aqueous suspension or emulsion method is generally preferred. Copolymers of VF and a wide variety of other monomers have been prepared. More recently, interpolymers of VF have been reported with tetrafluoroethylene and other highly fluorinated monomers, such as hexafluoropropylene, perfluorobutylethylene, and perfluoroethylvinylether.

STRUCTURE–PROPERTY RELATIONSHIP

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

1. PTFE has one of the lowest surface energies in polymers.
2. It is the most chemically resistant polymer.
3. It is one of the most thermally stable polymers.
4. Its melting point and specific gravity are more than double those of PE.

The differences between PTFE and PE 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:

1. Fluorine is the most electronegative of all elements (4 Paulings).
2. It has unshared electron pairs.
3. It is more easily converted to F^-.
4. Bond strength of C–F is higher than that of C–H.
5. It is larger than hydrogen.

The electronegativity of carbon at 2.5 Paulings is somewhat higher than that of hydrogen (2.1 Paulings) and lower than that 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 when compared with the C–H bond in which the carbon end is negatively charged.

The difference in the 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. At extremely high pressure, PTFE can be forced into such a conformation.[47] Below 19°C, PTFE crystallizes as a helix with 0.169 nm per repeat distance; it takes 13 carbon 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 a melting point (327°C).

The substitution of F for H in the C–H bond substantially increases the bond strength from 99.5 kcal/mol for the C–H bond to 116 kcal/mol for the C–F bond. Consequently, thermal stability and chemical resistance of PTFE are higher than those of PE because more energy is required to break the C–F bond. The polarity and the 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; while FEP, a copolymer of tetrafluoroethylene and hexafluoropropylene, 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 (Fig. 3) indicate degradation onset temperatures of 300°C for FEP (0.02% weight loss) and 425°C for PTFE (0.03% weight loss).

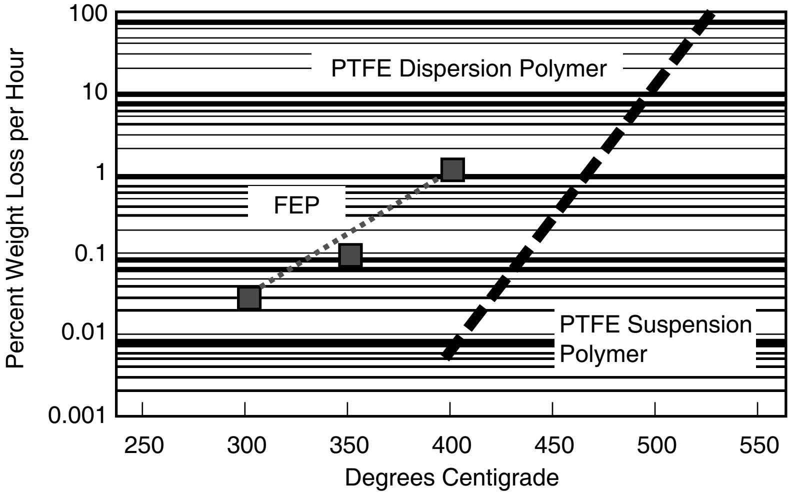


Fig. 3 A comparison of thermal degradation of FEP and PTFE in air. (From Ref.[48].) *(View this art in color at www.dekker.com.)*

POLYMER PROPERTIES

PTFE

It 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/cm^3 and melt viscosity in the range of 1–10 GPa sec.[28] 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.[49]

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 re-crystallizes 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 the 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 increasingly disorderly and the preferred crystallographic direction disappears, resulting in a large expansion in the specific volume of PTFE (1.8%),[50] which must be considered in measuring the dimensions of articles made from this plastics.

Polytetrafluoroethylene 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, and PTFE reacts with 80% sodium or potassium hydroxide and some strong Lewis bases including metal hydrides.

Mechanical properties of PTFE are generally inferior to that of engineering plastics at the room temperature. Compounding with fillers has been the strategy to overcome this shortage. In the normally used temperature range, PTFE has useful mechanical properties.

Also, 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. In air, PTFE is attacked by radiation and degradation, beginning at a dose of 0.02 Mrad.

PFA

These polymers are fully fluorinated and melt-processible.[51] They have chemical resistance and thermal stability comparable to those of PTFE. Specific gravity of PFA resins is in the range of 2.12–2.17. It 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 that of PTFE, the 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 defined as the amount of polymer melt that would flow through a capillary rheometer at a given temperature under a defined load (usually, grams in 10 min). It is inversely proportional to viscosity; viscosity is directly proportional to molecular weight of the polymer.

In contrast to the two transition temperatures for PTFE at 19 and 30°C, PFA exhibits one first order transition at -5°C. It has three second-order transitions at -100, -30 and 90°C.[18] It 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 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. In air, PFA is attacked by radiation and degradation, beginning at a somewhat higher dose than that of PTFE.

FEP

Fluorinated ethylene–propylene copolymers are fully fluorinated and melt-processible.[52] They have excellent chemical resistance and thermal stability. Specific gravity of FEP resins is in the range of 2.13–2.15. It has an upper continuous use temperature of 200°C.

Similar to that of PTFE, molecular weight of FEP cannot be measured by conventional techniques. As in the case of PFA, MFR is used to characterize the molecular weight of FEP. Molecular weight distribution is determined by measuring the dynamic moduli of the polymer melt, using rheological analyses. Crystallinity of virgin (unmelted) FEP is 65–75%. It exhibits a single first order transition that is its melting point. Relaxation temperature of FEP increases with hexafluoropropylene content of the copolymer. It 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. In air, FEP is attacked by radiation and its degradation begins at a dose of 0.2 Mrad (10 times higher than that of PTFE).

PCTFE

It is a semicrystalline polymer[44] with a helical polymer chain and a pseudohexagonal crystal. Crystal growth is spherulitic and consists of folded chains. The large size of chlorine constrains recrystallization after melting during the processing. This resin has good properties at cryogenic temperatures, though it is inferior to all fluoropolymers except PVDF.

In addition, PCTFE has exceptional barrier properties and superb chemical resistance. It is attacked by a number of organic solvents. It has low thermal stability and degrades upon reaching its melting point, requiring special care during processing.

ETFE

Equimolar ETFE and PVDF are isomers, but the former has a higher melting point and a lower dielectric loss than the latter. It crystallizes into unit cells believed to be orthorhombic or monoclinic.[53] The molecular conformation of ETFE is an extended zigzag. This polymer dissolves in some boiling esters at above 230°C, thus allowing the determination of molecular weight (weight-average) by light scattering. It 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.

Terpolymers of ETFE have good mechanical properties including tensile and cut-through resistance and lower creep than perfluoropolymers. It is more resistant to radiation than perfluoropolymers (modestly affected up to 20 Mrad) and can be cross-linked by radiation, such as electron beam. Cross-linking is used to strengthen cut-through resistance of ETFE wire insulation. It has a dielectric constant of 2.6–3.4 and a dissipation factor of 0.0006–0.010 as frequency increases from 10^2 to 10^{10} Hz. Terpolymers of ETFE are resistant to stress cracking and chemical attack by most compounds. Strong oxidizing acids, concentrated boiling sulfonic acids, organic bases (amines), and any chemical that affects PTFE, PFA, and FEP attack ETFE.

ECTFE

It is semicrystalline (50–60%) and melts at 240°C (commercial grade).[44] 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.

As in the case of ETFE, ECTFE terpolymers (same termonomers) have better mechanical, abrasion, and radiation resistance than those of PTFE and other perfluoropolymers. Dielectric constant of ECTFE is 2.5–2.6, and it is independent of temperature and frequency. Dissipation factor is 0.02 and much larger than ETFE's. ECTFE is resistant to most chemicals except for hot polar and chlorinated solvents. It does not stress crack dissolve in any solvents. It has better barrier properties to SO_2, Cl_2, HCl, and water than FEP and PVDF.

PVDF

Polyvinylidene fluoride is a semicrystalline polymer (35–70% crystallinity) with an extended zigzag chain.[33] 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. It has a number of transitions, and its density alters for each polymorph state. There are four known states, named as α, β, γ, and δ, and a proposed state. The most common phase is α-PVDF, which exhibits transitions at -70°C (γ), -38°C (β), 50°C (α''), and 100°C (α').

It 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. It exhibits compatibility with a number of polymers. Commercially useful blends with acrylics and methacrylics have been developed. Just as ETFE, PVDF readily cross-links as a result of exposure to radiation. Radiation (gamma rays) has modest effect on the mechanical properties of PVDF.

PVF

Poly(vinyl fluoride) is a semicrystalline polymer with a planar, zigzag conformation.[23,24] The degree of crystallinity can vary significantly from 20–60% 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 (52,53,62,63). Poly(vinyl flouride) 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 and 150°C have been reported.

Below about 100°C, PVF has low solubility in all solvents. 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 ranged 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.

It is transparent to radiation in the UV, visible, and near IR regions, transmitting 90% of the radiation from 350 to 2500 nm. It 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 polytetrafluoroethylene 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%. Hydrogen fluoride and a mixture of aromatic and aliphatic hydrocarbons are generated from the thermal degradation of PVF.

FABRICATION TECHNIQUES

With the exception of two fluoropolymers, PVF and PTFE, the rest of the resins described in this entry 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.

Metal powder processing techniques in which a preform is molded and ‘‘sintered’’ are used to process PTFE. Compression molding may also be used to fabricate PTFE parts. Its 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 parts are 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.

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 insulation, e.g., FEP in data communications.

Mechanical properties of fluoropolymers are beneficial in low-friction bearings and seals that resist attack by hydrocarbons and other fluids in automotive and office equipment. In food processing, the Food and Drug Administration approved grades are fabrication material for equipment. 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 on 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, where it 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.

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.

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. It has been shown that PVF does not cause any skin reaction in human beings.[1] Excessive human exposure to fluoropolymer dust resulted in no toxic effects, although urinary fluoride content increased.[2]

ECONOMY

Fluoropolymers are more costly to produce than polyolefins and many other plastics because of the 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 early 2004, the cost ranges from US$6 per kg for mechanical grade PTFE to US$70 per kg for specialty grade PFA. Soluble perfluoropolymers cost $10–20 per gram and are only used in high value applications.

CONCLUSIONS

Commercial fluoropolymers are based on tetrafluoroethylene, vinylidene fluoride, and, to a lesser extent, chlorotrifluoroethylene. Examples of comonomers include perfluoromethyl vinyl ether, perfluoroethyl vinyl ether, perfluoropropyl vinyl ether, hexafluoropropylene, chlorotrifluoroethylene, and perfluorobutyl ethylene. 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.

REFERENCES

1. Plunkett, R.J. The history of polytetrafluoroethylene: discovery and development. In *High Performance Polymers: Their Origin and Development*, Proceedings Symp. Hist. High Perf. Polymers at the ACS Meeting in New York, April, 1986; Seymour, R.B. Kirshenbaum G.S., Eds.; Elsevier: New York, 1987.
2. Teflon® AF; www.dupont.com/Teflon/AF (accessed 2003).
3. Ruff, O.; Bretschneider, O.Z. Anorg. Che. **1933**, *210*, 73.
4. Park, J.D. et al. Synthesis of tetrafluorethylene—pyrolisis of monochlorodifluoromethane. Ind. Eng. Chem. **1947**, *39*, 354.
5. Hamilton, J.M. In *Advances in Fluorine Chemistry*; Stacey, M., Eds.; Butterworth & Co., Ltd.: Kent, U.K., 1963; Vol. 3, 117.
6. Edwards, J.W.; Small, P.A. Nature **1964**, *202*, 1329.
7. Gozzo, F.; Patrick, C.R. Nature. **1964**, *202*, 80.
8. Hisazumi, M.; Shingu, H. Japanese Patent 60 15,353.
9. Scherer, O. et al US Patent 2,994,723, Assigned to Farbewerke Hoechst, August 1, 1961.
10. Edwards, J.W.; Sherratt, S.; Small, P.A. British Patent 960,309; Assigned to ICI, June 10, 1964.
11. Ukahashi, H.; Hisasne, M. US Patent 3,459,818; Assigned to Asahi Glass Co, August 5, 1969.
12. Sherratt, S. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Ed.; Standen, A., Ed.; Interscience Publishers, John Wiley & Sons: New York, 1966; Vol. 9, 805–831.
13. Dietrich, M.A.; Joyce, R.M. US Patent 2,407,405, Assigned to DuPont, September 10, 1946.
14. Downing, F.B.; Benning, A.F.; McHarness, R.C. US Patent 2,384,821, Assigned to DuPont, September 18, 1945.
15. Henne, A.L.; Woalkes, T.P. Fluorinated derivatives of propane and propylene. VI. J. Am. Chem. Soc. **1946**, *68*, 496.

16. Brice, T.J.; Pearlson, W.H. US Patent 2,713,593, Assigned to 3M Co, July 1955.
17. Carpenter, C.P.; Smyth, H.F.; Pozzani, U.C.J. Ind. Hygiene **1949**, *31*, 343.
18. Chandrasekaran, S. Chlorotrifluoroethylene polymers. In *Encyclopedia of Polymer Science and Engineering*, 2nd Ed.; John Wiley & Sons: New York, 1989; Vol. 3, 463–480.
19. Hauptschein, A.; Feinberg, A.H. US Patent 3,188,356, Assigned to Pennsalt Chemicals Corp, June 8, 1965.
20. Schultz, N.; Martens, P.; Vahlensieck, H.J. German Patent 2,659,712; Assigned to Dynamit Nobel AG, July 6, 1976
21. McBee, E.T. et al. Fluorinated derivatives of ethane. Ind. Eng. Chem. **1947**, *39* (3), 409–412.
22. Kaess, F.; Michaud, H. US Patent 3,600,450, Assigned to Sueddeutsche Kalkstickstoff-Werke AG, August 17, 1971
23. Ebnesajjad, S.; Snow, L.G. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Ed.; John Wiley & Sons, Inc.: New York, 1994; Vol. 11, 683–694.
24. Brasure, D.E.; Ebnesajjad, S. Vinyl fluoride polymers. In *Encyclopedia of Polymer Science and Engineering*, 2nd Ed.; John Wiley & Sons, Inc.: New York, 1989; Vol. 17, 468–491.
25. Coffman, D.D.; Cramer, R.; Rigby, G.W. Synthesis of chlorofluoropropanes. J. Am. Chem. Soc. **1949**, *71*, 979–980.
26. Coffman, D.D.; Raasch, M.I.; Rigby, G.W.; Barrich, P.L.; Hanford, W.E. Addition reactions of tetrafluoroethylene. J. Org. Chem. **1949**, *14*, 747–753.
27. Pajaczkowski, A.; Spoors, J.W. Chem. Ind. **1964**, *16*, 659.
28. Gangal, S.V. Polytetrafluoroethylene, homopolymers of tetrafluoroethylene. In *Encyclopedia of Polymer Science and Engineering*, 2nd Ed.; John Wiley & Sons: New York, 1989; Vol. 16, 577–600.
29. Clayton, J.W. Occup. Med. **1962**, *4*, 262–273.
30. Gibbs, H.H.; Warnell, J.J. British Patent 931,587; Assigned to DuPont, July 17, 1963
31. Carpenter, C.P.; Smyth, H.F.; Pozzani, U.C. The assay of acute vapor toxicity, and the grading and interpretation of results on 96 chemical compounds. J. Ind. Hygiene **1949**, *31*, 343.
32. Haszeldine, R.N.; Nyman, F.J. Chem. Soc. **1959**, 1085.
33. Dohany, J. Poly(vinylidene fluoride). In *Kirk-Othmer Encyclopedia Chemical Technology*, 4th Ed.; John Wiley & Sons: New York, 1994; Vol. 11, 694–712.
34. Ebnesajjad, S. Non-Melt Processible Fluoroplastics: The Definitive User's Guide and Data Book, *Plastics Design Library*. William Andrew Publishing: Norwich, NY, 2000.
35. Bro, M.I. US Patent 2,952,669, Assigned to DuPont Co, September 13, 1960.
36. Berry, K.L. US Patent 2,559,752, Assigned to DuPont Co, July 10, 1951.
37. Ebnesajjad, S. Melt Processible Fluoroplastics: The Definitive User's Guide and Data Book, *Plastics Design Library*. William Andrew Publishing: Norwich, NY, 2002.
38. Carlson, D.P. US Patent 3,674,758, Assigned to DuPont Co, July 15, 1972.
39. Carlson, D.P. Heat stable tetrafluoroethylene-perfluoro(alkyl vinyl ether) copolymers US Patent 4,599,386, Assigned to DuPont Co., July 8, 1986.
40. PCT Int. Appl. WO89,11,495, M.D. Buckmaster to DuPont Co., 1989.
41. Imbalzano, J.F.; Kerbow, D.L. Stable tetrafluoro thylene copolymers US Patent 4,743,658; Assigned to DuPont Co., May 10, 1988.
42. Goodman, J.; Andrews, S. Fluoride contamination from fluoropolymers in semiconductor manufacture. Solid State Technol., June 1990.
43. Carlson, D.P. US Patent 3,624,250, Assigned to DuPont Co, November 30, 1971.
44. Miller, W.A. Chlorotrifluoroethylene-ethylene copolymers. In *Encyclopedia of Polymer Science and Engineering*, 2nd Ed.; John Wiley & Sons: New York, 1989; Vol. 3, 480–491.
45. Ford, T.A.; Hanford, W.E. US Patent 2,435,537, Assigned to DuPont Co, February 3, 1948.
46. Ford, T.A. US Patent 2,468,054, Assigned to DuPont Co, April 26, 1949.
47. England, D.C. et al.; Proceedings of Robert A. Welch Conference on Chemical Research XXVI, R.A. Welch Foundation; 1982; 193–243.
48. Baker, B.B.; Kasprzak, D.J. Thermal degradation of commercial fluoropolymer in air. Polym. Degrad. Stabil. **1994**, *42*, 181–188.
49. Sperati, C.A., Starkweather, H.W., Jr. Adv. Polym. Sci. **1961**, *2*, 465.
50. McCrum, N.G. An internal friction study of polytetrafluoroethylene. J. Polym. Sci. **1959**, *34*, 355.
51. Gangal, S.V. Tetrafluoroethylene-perfluorovinyl ether copolymer. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Ed.; John Wiley & Sons: New York, 1994; Vol. 11, 671–683.
52. Gangal, S.V. Perfluorinated ethylene-propylene copolymer. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Ed.; John Wiley & Sons: New York, 1994; Vol. 11, 644–656.
53. Gangal, S.V. Tetrafluoroethylene-ethylene copolymers. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Ed.; John Wiley & Sons: New York, 1994; Vol. 11, 657–671.