PERFLUORINATED POLYMERS

1. Polytetrafluoroethylene

1.1. Introduction. Polytetrafluoroethylene (PTFE) [9002-84-0], more commonly known as Teflon (E.I. du Pont de Nemours & Co., Inc.), a perfluorinated straight-chain high polymer, has a most unique position in the plastics industry because of its chemical inertness, heat resistance, excellent electrical insulation properties, and low coefficient of friction over a wide temperature range. Polymerization of tetrafluoroethylene monomer gives this perfluorinated straight-chain high polymer with the formula $-(CF_2-CF_2)_n-$. The white to translucent solid polymer has an extremely high molecular weight, in the 10^6-10^7 range, and consequently has a viscosity in the range of 1–10 GPa·s ($10^{10}-10^{11}$ P) at 380°C. It is a highly crystalline polymer and has a crystalline melting point. Its high thermal stability results from the strong carbon–fluorine bond and characterizes PTFE as a useful high temperature polymer.

The discovery of PTFE (1) in 1938 opened the commercial field of perfluoropolymers. Initial production of PTFE was directed toward the World War II effort, and commercial production was delayed by DuPont until 1947. Commercial PTFE is manufactured by two different polymerization techniques that result in two different types of chemically identical polymer. Suspension polymerization produces a granular resin, and emulsion polymerization produces the coagulated dispersion that is often referred to as a fine powder or *PTFE dispersion*.

Because of its chemical inertness and high molecular weight, PTFE melt does not flow and cannot be fabricated by conventional techniques. The suspension-polymerized PTFE polymer (referred to as *granular PTFE*) is usually fabricated by modified powder metallurgy techniques. Emulsion-polymerized PTFE behaves entirely differently from granular PTFE. Coagulated dispersions are processed by a cold-extrusion process (like processing lead). Stabilized PTFE dispersions, made by emulsion polymerization, are usually processed according to latex processing techniques.

Manufacturers of PTFE include Daikin Kogyo (Polyflon), DuPont (Teflon), Dyneon, Asahi Glass, Solvay Solexis (Algoflon and Halon), and the CIS (Fluoroplast). India and The People's Republic of China also manufacture some PTFE products. Additional information on specific manufacturers' products can often be obtained by consulting their internet web sites (for example, www.dupont.com/teflon).

1.2. Monomer. *Preparation.* The manufacture of tetrafluoroethylene (TFE) [116-14-3] involves the following steps (2–9). The pyrolysis is often conducted at a PTFE manufacturing site because of the difficulty of handling TFE. New discoveries have made it somewhat easier to use it at remote places (10).

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,HF$$
$$CH_4 + 3\,Cl_2 \longrightarrow CHCl_3 + 3\,HCl$$
$$CHCl_3 + 2\,HF \xrightarrow{SbF_3} CHClF_2 + 2\,HCl$$
$$2\,CHClF_2 \xrightarrow{\Delta} CF_2{=}CF_2 + 2\,HCl$$

Pyrolysis of chlorodifluoromethane is a noncatalytic gas-phase reaction carried out in a flow reactor at atmospheric of subatmospheric pressure; yields can be as high as 95% at 590–900°C. The economics of monomer production is highly dependent on the yields of this process. A significant amount of hydrogen chloride waste product is generated during the formation of the carbon–fluorine bonds.

A large number of by-products are formed in this process, mostly in trace amounts; more significant quantities are obtained of hexafluoropropylene, perfluorocyclobutane, 1-chloro-1,1,2,2-tetrafluoroethane, and 2-chloro-1,1,1,2,3,3-hexafluoropropane. Small amounts of highly toxic perfluoroisobutylene, $CF_2{=}C(CF_3)_2$, are formed by the pyrolysis of chlorodifluoromethane.

In this pyrolysis, subatmospheric partial pressures are achieved by employing a diluent such as steam. Because of the corrosive nature of the acids (HF and HCl) formed, the reactor design should include a platinum-lined tubular reactor made of nickel to allow atmospheric pressure reactions to be run in the presence of a diluent. Because the pyrolysate contains numerous by-products that adversely affect polymerization, the TFE must be purified. Refinement of TFE is an extremely complex process, which contributes to the high cost of the monomer. Inhibitors are added to the purified monomer to avoid polymerization during storage; terpenes such as *d*-limonene and terpene B are effective (11).

Tetrafluoroethylene was first synthesized in 1933 from tetrafluoromethane, CF_4, in an electric arc furnace (12). Since then, a number of routes have been developed (13–19). Depolymerization of PTFE by heating at ca 600°C is probably the preferred method for obtaining small amounts of 97% pure monomer on a laboratory scale (20,21). Depolymerization products contain highly toxic perfluoroisobutylene and should be handled with care.

Properties. Tetrafluoroethylene (mol wt 100.02) is a colorless, tasteless, odorless, nontoxic gas (Table 1). It is stored as a liquid; vapor pressure at −20°C is 1 MPa (9.9 atm). It is usually polymerized above its critical temperature and below its critical pressure. The polymerization reaction is highly exothermic.

Tetrafluoroethylene undergoes addition reactions typical of an olefin. It burns in air to form carbon tetrafluoride, carbonyl fluoride, and carbon dioxide (25). Under controlled conditions, oxygenation produces an epoxide (26) or an explosive polymeric peroxide (25). Trifluorovinyl ethers, $RO{-}CF{=}CF_2$, are obtained by reaction with sodium salts of alcohols (27). An ozone–TFE reaction is accompanied by chemiluminescence (28). Dimerization at 600°C gives perfluorocyclobutane, C_4F_8; further heating gives hexafluoropropylene, $CF_2{=}CFCF_3$, and eventually perfluoroisobutylene, $CF_2{=}C(CF_3)_2$ (29). Purity is determined by both gas–liquid and gas–solid chromatography; the ir spectrum is complex and therefore of no value.

Uses. Besides polymerizing TFE to various types of high PTFE homopolymer, TFE is copolymerized with hexafluoropropylene (30), ethylene (31), perfluorinated ether (32,33) isobutylene (34), propylene (35), and in some cases it is used as a termonomer (36). It is used to prepare low molecular weight polyfluorocarbons (37) and carbonyl fluoride (38), as well as to form PTFE *in situ* on metal surfaces (39). Hexafluoropropylene [116-15-4] (40,41) perfluorinated ethers, and other oligomers are prepared from TFE.

In the absence of air, TFE disproportionates violently to give carbon and carbon tetrafluoride; the same amount of energy is generated as in black powder explosions. This type of decomposition is initiated thermally and equipment hot spots must be avoided. The flammability limits of TFE are 14–43%; it burns when mixed with air and forms explosive mixtures with air and oxygen. It can be stored in steel cylinders under controlled conditions inhibited with a suitable stabilizer. The oxygen content of the vapor phase should not exceed 10 ppm. Although TFE is nontoxic, it may be contaminated by highly toxic fluorocarbon compounds.

1.3. Manufacture of PTFE.

Engineering problems involved in the production of TFE seem simple as compared with those associated with polymerization and processing of PTFE resins. The monomer must be polymerized to an extremely high molecular weight in order to achieve the desired properties. The low molecular weight polymer does not have the strength needed in end use applications.

Polytetrafluoroethylene is manufactured and sold in three forms: granular, fine powder, and aqueous dispersion; each requires a different fabrication technique. Granular resins are manufactured in a wide variety of grades to obtain a different balance between powder flows and end use properties (Fig. 1). Fine powders that are made by coagulating aqueous dispersions are also available in various grades. Differences in fine powder grades correspond to their usefulness in specific applications and to the ease of fabrication. Aqueous dispersions are sold in latex form and are available in different grades. A variety of formulation techniques are used to tailor these dispersions for specific applications.

Polymerization. In aqueous medium, TFE is polymerized by two different procedures. When little or no dispersing agent is used and vigorous agitation is maintained, a precipitated resin is produced, commonly referred to as granular resin. In another procedure, called *aqueous dispersion polymerization*, a sufficient dispersing agent is employed and mild agitation produces small colloidal particles dispersed in the aqueous reaction medium; precipitation of the resin particles is avoided. The two products are distinctly different, even though both are high molecular weight PTFE polymers. The granular product can be molded in various forms, whereas the resin produced by the aqueous dispersion cannot be molded, but is fabricated by dispersion coating or conversion to powder for paste extrusion with a lubricant medium. Granular resin cannot be paste extruded or dispersion coated.

Granular Resins. Granular PTFE is made by polymerizing TFE alone or in the presence of trace amounts of comonomers (42–44). An initiator, a small amount of dispersing agent, and other additives (45) may be present; an alkaline buffer is occasionally used (46). In the early stages of polymerization, an unstable dispersion is formed, but lack of dispersing agent and vigorous agitation cause the polymer to partially coagulate; the remainder of the process is fairly complex. The polymerized product is stringy, irregular, and variable in shape. The dried granular polymer is ground to different average particle sizes, depending on the product requirements, eg, the flow and other properties. Coarser fabrication of particles leaves a higher void in the sintered article. A better balance between handleability and moldability (ability to mold and sinter in the absence of voids) is achieved by agglomerating the finely divided resin to ca 400−800 μm (47–49). For ram extrusion of granular resin into long tubes and rods, a partially presintered resin is preferred. Granular PTFE resin is nonflammable.

Fine Powder Resins. Fine powder resins are made by polymerizing TFE in an aqueous medium with an initiator and emulsifying agents (50). The polymerization mechanism is not a typical emulsion type, but is subject to some of the principles of emulsion polymerization. The process and ingredients have a significant effect on the product. It is extremely important that the dispersion remains sufficiently stable throughout polymerization, avoiding premature coagulation (51), but unstable enough to allow subsequent coagulation into a fine powder. Gentle stirring ensures dispersion stability. The amount of emulsifying agent in the polymerization process is usually less than its critical micelle concentration. The rate of polymerization and the particle shape are influenced by the amount of the emulsifying agent (52–55). The particle structure can be influenced by the polymerization process. Most of the particles are formed in the early stages of the polymerization process and the particles grow as the batch progresses; hence, the radial variation in molecular weight and polymer composition within the dispersion particle can be achieved by controlling the polymerization variables, including ingredients and operating conditions (56–62).

The thin dispersion rapidly thickens into a gelled matrix and coagulates into a water-repellent agglomeration that floats on the aqueous medium as the mechanical agitation is continued. The agglomeration is dried gently; shearing must be avoided.

Aqueous Dispersions. The dispersion is made by the polymerization process used to produce fine powders of different average particle sizes (63). The most common dispersion has an average particle size of about 0.2 μm, probably the optimum particle size for most applications. The raw dispersion is stabilized with a nonionic or anionic surfactant and concentrated to 60−65 wt% solids by electrodecantation, evaporation, or thermal concentration (64). The concentrated dispersion can be modified further with chemical additives. The fabrication characteristics of these dispersions depend on polymerization conditions and additives.

Filled Resins. Fillers such as glass fibers, graphite, asbestos, or powered metals are compounded into all three types of PTFE. Compounding is achieved by intimate mixing. Coagulation of the polymer with a filler produces a filled fine powder.

1.4. Properties. The properties described herein are related to the basic structure of PTFE and are exhibited by both granular and fine powder products. The carbon−carbon bonds, which form the backbone of the PTFE chain, and the carbon−fluorine bonds are extremely strong and are the key contributors in imparting an outstanding combination of properties. The fluorine atoms form a protective sheath over the chain of carbon atoms. If the atoms attached to the carbon-chain backbone were smaller or larger than fluorine, the sheath would not form a regular uniform cover. This sheath shields the carbon chain from attack and confers chemical inertness and stability. It also reduces the surface energy resulting in low coefficient of friction and nonstick properties.

Polytetrafluoroethylene does not dissolve in any common solvent; therefore, its molecular weight cannot be measured by the usual methods. A number-average molecular weight has been estimated by determining the concentration of end groups derived from the initiator. Earlier estimates, based on an iron bisulfite system containing radioactive sulfur, ^{35}S, ranged from 142×10^3 to 534×10^3 for low molecular weight polymer. The same technique applied to polymers of industrial interest gave molecular weights of $389 \times 10^3 - 8900 \times 10^3$ (65,66). In the absence of a normal molecular weight determination method, an estimated relative molecular weight is used for all practical purposes. It is obtained by measuring the specific gravity, following a standardized fabricating and sintering procedure (ASTM D1457-83). Because the rate of crystallization decreases with increasing molecular weight, samples prepared from the high molecular weight polymer and cooled from the melt at a constant slow rate have lower standard specific gravities than those prepared from low molecular weight polymer cooled at the same rate (67). The correlation between number-average molecular weight ($M_{\rm n}$) based on end group estimations, and standard specific gravity (SSG) is given by

$$\mathrm{SSG} = 2.612 - 0.058 \log_{10} M_{\rm n}$$

The SSG procedure assumes absence of voids (or constant void content). Voids depress the values of the measured specific gravity. The inaccuracies that result from voids can be corrected by applying ir techniques (68).

Melting and recrystallization behavior of virgin PTFE has been studied by dsc (69). A quantitative relationship was found between $M_{\rm n}$ and the heat of crystallization ($\Delta H_{\rm c}$) in the molecular weight range of $5.2 \times 10^5 - 4.5 \times 10^7$, where $\Delta H_{\rm c}$ is heat of crystallization in J/g, which is independent of cooling rates of 4–32°C/min.

$$M_{\rm n} = 2.1 \times 10^{10} \Delta H_c^{-5.16}$$

At ca 342°C, virgin PTFE changes from white crystalline material to almost transparent amorphous gel. Differential thermal analysis indicates that the first melting of virgin polymer is irreversible and that subsequent remeltings occur at 327°C, which is generally reported as the melting point. Most of the studies reported in the literature are based on previously sintered (ie, melted and recrystallized) polymer; very little work is reported on the virgin polymer. Melting is accompanied by a volume increase of ca 30%. Because the viscosity of the polymer at 380°C is 10 GPa·s (10^{11} P), the shape of the melt is stable. The melting point increases with increasing applied pressure at the rate of 1.52°C/MPa (0.154°C/atm) (70).

Virgin PTFE has a crystallinity in the range of 92–98%, which indicates an unbranched chain structure. The fluorine atoms are too large to allow a planar zigzag structure, which would permit chain flexibility; therefore the chains are rigid (71). Electron micrographs and diffraction patterns (72) of PTFE dispersion particles indicate that the rod-like particles present in virgin PTFE dispersions are fully extended chain crystals containing few defects. The spherical particles appear to be composed of similar rod-like entities that are wrapped around themselves in a more or less random fashion.

Between 50 and 300°C, PTFE obeys the relationship between stress τ and the apparent shear rate γ:$\tau = K\gamma^{1/4}$. Melting of PTFE begins near 300°C. Above this temperature, the shear stress at constant shear rate increases and the rheological exponent rises from 0.25 to 0.5 at the final melting point (73).

Transitions. Transitions observed by various investigators (74–80), their interpretation, and the modes of identification are shown in Table 2. Besides the transition at the melting point, the transition at 19°C is of great consequence because it occurs at ambient temperature and significantly affects the product behavior. Above 19°C, the triclinic pattern changes to a hexagonal unit cell. Around 19°C, a slight untwisting of the molecule from a 180° twist per 13 CF_2 groups to a 180° twist per 15 CF_2 groups occurs. At the first-order transition at 30°C, the hexagonal unit cell disappears and the rod-like hexagonal packing of the chains in the lateral direction is retained. Below 19°C there is almost perfect three-dimensional order; between 19 and 30°C, the chain segments are disordered; and above 30°C, the preferred crystallographic direction is lost and the molecular segments oscillate above their long axes with a random angular orientation in the lattice.

The dynamic mechanical properties of PTFE have been measured at frequencies from 0.033 to 90 Hz. Abrupt changes in the distribution of relaxation times are associated with the crystalline transitions at 19 and 30°C (81). The activation energies are 102.5 kJ/mol (24.5 kcal/mol) below 19°C, 510.4 kJ/mol (122 kcal/mol) between the transitions, and 31.4 kJ/mol (7.5 kcal/mol) above 30°C.

Polytetrafluorothylene transitions occur at specific combinations of temperature and mechanical or electrical vibrations. Transitions, sometimes called *dielectric relaxations*, can cause wide fluctuations in the dissipation factor.

Mechanical Properties. Mechanical properties of PTFE depend on processing variables, eg, preforming pressure, sintering temperature and time, cooling rate, void content, and crystallinity. Properties, such as the coefficient of friction, flexibility at low temperatures, and stability at high temperatures, are relatively independent of fabrication. Molding and sintering conditions affect flex life, permeability, stiffness, resiliency, and impact strength. The physical properties of PTFE have been reviewed and compiled (82–84) (Table 3).

A marked change in volume of 1.0−1.8% is observed for PTFE in the transition zone from 18 to 25°C. An article that has been machined on either side of this zone changes dimensions when passing through the transition zone; hence, the final operating temperature of a precision part must be accurately determined. Articles fabricated of PTFE resins exhibit high strength, toughness, and self-lubrication at low temperatures. They are useful from 5 K and are highly flexible from 194 K. They tend to return to their original dimensions after a deformation. At sintering temperature, they rapidly recover their original shapes. For most applications no special precautions are necessary because decomposition rates below the recommended maximum service temperature of 260°C are very low.

Impact strength is excellent over a wide range of temperatures. Static friction decreases with an increase in load. Static coefficient of friction is lower than the dynamic coefficient and therefore reduces stick–slip problems.

The surface of PTFE articles is slippery and smooth. Liquids with surface tensions below 18 mN/m (=dyn/cm) are spread completely on the PTFE surface; hence, solutions of various perfluorocarbon acids in water wet the polymer (85). Treatment with alkali metals promotes the adhesion between PTFE and other substances (86) but increases the coefficient of friction (87).

Filled Resins. Filled compositions meet the requirements of an increased variety of mechanical, electrical, and chemical applications. Physical properties of filled granular compounds are shown in Table 4 (88–89).

Chemical Properties. Vacuum thermal degradation of PTFE results in monomer formation. The degradation is a first-order reaction (90). Mass spectroscopic analysis shows that degradation begins at ca 440°C, peaks at 540°C, and continues until 590°C (91).

Radiation Effects. Polytetrafluoroethylene is attacked by radiation. In the absence of oxygen, stable secondary radicals are produced. An increase in stiffness in material irradicated in vacuum indicates cross-linking (92). Degradation is due to random scission of the chain; the relative stability of the radicals in vacuum protects the materials from rapid deterioration. Reactions take place in air or oxygen and accelerated scission and rapid degradation occur.

Crystallinity has been studied by x-ray irradiation (93). An initial increase caused by chain scission in the amorphous phase was followed (above 3 kGy or 3×10^5 rad) by a gradual decrease associated with a disordering of the crystallites. The amorphous component showed a maximum of radiation-induced broadening in the nmr at 7 kGy (7×10^5 rad).

In air, PTFE has a damage threshold of 200–700 Gy ($2\times10^4 - 7\times10^4$ rad) and retains 50% of initial tensile strength after a dose of 10^4 Gy (1 Mrad), 40% of initial tensile strength after a dose of 10^5 Gy (10^7 rad), and ultimate elongation of 100% or more for doses up to 2–5 KGy ($2 \times 10^5 - 5 \times 10^5$ rad). During irradiation, resistivity decreases, whereas the dielectric constant and the dissipation factor increase. After irradiation, these properties tend to return to their preexposure values. Dielectric properties at high frequency are less sensitive to radiation than are properties at low frequency. Radiation has very little effect on dielectric strength (94).

Absorption, Permeation, and Interactions. Polytetrafluoroethylene is chemically inert to industrial chemicals and solvents even at elevated temperatures and pressures (95). This compatibility is due to the strong interatomic bonds, the almost perfect shielding of the carbon backbone by fluorine atoms, and the high molecular weight of the polymer. Under some severe conditions PTFE is not compatible with certain materials. It reacts with molten alkali metals, fluorine, strong fluorinating agents, and sodium hydroxide above 300°C. Shapes of small cross section burn vertically upward after ignition in 100% oxygen. Because gases may be evolved, the weight loss during sintering of a blend of PTFE and white asbestos is many times greater than loss from pure PTFE. Finely divided aluminum and magnesium thoroughly mixed with finely divided PTFE react vigorously after ignition or at high temperatures.

Absorption of a liquid is usually a matter of the liquid dissolving in the polymer; however, in the case of PTFE, no interaction occurs between the polymer and other substances. Submicroscopic voids between the polymer molecules provide space for the material absorbed, which is indicated by a slight weight increase and sometimes by discoloration. Common acids or bases are not absorbed up to 200°C. Aqueous solutions are scarcely absorbed at atmospheric pressure. Even the absorption of organic solvents is slight, partially resulting from the low wettability of PTFE. Since absorption of chemicals or solvents has no substantial effect on the chemical bond within the fluorocarbon molecule, absorption should not be confused with degradation; it is a reversible physical process. The polymer does not suffer loss of mechanical or bulk electrical properties unless subjected to severely fluctuating conditions.

Dynamic mechanical measurements were made on PTFE samples saturated with various halocarbons (96). The peaks in loss modulus associated with the amorphous relaxation near −90°C and the crystalline relaxation near room temperature were not affected by these additives. An additional loss peak appeared near −30°C, and the modulus was reduced at all higher temperatures. The amorphous relaxation that appears as a peak in the loss compliance at 134°C is shifted to 45–70°C in the swollen samples.

The sorption behavior of perfluorocarbon polymers is typical of nonpolar partially crystalline polymers (97). The weight gain strongly depends on the solubility parameter. Little sorption of substances such as hydrocarbons and polar compounds occurs.

As an excellent barrier resin, PTFE is widely used in the chemical industry. However, it is a poor barrier for fluorocarbon oils because similarity in the chemical composition of a barrier and a permeant increases permeation. Most liquids and gases (other than fluorocarbons) do not permeate highly crystalline PTFE. Permeabilities at 30°C [in $10^{15} \times \mathrm{mol/(m{\cdot}s{\cdot}Pa)}$] are as follows: CO_2, 0.93; N_2, 0.18; He, 2.47; anhydrous HCl, <0.01.

Gases and vapors diffuse through PTFE more slowly than through most other polymers (Table 5). The higher the crystallinity, and the less space between polymer molecules, the slower the permeation. Voids greater than molecular size cause an increase in permeability. However, the permeability of the finished article can be controlled by molding the resin to low porosity and high density. The optimum specific gravity for low permeability and good flexural properties is 2.16–2.195. Permeability increases with temperature as a result of the increase in activity of the solvent molecules and because of the increase in vapor pressure of the liquids. Swelling of PTFE resins and film is very low.

Electrical Properties. Polytetrafluoroethylene is an excellent electrical insulator because of its mechanical strength and chemical and thermal stability, as well as excellent electrical properties (Table 6).

It does not absorb water and volume resistivity remains unchanged even after prolonged soaking. The dielectric constant remains constant at 2.1 for a temperature range of −40 to 250°C and a frequency range of 5–10 GHz.

Articles fabricated according to standard practice should have dielectric constants in the range of 2.05 ± 0.5 when tested at room temperature (RT). The dielectric constant varies with density and factors that affect density. Machined components can be fabricated to a predetermined dielectric constant by controlling the rod density during processing by adjusting the preforming pressure on the resin and cooling after sintering. The dielectric constant and the density have a linear relationship. Predictable variations in the dielectric constant result from density changes that accompany thermal expansion occurring with increasing temperature. The dielectric constant did not change over two to three years of measurements.

The dissipation factor (the ratio of the energy dissipated to the energy stored per cycle) is affected by the frequency, temperature, crystallinity, and void content of the fabricated structure. At certain temperatures and frequencies, the crystalline and amorphous regions become resonant. Because of the molecular vibrations, applied electrical energy is lost by internal friction within the polymer, which results in an increase in the dissipation factor. The dissipation factor peaks for these resins correspond to well-defined transitions, but the magnitude of the variation is minor as compared to other polymers. The low temperature transition at -97°C causes the only meaningful dissipation factor peak. The dissipation factor has a maximum of 10^8–10^9 Hz at RT; at high crystallinity (93%) the peak at 10^8–10^9 Hz is absent.

As crystallinity increases, the internal molecular friction and the dissipation factor decrease. Voids reduce the dissipation factor in proportion to the percentage of microvoids present. Certain extruded shapes utilize air to reduce the effective dielectric constant and dissipation factor of a coaxial cable. The dielectric strength of these resins is high and is unaffected by thermal aging at 200°C. Frequency has a marked effect on the dielectric strength because corona discharge becomes more continuous as frequency increases. If the voltage stress is not high enough to cause corona ignition, a very long dielectric life is anticipated at any frequency. Corona discharges on the surface or in a void initiate dielectric breakdown (99). Surface arc resistance of these resins is high and not affected by heat aging. The resins do not track or form a carbonized conducting path when subjected to a surface arc in air. Polytetrafluoroethylene resins are capable of continuous service up to 260°C and can withstand much higher temperatures for limited periods of time. They do not melt or flow and retain some strength even in the gel state which begins at 327°C.

1.5. Fabrication. *Granular Resins.* These resins are sold in different forms; an optimum balance between handleability and product properties is desired. A free-flowing resin is used in small and automatic moldings. A finely divided resin is more difficult to handle but it distributes evenly in large moldings and has superior properties in sintered articles; it is used for large billet- and sheet-molding operations. A presintered resin with low crystallinity and superior handleability is highly suitable for ram extrusion.

Virgin PTFE melts at about 342°C; viscosity, even at 380°C, is 10 GPa·s (10^{11} P). This eliminates processing by normal thermoplastic techniques, and other fabrication techniques had to be developed: the dry powder is compressed into handleable form by heating above the melting point. This coalesces the particles into a strong homogeneous structure; cooling at a controlled rate achieves the desired degree of crystallinity.

Molding. Many PTFE manufacturers give detailed descriptions of molding equipment, and procedures are presented in Reference 100. Round piston molds for the production of solid or hollow cylinders are the most widely used.

Because preforming usually takes place below 100°C, carbon steel is a suitable material of construction. The compression ratio (ie, the bulk volume of the powder to the specific volume of the unsintered molding) for granular resins is 3:1 to 6:1. The powder should be evenly distributed and leveled in the mold, and to ensure adequate compression uniformly throughout the preform, maximum pressure should be maintained for a sufficient length of time, and then be released slowly.

Automatic molding permits high speed mass production and can be effective. Automatic presses can be operated mechanically, pneumatically, or hydraulically. The mold is filled by means of a special metering system from a storage hopper containing a free-flowing resin. Loading buckets that shuttle back and forth over the single-cavity mold are also used. Because automatic molding requires short cycles, the powder is usually compressed at high speed with a high preform pressure. Small articles such as rings, bushings, washers, gaskets, and ball-valve seats can be molded by this technique.

Isostatic molding allows uniform compression from all directions. A flexible mold is filled with a free-flowing granular powder and evacuated, tightly sealed, and placed in an autoclave containing a liquid that can be raised to the pressure required for performing. The moldings require subsequent finishing because close tolerance cannot be achieved.

Sintering. Electrical ovens with air circulation and service temperatures up to 400°C are satisfactory for sintering. In free sintering—the cheapest and most widely used process—a preformed mold is placed in an oven with a temperature variation of ±2°C. In pressure sintering, the preform is not removed from the mold; instead the mold containing the preform is heated in an oven until the sintering temperature is reached. During sintering and cooling, the mold is again placed under pressure but lower than the preform pressure. Pressure-sintered products have internal stresses that can be relieved by subsequent annealing. In the pressure-cooling process, pressure is applied on the molded article after it has reached sintering temperature and is maintained throughout the cooling period. The final product has a lower void content than the free-sintered mold.

To improve homogenity, the preformed article is heated to 370–390°C. The time required for heating and sintering depends on the mold dimensions; cooling, which affects the crystallinity and product properties, should be slow.

Free-sintered articles do not have the same dimensions as the mold cavity because they shrink at right angles to the direction of the preform pressure and grow in the direction of the applied pressure.

For processing after sintering, in the least expensive method for sintered PTFE tape or sheet, a large billet is skived on a lathe after it has been sintered and cooled. High precision articles are machined from ram-extruded rods.

Articles that are too complicated to be made by machining are made by coining. A sintered molding is heated to its melting point, transferred to a mold, and quickly deformed at low pressure, where it is held until it has cooled sufficiently to retain the improved shape. However, the coined molding, if reheated to a high temperature, returns to its original shape, and hence there is a limit on the maximum temperature to which coined moldings can be heated.

Ram Extrusion. Compression molding is not suitable for the manufacture of continuous long moldings such as pipes or rods. In ram extrusion, a small charge of PTFE powder is preformed by a reciprocating ram and sintered. Subsequent charges are fused into the first charge, and this process continues to form homogeneous long rods (101). The die tube, which is made of a corrosion-resistant material, is heated by resistance heating. Good temperature control is essential, and the melted and compacted powder must not pass any constrictions in its path. Thermal expansion and friction produce great resistance to movement, and as a result, a considerable force is required to push the polymer through the tube. A high quality surface finish on the inside of the tube reduces the pressure. If adequate bond strength between successive charges is not developed, the extrudate may break at the interface (poker chipping). Free-flowing powders and presintered resins are preferred for ram extrusion. Ram-extruded rods are used for automatic screw machining. Tubing is used as pipe liners or stock from which seals, gaskets, and bellows are machined.

Fine Powder Resins. Fine powder PTFE resins are extremely sensitive to shear. They must be handled gently to avoid shear, which prevents processing. However, fine powder is suitable for the manufacture of tubing and wire insulation for which compression molding is not suitable. A paste-extrusion process may be applied to the fabrication of tubes with diameters from fractions of a millimeter to about a meter, walls from thicknesses of 100–400 μm, thin rods with up to 50-mm diameters, and cable sheathing. Calendering unsintered extruded solid rods produces thread-sealant tape and gaskets.

The paste-extrusion process includes the incorporation of ca 16–25 wt% of the lubricant (usually a petroleum fraction); the mixture is rolled to obtain uniform lubricant distribution. This wetted powder is shaped into a preform at low pressure (2.0–7.8 MPa or 19–77 atm), which is pushed through a die mounted in the extruder at ambient temperature. The shear stress exerted on the powder during extrusion confers longitudinal strength to the polymer by fibrillation. The lubricant is evaporated and the extrudate is sintered at ca 380°C.

The exact amount of lubricant required for extrusion depends on the design of the extruder, the reduction ratio (ie, ratio of the cross-sectional preform area to the cross-sectional area in the die), and the quality of the lubricant. A low lubricant content results in a high extrusion pressure, whereas a high lubricant content causes a poor coalescence and generates defects in the extrudate.

Fine powder resins can be colored with pigments that can withstand the sintering temperature. The pigment should be thoroughly mixed with the powder by rolling the mixture before adding the lubricant. Detailed design parameters of the paste extruder are given in References 100, 102 and 103.

The extrudate is dried and sintered by passing it through a multistage oven located immediately after the extruder. Pipes and rods may be heated up to 380°C. The throughput rate depends on the length of the sintering oven. Residence time varies from a few seconds for thin-walled insulations on a wire to a few minutes for large diameter tubing. For short residence times temperatures may be as high as ca 480°C. The extrusion pressure depends on the reduction ratio, the extrusion rate, the lubricant content, and the characteristics of the extruder.

To produce unsintered tape by paste extrusion, the fine powder is lubricated and preformed according to the procedure described earlier. The preform is extruded in the form of rods, which are calendered on hot rolls to the desired width and thickness. (104).

Different resins have been developed for use in different reduction–ratio application ranges (105,106). The powders suitable for high reduction–ratio applications, such as wire coatings, are not necessarily suitable for the medium reduction–ratio applications, such as tubings, or the low reduction–ratio applications, such as thread-sealant tapes or pipe liners. Applications and processing techniques are being used, which utilize the unique combination of properties offered by PTFE in fine powder form (107–109).

Dispersion Resins. Polytetrafluoroethylene dispersions in aqueous medium contain 30–60 wt% polymer particles and some surfactant. The type of surfactant and the particle characteristics depend on the application. These dispersions are applied to various substrates by spraying, flow coating, dipping, coagulating, or electrodepositing (110).

Aqueous dispersion is sprayed on metal substrates to provide chemical resistance, nonstick, and low friction properties. The coated surface is dried and sintered. Impregnation of fibrous or porous materials with these dispersions combines the properties of the materials with those of PTFE. Some materials require only a single dipping, eg, asbestos. The material is usually dried after dipping. For high pressure sealing applications, sintering at 380–400°C increases strength and dimensional stability. For film castings, the dispersion is poured on a smooth surface; the formed film is dried and sintered and peeled from the supporting surface.

Aqueous dispersions are used for spinning PTFE fibers. The dispersion is mixed with a matrix-forming medium (111,112) and forced through a spinneret into a coagulating bath. The matrix material is removed by heating and the fibers are sintered and drawn molten to develop their full strength.

Effects of Fabrication on Physical Properties of Molded Parts. The physical properties are affected by molecular weight, void content, and crystallinity. Molecular weight can be reduced by degradation but not increased during processing. These factors can be controlled during molding by the choice of resin and fabricating conditions. Void distribution (or size and orientation) also affects properties; however, it is not easily measured.

Preforming primarily affects void content, sintering controls molecular weight, and cooling determines crystallinity. Voids caused by insufficient consolidation of particles during preforming may appear in the finished articles. Densities below 2.10 g/cm^3 indicate a high void content. Electrical and chemical applications require a minimum density of 2.12–2.14 g/cm^3. Particle size, shape, and porosity are also important in determining void content. Although void content is determined largely by particle characteristics and preforming conditions, sintering conditions can also have an effect. Temperatures too high or too low increase void content. Excessively high sintering temperature can decrease the molecular weight. The final crystallinity of a molding depends on the initial molecular weight of the polymer, the rate of cooling of the molding, and to a lesser extent on sintering conditions. The degree of crystallinity of moldings is affected by the cooling or annealing conditions.

Flexural modulus increases by a factor of 5 as crystallinity increases from 50 to 90% with a void content of 0.2%; however, recovery decreases with increasing crystallinity. Therefore, the balance between stiffness and recovery depends on the application requirements. Crystallinity is reduced by rapid cooling but increased by slow cooling. The stress-crack resistance of various PTFE insulations is correlated with the crystallinity and change in density due to thermal mechanical stress (113).

1.6. Economic Aspects. Polytetrafluoroethylene (PTFE) is not melt processible, but is the largest volume fluoropolymer of commerce in the world. PTFE accounted for 60–65% by weight of all fluoropolymers consumed in the United States, Western Europe, and Japan in 2001. Consumed in smaller amounts are the melt-processible resins and these include FEP, ETFE, and PFA.

World consumption of fluropolymers reached 112×10^3 t in 2001. This total was valued at $\$2.1 \times 10^9$. Capacity in 2001 was about 142×10^3 t. World trade reached a level of about $39–46 \times 10^3$ t, representing 37% of total consumption. Growth in world consumption of fluoropolymers should average about 5%/yr through 2006 (114).

Polytetrafluoroethylene homopolymers are more expensive than most other thermoplastics because of high monomer refining costs. For extremely high molecular weights, ingredients and manufacturing process must be free of impurities, which increases costs. In the United States, the 2000 list prices from primary producers were between $15.2/kg and $20.4/kg, depending on the resin type. For example, granular PTFE resins cost $15.2–20.4/kg supplied in 45.45-kg containers. The coagulated fine powders cost $23.2–30.3/kg packaged in 45.45-kg containers. Formulated dispersions are $21.9–35.4/kg in 19- or 113-L containers. Although fine powder sales have increased in recent years, the sales of granular PTFE are the highest on a worldwide basis.

DuPont is the leader in the fluorocarbon industry. Other major participants in the total fluoropolymer market are ATOFINA, Daikin, Dyncon, Ashai Glass, and Solvay. China, Russia, India, and Poland are emerging as suppliers, however, products from these countries have not yet reached the high standards of users in developed regions of the world.

When fluropolymers are produced, the fluorocarbon feedstocks become solid and are not emitted into the environment. Ozone depletion is, however, a very important issue and could affect the future supply of fluorocarbon feedstocks (114).

1.7. Testing and Standards. A description of PTFE resins and their classification are given in ASTM D1457-83. A comprehensive listing of industrial and military specifications covering mechanical, electrical, and chemical applications of PTFE can be found in Reference 115.

1.8. Health and Safety Factors. Exposure to PTFE can arise from ingestion, skin contact, or inhalation. The polymer has no irritating effect to the skin, and test animals fed with the sintered polymer have not shown adverse reactions. Dust generated by grinding the resin also has no effect on test animals. Formation of toxic products is unlikely. Only the heated polymer is a source of a possible health hazard (116,117).

Because PTFE resins decompose slowly, they may be heated to a high temperature. The toxicity of the pyrolysis products warrants care where exposure of personnel is likely to occur. Above 230°C decomposition rates become measurable (0.0001% per hour). Small amounts of toxic perfluoroisobutylene have been isolated at 400°C and above; free fluorine has never been found. Above 690°C the decomposition products burn but do not support combustion if the heat is removed. Combustion products consist primarily of carbon dioxide, carbon tetrafluoride, and small quantities of toxic and corrosive hydrogen fluoride. The PTFE resins are nonflammable and do not propagate flame.

Prolonged exposure to thermal decomposition products causes so-called polymer fume fever, a temporary influenza-like condition. It may be contracted by smoking tobacco that has been contaminated with the polymer. It occurs several hours after exposure and passes within 36–48 h; the temporary effects are not cumulative.

Large quantities of PTFE resins have been manufactured and processed above 370°C. In various applications they are heated above the recommended use temperatures. No cases of serious injury, prolonged illness, or death have been reported resulting from the handling of these resins. However, when high molecular weight PTFE is converted to micropowder by thermal degradation, highly toxic products result.

Micropowders are added to a wide variety of material used in industry, where they provide nonstick and sliding properties (111). They are incorporated into the product by blending and grinding. To disperse well, the powder must have good flow properties. Conditions that make the powder sticky should be avoided.

The PTFE micropowders are commonly used in plastics, inks, lubricants, and finishes such as lacquer. Lubricants containing micropowders are used for bearings, valve components, and other moving parts where sliding friction must be minimized or eliminated. Nonstick finished that require good release properties, for example, in the food and packaging industry, commonly use PTFE micropowders.

In some applications the high heat stability of the micropowder can be utilized over a reasonably wide temperature range. A maximum service temperature is normally 260°C, provided the crystalline melting point is between 320 and 335°C. Exposure above 300°C leads to degradation and possible evolution of toxic decomposition products.

The particulate morphology of PTFE micropowder in printing inks provides desirable gloss to the printed product. Its inherent lubricity results in good wear and slip properties and surface smoothness. The chemical resistance of the micropowder is as high as that of high molecular weight PTFE. It is therefore used in applications requiring service in strong or corrosive chemical environments such as concentrated mineral acids and alkalies.

1.9. Applications. Consumption of PTFE increases continuously as new applications are being developed. Electrical applications consume half of the PTFE produced; mechanical and chemical applications share equally the other half. Various grades of PTFE and their applications are shown in Table 7.

Electrical Applications. The largest application of PTFE is for hookup and hookup-type wire used in electronic equipment in the military and aerospace industries. Coaxial cables, the second largest application, use tapes made from fine powder resins and some from granular resin. Interconnecting wire applications include airframes. Other electrical applications include computer wire, electrical tape, electrical components, and spaghetti tubing.

Mechanical Applications. Seals and piston rings, basic shapes, and antistick uses constitute two-thirds of the resin consumed in mechanical applications. Bearings, mechanical tapes, and coated glass fabrics also consume a large amount of PTFE resins. Seals and piston rings, bearings, and basic shapes are manufactured from granular resins, whereas the dispersion is used for glass–fabric coating and antistick applications. Most pressure-sensitive mechanical tapes are made from granular resins.

Chemical Applications. The chemical processing industry uses large amounts of granular and fine powder PTFE. Soft packing applications are manufactured from dispersions, and hard packings are molded or machined from stocks and shapes made from granular resin.

Overbraided hose liners are made from fine powder resins by paste extrusion, and thread-sealant tapes are produced from fine powder by calendering. Fabricated gaskets are made from granular resins and pipe liners are produced from fine powder resins. Fibers and filament forms are also available.

Highly porous fabric structures, eg, Gore-Tex, that can be used as membranes have been developed by exploiting the unique fibrillation capability of dispersion-polymerized PTFE (107).

Micropowders. The PTFE micropowders, also called waxes, are TFE homopolymers with molecular weights significantly lower than that of normal PTFE (118). The molecular weight for micropowders varies from 2.5×10^4 to 25×10^4, whereas that of normal PTFE is of the order of 10×10^6. Micropowders are generally white in color and are friable. The average agglomerate particle size is between 5 and 10 μm and is composed of smaller, "as polymerized" primary particles which are approximately 0.2 μm in diameter. The dsc curves of lower molecular weight micropowder show a higher heat of crystallization and melting (second heating) than normal PTFE. This is due to the higher crystallinity of the micropowder.

The production of micropowders involves the scission of the high molecular weight PTFE chain by gamma or electron beam irradiation at a variety of dosage levels. An increase in dosage reduces the molecular weight. The irradiated low molecular weight material is ground to a particle size ranging from 1 to 25 μm in the final product.

2. Perfluorinated Ethylene–Propylene Copolymers

2.1. Introduction.

Perfluorinated ethylene–propylene (FEP) resin is a copolymer of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) [116-15-4]; thus, its branched structure contains units of $-CF_2-CF_2-$ and of $-CF_2-CF(CF_3)-$. It retains most of the desirable characteristics of polytetrafluoroethylene (PTFE) but with a melt viscosity (MV) low enough for conventional melt processing. The introduction of HFP lowers the melting point of PTFE from 325°C to about 260°C.

The desire for a resin with PTFE properties yet capable of being fabricated by conventional melt processing led to the discovery of this product (119).

It allows melt extrusion of wire insulations of longer continuous lengths than the batchwise paste extrusion of PTFE as well as the injection molding of intricately shaped parts. The FEP polymer is melt-fabricable without severe sacrifice in mechanical properties because the perfluoromethyl side groups on the main polymer chain reduce crystallinity, which varies between 30 and 45%. This change in the crystallinity causes FEP and other copolymer particles to behave differently from PTFE particles; they do not fibrillate like PTFE particles and therefore do not agglomerate easily.

As a true thermoplastic, FEP copolymer can be melt-processed by extrusion and compression, injection, and blow molding. Films can be heat-bonded and sealed, vacuum-formed, and laminated to various substrates. Chemical inertness and corrosion resistance make FEP highly suitable for chemical services; its dielectric and insulating properties favor it for electrical and electronic services; and its low frictional properties, mechanical toughness, thermal stability, and nonstick quality make it highly suitable for bearings and seals, high temperature components, and nonstick surfaces.

Mechanical properties are retained up to 200°C, even in continuous service, which is better than with most plastics. At high temperatures, these copolymers react with fluorine, fluorinating agents, and molten alkali metals. They are commercially available under the DuPont trademark Teflon FEP fluorocarbon resin. A similar product is manufactured by Daikin Kogyo and Dyneon and sold under the trademarks Neoflon and Hostaflon, respectively. The People's Republic of China also manufactures some FEP products. Additional information on specific manufacturers' products can often be obtained by consulting their internet web sites (for example, www.dupont.com/teflon).

2.2. Monomers.

Preparation. The preparation, properties, and uses of TFE have been described. Hexafluoropropylene was initially prepared by pyrolysis of PTFE (120,121) and by fluorination of 1,2,3-trichloropropane followed by dehalogenation (122). A number of other routes are described in the patent literature (123–128). Hexafluoropropylene can be prepared in high yield by thermally cracking TFE at reduced pressure at 700−800°C (129,130). Pyrolysis ofPTFE at 860°C under vacuum gives a 58% yield of HFP (131). Fluorination of 3-chloropentafluoro-1-propene [79-47-0] at 200°C over activated carbon catalyst yields HFP (132). Decomposition of fluoroform [75-46-7] at 800−1000°C in a platinum-lined nickel tube is another route (133). The thermal decomposition of sodium heptafluorobutyrate [2218-84-4], $CF_3CF_2CF_2CO_2Na$ (134), and copyrolyses of fluoroform and chlorotrifluoroethylene [79-38-9] (135), and chlorodifluoromethane [75-45-6] and 1-chloro-1,2,2,2-tetrafluoroethane [2837-89-0] (136) give good yields of HFP.

Properties. The properties of HFP are shown in Table 8. It does not homopolymerize easily and hence can be stored as a liquid. It undergoes many addition reactions typical of an olefin. Reactions include preparation of linear dimers and trimers and cyclic dimers (139,140); decomposition at 600°C with subsequent formation of octafluoro-2-butene and octafluoroisobutylene (141); oxidation with formation of an epoxide (142), an intermediate for a number of perfluoroalkyl perfluorovinyl ethers (143,144); and homopolymerization to low molecular weight liquids (145,146) and high molecular weight solids (147,148). Hexafluoropropylene reacts with hydrogen (149), alcohols (150), ammonia (151), and the halogens and their acids, except I_2 and HI (149,152–154). It is used as a comonomer to produce elastomers and other copolymers (155–159). The toxicological properties are discussed in Reference 160.

2.3. Copolymers. Hexafluoropropylene and tetrafluoroethylene are copolymerized, with trichloracetyl peroxide as the catalyst, at low temperature (161). Newer catalytic methods, including irradiation, achieve copolymerization at different temperatures (162,163). Aqueous and nonaqueous dispersion polymerizations appear to be the most convenient routes to commercial production (119,164–168). The polymerization conditions are similar to those of TFE homopolymer dispersion polymerization. The copolymer of HFP–TFE is a *random copolymer*; that is, HFP units add to the growing chains at random intervals. The optimal composition of the copolymer requires that the mechanical properties are retained in the usable range and that the MV is low enough for easy melt processing.

Hexafluoropropylene–tetrafluoroethylene copolymers are available in low MV, extrusion grade, intermediate viscosity, high MV, and as dispersions. The low MV resin can be injection molded by conventional thermoplastic molding techniques. It is more suitable for injection molding than other FEP resins (169).

The extrusion grade is suitable for tubing, wire coating, and cable jacketing. It is less suitable for injection molding than the low MV resin because of its relatively high MV. The intermediate MV (Teflon FEP-140) resin is used for insulation of wires larger than AWG 12 (American wire gauge) and applications involving smaller wire sizes, where high current loads or excessive thermal cycling may occur. It is also ideal for jacketing wire braid construction, such as coaxial cables, and for heater cable jackets.

The high MV resin is used as liners for process equipment. Its MV is significantly higher than that of other resins, and therefore it is unsuitable for conventional injection molding. Stress-crack resistance and mechanical properties are superior to those of the other three products (170) (Table 9).

Modified HFP–TFE polymers offer a combination of high stress-crack resistance and high extrusion rates. Use of perfluorovinyl ethers as modifiers make it possible to achieve the superior performance without losing excellent chemical inertness and thermal stability (171–173).

Both high and low color concentrates are available for pigmenting extruded coatings of FEP resins. The concentrates are prepared for melt dispersion in extrusion applications. The pigments (thermally stable) are purified and carefully selected to meet electrical, mechanical, and thermal end use specifications. Color concentrate pellets are easily dispersed among clear pellets by conventional tumbling. The ratio of concentrate to natural resin varies, depending on the wire size, insulation thickness, and color intensity desired.

An FEP copolymer dispersion is available as a 55-wt% aqueous dispersion containing 6% nonionic surfactant (on a solids basis) and a small amount of anionic dispersing agent. Its average particle size is ca 0.2 μm.

2.4. Properties. The crystallinity of FEP polymer is significantly lower than that of PTFE (70 vs 98%). The structure resembles that of PTFE, except for a random replacement of a fluorine atom by a perfluoromethyl group (CF_3). The crystallinity after processing depends on the rate of cooling the molten polymer.

The presence of HFP in the polymer chain tends to distort the highly crystallized structure of the PTFE chain and results in a higher amorphous fraction.

In the free-radical polymerization of FEP copolymers, chain termination occurs by binary coupling of chain ends, thus contributing to high molecular weights. Linear viscoelastic properties of these polymers in the amorphous melts were measured by dynamic rheometry. The FEP samples had high molecular weights and were found to verify the relation of zero shear viscosity vs (mol wt)^3 predicted by the reptation theory. At lower molecular weights, the empirical relation of viscosity vs (mol wt)$^{3.4}$ holds (174).

Transitions and Relaxations. Only one first-order transition is observed, the melting point. Increasing the pressure raises the melting point. At low pressures, the rate of increase in the melting point is ca 1.74°C/MPa (0.012°C/psi); at high pressures this rate decreases to ca 0.725°C/MPa (0.005°C/psi). Melting increases the volume by 8%. In the presence of the HFP comonomer, crystal distortion occurs with an increase in intramolecular distance that, in turn, reduces the melting point (175).

The relaxation temperature appears to increase with increasing HFP content. Relaxation involves 5–13 of the chain carbon atoms. Besides α and γ relaxations, one other dielectric relaxation was observed below −150°C, which did not vary in temperature or in magnitude with comonomer content or copolymer density (176). The α relaxation (also called Glass I) is a high temperature transition (157°C), and γ relaxation (Glass II) (internal friction maxima) occurs between −5 and 29°C. The chain conformation and crystal structure of a series of HFP–TFE copolymers containing up to 50 mol% of HFP were studied (177). Increasing HFP content leads to significant departures from the highly ordered crystalline structure of PTFE. The helical conformation of the chain relaxes and untwists to accommodate the $-CF_3$ pendant group in the HFP unit.

Thermal Stability. The polymer is thermally stable and can be processed at ca 270°C. Thermal degradation is a function of temperature and time, and the stability is therefore limited. The melt-flow rate (thermal degradation) increases significantly for short periods above 280°C, and degradation occurs at lower temperatures with longer hold times. The hourly weight loss is 0.0004% at 230°C, 0.001% at 260°C, 0.01% at 290°C, 0.02% at 320°C, 0.08% at 340°C, and 0.3% at 370°C. Degradation is not significant if the change in melt-flow rate during molding is $<$10%. Physical strength decreases after prolonged exposure above 205°C, which accounts for the lower temperature rating of FEP resins (178).

Radiation Effects. The primary effect of radiation is the degradation of large molecules to small molecules. Molecular weight reduction can be minimized by excluding oxygen. If FEP is lightly irradiated at elevated temperatures in the absence of oxygen, cross-linking offsets molecular breakdown (176,179).

The degree to which radiation exposure affects FEP resins is determined by the energy absorbed, regardless of the type of radiation. Changes in mechanical properties depend on total dosage, but are independent of dose rate. The radiation tolerance of FEP in the presence or absence of oxygen is higher than that of PTFE by a factor of 10:1. Vacuum uv irradiation seems to provide a high potential for surface modification as compared to plasma treatment (180).

Mechanical Properties. Extensive lists of the physical properties of FEP copolymers are given in References 181–186. Mechanical properties are shown in Table 10. Most of the important properties of FEP are similar to those of PTFE; the main difference is the lower continuous service temperature of 204°C of FEP compared to that of 260°C of PTFE. The flexibility at low temperatures and the low coefficients of friction and stability at high temperatures are relatively independent of fabrication conditions. Unlike PTFE, FEP resins do not exhibit a marked change in volume at room temperature because they do not have a first-order transition at 19°C. They are useful above −267°C and are highly flexible above −79°C (187).

Static friction decreases with an increase in load, and the static coefficient of friction is lower than the dynamic coefficient. The tendency to creep must be considered carefully in FEP products designed for service under continuous stress. Creep can be minimized by suitable fillers. Fillers are also used to improve wear resistance and stiffness. Compositions such as 30% bronze-filled FEP, 20% graphite-filled FEP, and 10% glass-fiber-filled FEP offer high PV values [~400(kPa·m)/s] and are suitable for bearings.

Articles fabricated from FEP resins can be made bondable by surface treatment with a solution of sodium in liquid ammonia, or naphthalenyl sodium in tetrahydrofuran (187) to facilitate subsequent wetting. Exposing the surface to corona discharge (188) or amines at elevated temperatures in an oxidizing atmosphere (189) also makes the resins bondable. Some of the more recent work is described in References 190–192.

Vibration-dampening properties at sonic and ultrasonic frequencies are excellent. However, the thickness of the resin must be sufficient to absorb the energy produced; this is usually determined experimentally.

Electrical Properties. Because of excellent electrical properties, FEP is a valuable and versatile electrical insulator. Within the recommended service temperature range, PTFE and FEP have identical properties as electrical insulators. Volume resistivity, which is $>10^{17}\,\Omega\cdot$cm, remains unchanged even after prolonged soaking in water; surface resistivity is $>10^{15}\,\Omega$/sq.

At low frequencies, the dielectric constant of FEP remains the same (~2). However, at >100 MHz the constant drops slightly with increasing frequency. As a true thermoplastic, FEP has a void content of zero and most of the fabricated material has a density of 2.14–2.17 g/cm^3. The National Bureau of Standards has selected Teflon FEP resins for dielectric reference specimens because of the stability of their dielectric constant. The dissipation factor has several peaks as a function of temperature and frequency (3×10^{-4} at 100 kHz; 7×10^{-4} at 1 MHz). The magnitude of the dissipation factor peak is greater for FEP than for PTFE because the molecular structure of the former is less symmetrical. The dissipation factor is hardly affected by irradiation annealing (193) and unaffected by humidity. The dielectric strength is high (80 GV/mm for 0.25-mm film at 23°C) and unaffected by thermal aging at 200°C. At high frequencies, the dielectric properties deteriorate in the presence of corona. If the voltage stress is not high enough to cause corona ignition, an infinitely long dielectric life is expected at any frequency. Corona discharges on the surface or in a void initiate dielectric breakdown (194). The FEP resins are recommended for continuous service up to 205°C. Although they begin to melt flow at 270°C, they retain some structural integrity up to 250°C (193).

Chemical Properties. The FEP resin is inert to most chemicals and solvents, even at elevated temperatures and pressures. However, it reacts with fluorine, molten alkali metal, and molten sodium hydroxide. Acids or bases are not absorbed at 200°C and exposures of 1 year. The absorption of organic solvents is less than 1% at elevated temperatures and long exposure times. Absorption of chemicals or solvents has no effect on the chemical integrity of the FEP molecule and is a reversible physical process.

Gases and vapors permeate FEP resin at a rate that is considerably lower than that of most plastics. Because FEP resins are melt processed, they are void-free and permeation occurs only by molecular diffusion. Variation in crystallinity and density is limited, except in unusual melt-processing conditions.

Because of its low permeability, FEP polymer is used extensively in the chemical industry. Its permeation characteristics are similar to those of PTFE (Table 11). An inverse relationship between permeability and film thickness applies to FEP.

Weathering. Articles fabricated from FEP are unaffected by weather, and their resistance to extreme heat, cold, and uv irradiation suits them for applications in radar and other electronic components. For example, after 15 years of solar exposure in Florida, the tensile strength and light transmission (96%) of a 25-μm-thick film was unchanged and the film remained crystal clear (196). Elongation increased slightly for the first 5–7 years of outdoor exposure, probably as a result of stress relaxation. Beyond 10 years, a small decrease was observed.

Optical Properties. Teflon FEP fluorocarbon film transmits more ultraviolet, visible light, and infrared radiation than ordinary window glass. The refractive index of FEP film is 1.341–1.347 (197).

2.5. Fabrication. Standard thermoplastic processing techniques can be used to fabricate FEP. Thermal degradation must be avoided, and a homogeneous structure and good surface quality must be maintained.

Injection Molding. Compared to most thermoplastic products, even the low MV resin has a significantly higher MV and therefore requires higher processing temperatures, slower injection rates, special mold design, and corrosion-resistant material of construction. When the flow velocity in melt processing exceeds a critical value, melt fracture occurs. The critical shear rate of FEP is much lower than that of other thermoplastics. Recommendations for materials of construction and the screw design, valves, smear heads, nozzle, operating conditions, and mold design are given in References 170, 198, and 199.

Pigments (thermally stable at processing temperature) are dry blended with the resin before molding. At loadings of 0.1–1%, pigments have no appreciable effect on the dielectric strength, dielectric constant, or mechanical properties. The dissipation factor of pigmented resin varies with the pigment and its amount (200).

Extrusion. Conventional melt-extrusion equipment is used in processing FEP resins. Commercial pigments are mixed with the resin before extrusion into wire coating, tubing, rods, molding, beading channels, etc. Coating thicknesses of 0.076–2.54 mm have been extruded over such materials as silicone rubber, poly(vinyl chloride), glass braid, metal-shielded cables, twisted conductors, and parallel multiconductor cables.

For primary insulation or cable jackets, high production rates are achieved by extruding a tube of resin with a larger internal diameter than the base wire and a thicker wall than the final insulation. The tube is then drawn down to the desired size. An operating temperature of 315–400°C is preferred, depending on holdup time. The surface roughness caused by melt fracture determines the upper limit of production rates under specific extrusion conditions (201,202). Corrosion-resistant metals should be used for all parts of the extrusion equipment that come in contact with the molten polymer (203).

Tubing is made in a wide range of sizes and is used as slip-on electrical insulation, instrument tubing, and for hoses. Small tubing, called spaghetti tubing, can be produced by a free-extrusion technique, whereas hose-size tubing is produced by conventional forming-box techniques; FEP also is extruded into films.

Dispersion Processing. The commercial aqueous dispersion of FEP contains 55 wt% of hydrophobic, negatively charged FEP particles and ca 6 wt% (based on FEP) of a mixture of nonionic and anionic surface-active agents. The average particle size is ca 0.2 µm. The dispersion is processed by the same technique used for PTFE dispersion. For example, the fabric is coated with FEP dispersion, the water is evaporated from the coating, the wetting agent is removed, and the FEP layer is fused with the fabric.

Dispersion is used as a coating for glass fabric, chemical barriers, and wire-insulating tapes; as adhesive coatings for bonding seals and bearings of PTFE to metallic and nonmetallic components; and as antifriction or antistick coatings for metals. The fusion of FEP to provide a continuous film depends on a time–temperature relationship; 1 min at 400°C or 40 min at 290°C is sufficient to achieve good fusion (204).

Other Techniques. The FEP resin is bonded to metal surfaces by the application of heat and pressure; it can be heat sealed or hot-gas welded. Heating FEP at 260°C and allowing it to cool slowly results in stress relieving, or annealing. The FEP film is used to weld PTFE-coated surfaces.

Effects of Fabrication on Product Properties. Extrusion conditions have a significant effect on the quality of the product (203). Contamination can be the result of corrosion, traces of another resin, or improper handling. Corrosion-resistant Hastelloy C parts should be used in the extruder. Surface roughness is the result of melt fracture or mechanical deformation. Melt fracture can be eliminated by increasing the die opening, die temperature, and the melt temperature and by reducing the extrusion rate. Bubbles and discoloration are caused by resin degradation, air entrapment, or condensed moisture. Excessive drawdown, resin degradation, or contamination can result in pinholes, tears, and cone breaks. The blisters are caused by degassing of primary coatings, and loose coatings are caused by rapid cooling and long cones.

2.6. Testing and Standards. Requirements for extrusion and molding grades are cited in ASTM specifications (205) and in Federal specification LP-389A of May 1964 (206). For fabricated shapes, FEP film and sheet are covered by Aeronautical Material Specifications (AMS) 3647 and LP-523 (207). Besides the specifications covered by the Fluorocarbons Division of the Society of the Plastics Industry, Inc. (208), other specifications are listed in Reference 209.

2.7. Economic Aspects. Because of the high cost of HFP, FEP is more expensive than PTFE. In the United States, in 2000, FEP sold at prices up to \$35.2/kg, depending on the type and quantity. Most grades are marketed in a colorless, translucent, extruded pellet form. The dispersion containing about 55% solids is priced at ca \$44/kg. FEP sales have increased rapidly because of usage in plenum cable.

2.8. Health and Safety Factors. The safety precautions required in handling HFP–TFE copolymers are the same as those applied to handling PTFE (117). Large quantities have been processed safely by many different fabricators in a variety of operations. With proper ventilation, the polymer can be processed and used at elevated temperatures without hazard. The fumes from heated FEP or its thermal decomposition products are toxic in high concentrations, like the fumes or decomposition products of other polymers. Ventilation should be provided in areas where the resin is at processing temperature (270–400°C). At ambient temperatures, FEP resin is essentially inert. Inhalation of fumes given off by heated FEP resin may result in influenza-like symptoms. They may occur several hours after exposure and disappear within 35–48 h, even in the absence of treatment; the effects are not cumulative (52). Such attacks usually follow exposure to vapors evolved from the polymer without adequate ventilation or from smoking tobacco or cigarettes contaminated with the polymer. Toxicology study of the particulates and fumes is reported in Reference (210).

2.9. Applications. The principal electrical applications include hookup wire, interconnecting wire, coaxial cable, computer wire, thermocouple wire, plenum cable, and molded electrical parts. Principal chemical applications are lined pipes and fittings, over-braided hose, heat exchangers, and laboratory ware. Mechanical uses include antistick applications, such as conveyor belts and roll covers. A recent development of FEP film for solar collector windows takes advantage of light weight, excellent weatherability, and high solar transmission. Solar collectors made of FEP film are efficient, and installation is easy and inexpensive.

3. Tetrafluoroethylene–Ethylene Copolymers

3.1. Introduction. Copolymers of ethylene [74-85-1] and tetrafluoroethylene [116-14-3] (ETFE) have been a laboratory curiosity for more than half a century. These polymers were studied in connection with a search for a melt-fabricable polytetrafluroethylene (PTFE) resin (211–215) interest in them fell with the discovery of TFE–HFP (FEP) copolymers (216). In the 1960s, however, it became evident that a melt-fabricable fluorocarbon resin was needed with higher strength and stiffness than those of PTFE resins. Earlier studies indicated that ETFE [11939-51-6] might have the right combination of properties. Subsequent research efforts (217) led to the introduction of modified ETFE polymer [25038-71-5] (Tefzel) by E. I. du Pont de Nemours & Co., Inc., in 1970.

Modified ETFE are the products of real commercial value because they have good tensile strength, moderate stiffness, high flex life, and outstanding impact strength, abrasion resistance, and cut-through resistance. Electrical properties include low dielectric constant, high dielectric strength, excellent resistivity, and low dissipation factor. Thermal and cryogenic performance and chemical resistance are good. These properties, combined with elasticity, make this material an ideal candidate for heat-shrinkable film and tubing. This family of copolymers can be processed by conventional methods such as melt extrusion, injection molding, transfer molding, and rotational molding. The properties of the copolymers vary with composition; polymers containing 40–90% TFE (by weight) soften between 200 and 300°C, depending on composition (211). The TFE segments of the molecules account for $>75\%$ of the weight of an approximately 1:1 mole ratio copolymer. The two monomers combine readily into a nearly 1:1 alternating structure. Such polymers exhibit a unique combination of mechanical, chemical, and electrical properties as well as excellent weatherability. However, thermal stress-crack resistance is poor. The copolymer can be modified with a termonomer that undergoes free-radical polymerization and does not cause undesirable chain transfer or termination during polymerization. The modified copolymer exhibits almost the identical physical, chemical, and electrical properties characteristic of the 1:1 alternating copolymer, but retains high ultimate elongation up to 200°C.

Ethylene and TFE are copolymerized in aqueous, nonaqueous, or mixed medium with free-radical initiators. The polymer is isolated and converted into extruded cubes, powders, and beads, or a dispersion. This family of products is manufactured by DuPont, Dyneon, Daikin, Asahi Glass, and Solvay Solexis and sold under the trade names of Tefzel, Hostaflon ET, Neoflon EP, Aflon COP, and Halon ET, respectively. Additional information on specific manufacturers' products can often be obtained by consulting their internet web sites (for example, www.dupont.com/teflon).

3.2. Monomers. Tetrafluoroethylene of purity suitable for granular or dispersion polymerizations is acceptable for copolymerization with ethylene. Polymerization-grade ethylene is suitable for copolymerization with TFE. Modifying termonomers, eg, perfluorobutylethylene and perfluoropropylene, are incorporated by free-radical polymerization.

3.3. Manufacture. Tetrafluoroethylene–ethylene copolymers have tensile strengths two to three times as high as the tensile strength of PTFE or of the ethylene homopolymer (211). Because these copolymers are highly crystalline and fragile at high temperature, they are modified with a third monomer, usually a vinyl monomer free of telegenic activity. The termonomer provides the copolymer with side chains of at least two carbon atoms, such as perfluoroalkylvinyl or vinylidene compounds, perfluoroalkyl ethylenes, and perfluoroalkoxy vinyl compounds. For high tensile properties and cut-through resistance, a molar ratio of ethylene and TFE between 60:40 and 40:60 is required (218,219).

Copolymerization is effected by suspension or emulsion techniques under such conditions that TFE, but not ethylene, may homopolymerize. Bulk polymerization is not commercially feasible because of heat-transfer limitations and explosion hazard of the comonomer mixture. Polymerizations typically take place below 100°C and 5 MPa (50 atm). Initiators include peroxides, redox systems (220), free-radical sources (221), and ionizing radiation (222). Mixtures of inert solvent and water can be used, where the polymerization occurs in the solvent medium, while the water serves to lower the viscosity of the mixture and to remove the heat of polymerization (223,224).

Purely aqueous polymerization systems give copolymers that are not wetted by the reaction medium. The products agglomerate and plug valves, nozzles, and tubing, and adhere to stirrer blades, thermocouples, or reactor walls. These problems do not occur in organic media or mixtures of these with water.

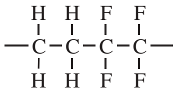
Aqueous emulsion polymerization is carried out using a fluorinated emulsifier, a chain-transfer agent to control molecular weight, and dispersion stabilizers such as manganic acid salts and ammonium oxalate (225,226).

To obtain a 50:50 molar ratio of monomers in the polymer, a mixture of about 75:25 TFE to ethylene must be initially charged to the reactor, depending on reactor pressure and temperature. Reactivity ratios for this system have been studied (227,228). The effects of temperature, addition of termonomer, and ethylene/TFE ratio on degree of alternation and on molecular structure have been studied (229). Melting point of ETFE are higher than would be predicted based upon a linear relationship between polyethylene and PTFE melting points. ETFE is unique in this respect. All other common copolymers of TFE exhibit either linear or depressed melting points when compared to a line between the respective homopolymer melting point and that of PTFE. This positive melting point deviation occurs from about 35:65 to 65:35 mole ratios and is at a maximum at the 50:50 alternating copolymer, which melts at about 285°C, compared to about 235°C for the 65:35 TFE/ethylene composition. Melting points are lowered by the incorporation of modifier, but the overall shape of a curve of the positive melting point deviation is unaltered. The ability of adjacent chains to interpenetrate is thought to be responsible for this behavior. For the same reason, stiffness follows a similar positive deviation, also reaching a maximum at the 50:50 composition. Reactivity ratios of ethylene and TFE are as follows:

Temperature, °C	$r(C_2F_4)$	$r(C_2H_4)$
−35	0.014 ± 0.008	0.010 ± 0.02
65	0.045 ± 0.010	0.14 ± 0.03

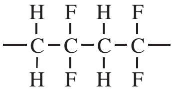
These values indicate strong alternation tendencies that decrease with increasing temperature. Computations show that 1:1 ETFE obtained at −30 and 65°C should have about 97 and 93%, respectively, of alternating sequences (230).

3.4. Properties. The equimolar copolymer of ethylene and TFE is isomeric with poly(vinylidene fluoride) but has a higher melting point (231,232) and a lower dielectric loss (233,234). A copolymer with the degree of alternation of about 0.88 was used to study the structure (235). The unit cell was determined by x-ray diffraction (236,237). Despite irregularities in the chain structure and low crystallinity, a unit cell and structure was derived that gave a calculated crystalline density of 1.9 g/cm^3. The unit cell is believed to be orthorhombic or monoclinic ($a = 0.96$ nm, $b = 0.925$ nm, $c = 0.50$ nm; $\gamma = 96°$).



$-\mathrm{CH_2-CH_2-CF_2-CF_2}-$

Ethylene-tetrafluoroethylene unit



$-\mathrm{CH_2-CF_2-CH_2-CF_2}-$

Poly(vinylidene fluoride) segment

The molecular conformation is that of extended zigzag. Molecular packing appears to be orthorhombic, each molecule having four nearest neighbors with the CH_2 groups of one chain adjacent to the CF_2 groups of the next. The x-ray spectrum of a 1:1 copolymer has two main peaks at $Z_0 = 19.63^\circ$ and $Z_0 = 21.00^\circ$, corresponding to Bragg distances of 0.45 and 0.42 nm, respectively. Compression-molded samples are 50–60% crystalline; however, crystallinity is greatly affected by composition, quench rate, and temperature.

Alternation is usually above 90%. Nearly perfect alternation of isomeric units in a ca 1:1 monomer ratio has been confirmed by infrared spectroscopy. Bands at 733 and 721 cm^{-1} have an intensity proportional to the concentration of $(CH_2)_n$ groups ($n = 4$ and <6, respectively) present in a copolymer containing 46 mol% TFE; intensity decreases with increasing concentration of fluorinated monomer.

The molecular weight and its distribution have been determined by laser light scattering, employing a new apparatus for ETFE dissolution and solution clarification at high temperature; diisobutyl adipate is the solvent at 240°C. The molecular weight of molten ETFE is determined by high temperature rheometry (238).

This polymer can be dissolved in certain high boiling esters at temperatures above 230°C (239–241), permitting a weight-average molecular weight determination by light scattering. Solution viscosity data suggest that the polymer exists as a slightly expanded coil under similar conditions (242).

Transitions. Samples containing 50 mol% TFE with ca 92% alternation were quenched in ice water or cooled slowly from the melt to minimize or maximize crystallinity, respectively (234). Internal motions were studied by dynamic mechanical and dielectric measurements, and by nuclear magnetic resonance. The dynamic mechanical behavior showed that the α relaxation occurs at 110°C in the quenched sample; in the slowly cooled sample it is shifted to 135°C. The β relaxation appears near -25°C. The γ relaxation at -120°C in the quenched sample is reduced in peak height in the slowly cooled sample and shifted to a slightly higher temperature. The α and γ relaxations reflect motions in the amorphous regions, whereas the β relaxation occurs in the crystalline regions. The γ relaxation at -120°C in dynamic mechanical measurements at 1 Hz appears at -35°C in dielectric measurements at 10^5 Hz. The temperature of the α relaxation varies from 145°C at 100 Hz to 170°C at 10^5 Hz. In the mechanical measurement it is 110°C. There is no evidence for relaxation in the dielectric data.

The activation energy is 318.1 kJ/mol (76 kcal/mol) for the α relaxation and 44.3 kJ/mol (10.6 kcal/mol) for the γ relaxation. These relaxations are attributed to the motion of long and short segments in the amorphous regions, respectively. As ETFE is isomeric with poly(vinylidene fluoride) (233), the γ relaxations occur at about the same temperature. Activation energies are similar and are attributed to the motion of short amorphous segments. The β relaxation in PVF_2 is considered to be the main-chain amorphous relaxation and is analogous to the α relaxation in the ETFE. However, the arrangement of dipoles in the all-trans conformation is more symmetrical.

Physical and Mechanical Properties. Modified ETFE has a good combination of mechanical properties, including excellent cut-through and abrasion resistance, high flex life, and exceptional impact strength. As wire insulation, it withstands physical abuse during and after installation. Lightweight wire constructions are designed with a minimum diameter and are useful as single, general-purpose insulation and for multiple or composite constructions.

Modified ETFE is less dense, tougher, and stiffer and exhibits a higher tensile strength and creep resistance than PTFE, PFA, or FEP resins. It is ductile, and displays in various compositions the characteristic of a nonlinear stress–strain relationship. Typical physical properties of Tefzel products are shown in Table 12 (243,244). Properties such as elongation and flex life depend on crystallinity, which is affected by the rate of crystallization; values depend on fabrication conditions and melt cooling rates.

Light transmittance of 25-μm films in the visible-to-ir range varies from 91 to 95% for Tefzel 200 and from 89 to 93% for Tefzel 280. In the uv range, transmittance increases from 50% at 200 nm to 90% at 400 nm.

Thermal Properties. Modified ETFE has a broad operating temperature range up to 150°C for continuous exposure (243). Cross-linking by radiation improves the high temperature capability further. However, prolonged exposure to higher temperatures gradually impairs the mechanical properties and results in discoloration. Thermal and oxidative degradation studies (245,246) suggest that main carbon chain sequences of two or more ethylene links are thought to be subject to thermal and oxidative degradation. To enhance the thermal stability of ETFE resins stabilizers may be added for high temperature applications (247). The copolymer will not support combustion in air. Limiting oxygen index (LOI) is about 30–31, depending on monomer ratio. LOI increases gradually as fluorocarbon content is increased up to the alternating composition. It then increases rapidly to the index of PTFE (248).

The thermodynamic properties of Tefzel 200 and 280 are shown in Table 13; the annual rate of loss of weight with thermal aging for Tefzel 200 ranges from 0.0006 g/g at 135°C to 0.006 g/g at 180°C after an initial loss of absorbed gases of 0.0013 g/g at elevated temperature. The excellent thermal stability of ETFE is demonstrated by aging at 180°C; at this temperature, the annual weight loss of six parts per 1000, or a 1% weight loss, takes almost two years.

Friction and Bearing Wear of the Glass-Reinforced Copolymer. Glass reinforcement improves the frictional and wear properties of modified ETFE resins (HT-2004). For example, the dynamic coefficient of friction [689.5 kPa (100 psi) at >3 m/min] for Tefzel 200 is 0.4, which drops to 0.3 for the 25% glass-reinforced product at these conditions (243). The wear factor also improves from 12×10^{-14} to 32×10^{-17} 1/Pa [$6000 \times 10^{-10} - 16 \times 10^{-10}$ (in.^{3}·min)/(ft·lbf·h)]. These frictional and wear characteristics, combined with outstanding creep resistance, indicate suitability for bearing applications. Glass-reinforced ETFE is less abrasive on mating surfaces than most glass-reinforced polymers. Its static coefficient of friction depends on bearing pressure; for Tefzel HT-2004 the coefficient of friction changes from 0.51 at 68 Pa to 0.34 at 3.43 kPa (0.5 psi).

Dynamic friction depends on pressure and rubbing velocity (PV). The generation of frictional heat depends on the coefficient of friction and the PV factor. For the glass-reinforced product, temperature buildup begins at about PV 10,000 and thermal runaway occurs just below PV 20,000. High wear rates begin above PV 15,000. The wear rate depends on the type of metal rubbing surface and finish, lubrication, and clearances. Lubrication, hard shaft surfaces, and high finishes improve wear rates. Table 14 gives wear factors for steel and aluminum. Because the wear rate of both ETFE and the metal is much higher for aluminum than for steel, an anodized surface is preferred with aluminum.

Electrical Properties. Modified ETFE is an excellent dielectric (Table 15). Its low dielectric constant confers a high corona-ignition voltage. The dielectric constant does not vary with frequency or temperature. Both dielectric strength (ASTM D149) and resistivity are high. The loss characteristics are minimum; the dissipation factor, although low, increases at higher frequencies. Glass reinforcement increases losses and the dielectric constant rises from 2.6 to 3.4 (from 10^2 to 10^{10} Hz); the dissipation factor is increased by 10-fold. Exposure to radiation also increases losses. Dielectric strength is not reduced by thermal aging, unless a physical break occurs in the material. The short-time test of ASTM D149 gives values of 16–20 kV/mm with 3-mm-thick specimens to 160–200 kV/mm with films 25–75 μm thick. Tracking resistance is about 70 s by ASTM D495. This is comparable to materials considered to be nontracking; under unusual conditions tracking occurs. When these resins are foamed they provide insulation with even lower dielectric constant (249).

Chemical Resistance and Hydrolytic Stability. Modified ETFE are resistant to chemicals and solvents (Table 16) that often cause rapid degradation in other plastic materials. Performance is similar to that of perfluorinated polymers (250), which are not attacked by strong mineral acids, inorganic bases, halogens, and metal salt solutions. Organic compounds and solvents have little effect. Strong oxidizing acids, organic bases, and sulfonic acids at high concentrations and near their boiling points affect ETFE to varying degrees.

Physical properties remain stable after long exposure to boiling water. Tensile strength and elongation of Tefzel 200 are unaffected after 3000 h in boiling water. The higher molecular weight ETFE behaves similarly, whereas the glass-reinforced product shows a reduction of 25–35% in tensile strength with loss of reinforcement.

Water absorption of Tefzel is low (0.029 wt%), which contributes to its outstanding dimensional stability as well as to the stability of mechanical and electrical properties regardless of humidity.

High temperature resistance of ETFE and other fluoropolymers in automotive fuels and their permeation resistance have been discussed (251,252).

The ETFE can be cross-linked by radiation (253), despite the high content of TFE units. The recommended upper continuous use temperature for commercial

ETFE is 150°C. Physical strength can be maintained at higher temperatures when cross-linking agents are incorporated and cured by peroxide or ionizing radiation (254). The cut-through resistance of thin-wall wire insulation to a physical abuse during installation or use is increased at temperature up to 200°C. Short-term excursions to 240°C are possible for highly cross-linked resins. Cross-linking reduces plasticity but enhances high temperature properties and nondrip performance. The irradiated resin withstands a 400°C solder iron for 10 min without noticeable effect.

Modified ETFE has excellent weather resistance; tensile strength and elongation are not affected. On the other hand, tensile and elongation properties of the glass-reinforced compound show a significant reduction.

Modified ETFE films are used as windows in greenhouses and conservatories because of their high transparency to both uv and visible light and excellent resistance to weathering (255). Pigmented films are applied on white boards and in outdoor advertising laminates. Biaxially oriented films have tensile properties and toughness similar to polyester films (256).

Vacuum Outgassing and Permeability. Under vacuum, modified ETFE give off little gas at elevated temperatures. The loss rate is about one-tenth of the acceptable maximum rates for spacecraft uses. Exposing 750-μm specimens for 24 h at 149°C to a high vacuum results in a maximum weight loss of 0.12%; volatile condensible material is less than 0.02%.

The following permeability values were determined on Tefzel film (100 μm, ASTM D1434) at 25°C [1 nmol (m·s·GPa) = 0.5 (cm^3·mil)/(100 in.^{2}dia·atm)]:

material	nmol/(m·s·GPa)
carbon dioxide	500
nitrogen	60
oxygen	200
helium	1800
water vapor (ASTM E96)	3.3

3.5. Fabrication. Modified ETFE are commercially available in a variety of physical forms (Table 17) and can be fabricated by conventional thermoplastic techniques. Commercial ETFE resins are marketed in melt-extruded cubes, that are sold in 20-kg bags or 150-kg drums.

Like other thermoplastics, they exhibit melt fracture (257) above certain critical shear rates. In extrusion, many variables control product quality and performance (258).

Melt Processing. Articles are made by injection molding, compression molding, blow molding, transfer molding, rotational molding, extrusion, and coating. Films can be thermoformed and heat sealed (243). Because of high melt viscosity, ETFE resins are usually processed at high temperatures (300–340°C).

Injection-molded articles shrink about 1.5–2.0% in the direction of resin flow and about 3.5–4.5% in the transverse direction under normal molding conditions. A 25% glass-reinforced composition shrinks only about 0.2–0.3% in the flow direction and about 3.0% in the transverse direction. Although shrinkage depends on shape and processing conditions, uniformity is excellent.

Molten ETFE polymers corrode most metals, and special corrosion-resistant alloys are recommended for long-term processing equipment; short-term prototype runs are possible in standard equipment.

Forming and Machining. Articles can be formed below the melting point with conventional metal-forming techniques. Tetrafluoroethylene–ethylene copolymers are readily machined with the same tools and feed rates as are used for nylon and acetal. For best dimensional stability, the article should be annealed at the expected use temperature before the final machine cut.

Coloring and Decorating. Commercial pigments that are thermally stable at the resin processing temperature may be used. Pigments may be dry-blended with the resin, or ETFE pellets may be blended with color concentrates, which are available in pellet form.

Nontreated surfaces can be hot-printed with special foils in a manner similar to a typewriter ribbon. The type is heated to about 321°C, and a printing pressure of 172–206 kPa (25–30 psi) is applied for about 0.25 s; no further treatment is required.

Stripes may be applied to wire coated with ETFE fluoropolymer over DuLite 817-5002 fluoropolymer clear enamel or other bases. Thermally stable pigments are required. Stripes may be applied by gravure-wheel-type applicators and oven-cured in-line.

Assembly. The success of many applications depends on the ability of ETFE fluoropolymer to be economically assembled.

Screw Assembly. Self-tapping screws are used for joining ETFE parts. For maximum holding power, the boss diameter should be about double the screw diameter, and the engagement length about 2.5 times the screw diameter; lubricants should be avoided. Threaded inserts can be molded in place, pressed in, or driven in ultrasonically.

Snap-Fit and Press-Fit Joints. Snap-fit joints offer the advantage that the strength of the joint does not diminish with time because of creep. Press-fit joints are simple and inexpensive, but lose holding power. Creep and stress relaxation reduce the effective interference, as do temperature variations, particularly with materials with different thermal expansions.

Cold or Hot Heading. Rivets or studs can be used in forming permanent mechanical joints. The heading is made with special tools and preferably with the rivet at elevated temperatures. Formed heads tend to recover part of their original shape if exposed to elevated temperatures, resulting in loose joints. Forming at elevated temperature reduces recovery.

Spin Welding. Spin welding is an efficient technique for joining circular surfaces of similar materials. The matching surfaces are rotated at high speed relative to each other and then brought into contact. Frictional heat melts the interface and, when motion is stopped, the weld is allowed to solidify under pressure.

Ultrasonic Welding. Ultrasonic welding has been applied to Tefzel with weld strength up to 80% of the strength of the base resin. Typical conditions include a contact pressure of 172 kPa (25 psi) and 1–2 s cycle time. The two basic designs, the shear and butt joints, employ a small initial contact area to concentrate and direct the high frequency vibrational energy.

Potting. Potting of wire insulated with Tefzel has been accomplished with the aid of a coating of a colloidal silica dispersion. The pots produced with a polysulfide potting compound meeting MIL-S-8516C Class 2 standards exhibit pull-out strengths of 111–155 N (25–35 lbf).

Bonding. Surface treatment, such as chemical etch, corona, or flame treatments, is required for adhesive bonding of Tefzel. Polyster and epoxy compounds are suitable adhesives.

ETFE respond well to melt bonding to untreated aluminum, steel, and copper with peel strengths above 3.5 kN/m (20 lbf/in.). For melt bonding to itself, hot-plate welding is used. The material is heated to 271–276°C, and the parts are pressed together during cooling.

The plasma surface treatment of ETFE to improve adhesion has been studied (259).

3.6. Testing and Standards. A description of modified ETFE and their classification is given by the American Society for Testing and Materials under the designation D3159-83 (260). A comprehensive listing of industrial and military specifications is available (261).

3.7. Applications. Tefzel 200 is a general-purpose, high temperature resin for insulating and jacketing low voltage power wiring for mass transport systems, wiring for chemical plants, and control and instrumentation wiring for utilities. In injection-molded form, it is used for sockets, connectors, and switch components (262). Because of excellent mechanical properties it provides good service in seal glands, pipe plugs, corrugated tubing, fasteners, and pump vanes. In chemical service, it is used for valve components, laboratory ware, packing, pump impellers, and battery and instrument components.

Tefzel 210, the high melt-flow resin, provides a high speed processing product for use in coating of fine wire and injection molding of thin-walled or intricate shapes. It is also used for other fine-wire applications requiring high line speeds and mechanical strength, but where harsh environmental conditions are not anticipated.

For high temperature wiring with mechanical strength and stress-crack and chemical resistance, Tefzel 280 is preferred. Rated by UL at 150°C, it is widely used for insulating and jacketing heater cables and automotive wiring and for other heavy-wall application where temperatures up to 200°C are experienced for short peirod of time or where repeated mechanical stress at 150°C is encountered. It is also suitable for oil-well logging cables and is used in transfer moldings and extrusions for lined chemical equipment. It is injection molded into articles with metal inserts, thick sections, and stock shapes.

3.8. Health and Safety Factors. Large quantities of Tefzel have been processed and used in many demanding service applications. No cases of permanent injury have been attributed to these resins, and only limited instances of temporary irritation to the upper respiratory tract have been reported (117).

As with other melt-processible fluoropolymers, trace quantities of harmful gases, including hydrogen fluoride, diffuse from the resin even at room temperature. Therefore, the resins should be used in well-ventilated areas. Even though the resin is physiologically inert and nonirritating to the skin, it is recommended that spills on the skin be washed with soap and water. These resins are stable at 150°C and are recommended for continuous use at this temperature. Degradation, as measured by weight loss, is insignificant up to the melting point of 270°C. At processing temperatures sufficient quantities of irritating and toxic gases are generated to require removal of the gases by exhaust hoods over the die and at the hopper heater. For extrusion into water, a quench tank or partially filled container for purging is recommended. In extrusion operations proper procedures must be maintained to control temperature and pressure. The weight loss with increasing temperature is as follows:

Temperature, °C	Hourly weight loss, %
300	0.05
330	0.26
350	0.86
370	1.60

To remove all decomposition products, a “total-capture” exhaust hood is recommended.

Under normal processing conditions at 300–350°C, Tefzel resins are not subject to autocatalytic degradation. However, extended overheating can result in “blow-backs” through extruder feed hopper or barrel front.

Prolonged soldering in confined spaces with restricted air circulation requires ventilation. A small duct fan is recommended for hot-wire stripping. Tefzel articles should not be exposed to welding conditions.

The limiting oxygen index of Tefzel as measured by the candle test (ASTM D2863) is 30%. Tefzel is rated 94 V-0 by Underwriters, Laboratories, Inc., in their burning test classification for polymeric materials. As a fuel, it has a comparatively low rating. Its heat of combustion is 13.7 MJ/kg (32,500 kcal/kg) compared to 14.9 MJ/kg (35,000 kcal/kg) for poly(vinylidene fluoride) and 46.5 MJ/kg (110,000 kcal/kg) for polyethylene.

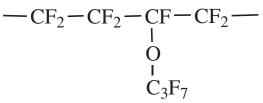
Bulk quantities of Tefzel fluoropolymer resins should be stored away from flammable materials. In the event of fire, personnel entering the area should have full protection, including acid-resistant clothing and self-contained breathing apparatus with a full facepiece operated in the pressure-demand or other positive-pressure mode. All types of chemical extinguishers may be used to fight fire involving Tefzel resins. Large quantities of water may be used to cool and extinguish the fire.

The DuPont Haskell Laboratory for Toxicology and Industrial Medicine has conducted a study to determine the acute inhalation toxicity of fumes evolved from Tefzel fluoropolymers when heated at elevated temperatures. Rats were exposed to decomposition products of Tefzel for 4 h at various temperatures. The approximate lethal temperature (ALT) for Tefzel resins was determined to be 335–350°C. All rats survived exposure to pyrolysis products from Tefzel heated to 300°C for this time period. At the ALT level, death was from pulmonary edema; carbon monoxide poisoning was probably a contributing factor.

Hydrolyzable fluoride was present in the pyrolysis products, with concentration dependent on temperature.

4. Tetrafluoroethylene–Perfluorovinyl Ether

4.1. Introduction. Perfluoroalkoxy (PFA) fluorocarbon resins are designed to meet industry's needs in chemical, electrical, and mechanical applications. These melt-processible copolymers contain a fluorocarbon backbone in the main chain and randomly distributed perfluorinated ether side chains:



$$-CF_2-CF_2-\underset{\underset{\displaystyle C_3F_7}{\underset{|}{\underset{\displaystyle O}{|}}}}{CF}-CF_2-$$

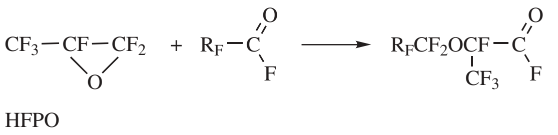
(**1**)

A combination of excellent chemical and mechanical properties at elevated temperatures results in reliable, high performance service to the chemical processing and related industries. Chemical inertness, heat resistance, toughness and flexibility, stress-crack resistance, excellent flex life, antistick characteristics, little moisture absorption, nonflammability, and exceptional dielectric properties are among the characteristics of these resins.

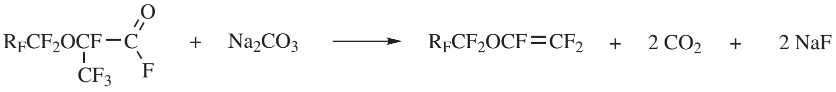
The introduction of a perfluoromethyl side chain (Teflon FEP) greatly reduces the crystallinity of polytetrafluoroethylene (PTFE). Crystallinity is reduced even further by replacing the short side chain with a long side chain, such as perfluoropropyl ether. In contrast to Teflon FEP, only a small amount of vinyl ether is required to reduce crystallinity and develop adequate toughness.

Tetrafluoroethylene (TFE) [116-14-3] and perfluorovinyl ether are copolymerized in aqueous (263,264) or nonaqueous (265) media. The polymer is separated and converted into various forms, such as extruded cubes, powders, beads, or dispersions. This family of products is manufactured by DuPont, Daikin, Dyneon, and Asahi Glass and sold under the trade names of Teflon PFA, Neoflon AP, Hostaflon TFA, and Aflon PFA, respectively. Additional information on specific manufacturers' products can often be obtained by consulting their internet web sites (for example, www.dupont.com/teflon).

4.2. Monomers. *Preparation.* The preparation of TFE has been described previously. Perfluorovinyl ethers (266–269) are prepared by the following steps. Hexafluoropropylene (HFP) [116-15-4] is oxidized to an epoxide HFPO [428-59-1] (270) which, on reaction with perfluorinated acyl fluorides, gives an alkoxyacyl fluoride.



The alkoxyacyl fluoride is converted to vinyl ethers by treatment with base at ca 300°C (270).



$$R_FCF_2O\underset{CF_3}{CF}-C(=O)F + Na_2CO_3 \longrightarrow R_FCF_2OCF{=}CF_2 + 2\,CO_2 + 2\,NaF$$

where $R_F = F(CF_2)_n$.

Alkoxyacyl fluorides are also produced by an electrochemical process (271).

The preparation of perfluoromethyl and perfluoroethyl vinyl ethers is described in References 272 and 273.

Properties. Properties of perfluoropropyl vinyl ether (PPVE) [1623-05-8], a colorless, odorless liquid (mol. wt. 266), are shown in Table 18. Perfluoropropyl vinyl ether is an extremely flammable liquid and burns with a colorless flame. It is significantly less toxic than HFP; the average lethal concentration (ALC) is 50,000 ppm (274).

4.3. Copolymerization. Tetrafluoroethylene–perfluoropropyl vinyl ether copolymers [26655-00-5] are made in aqueous (263,264) or nonaqueous media (265). In aqueous copolymerizations water-soluble initiators and a perfluorinated emulsifying agent are used. Molecular weight and molecular weight distribution are controlled by a chain-transfer agent. Sometimes a second phase is added to the reaction medium to improve the distribution of the vinyl ether in the polymer (275); a buffer is also added. In nonaqueous copolymerization, fluorinated acyl peroxides are used as initiators that are soluble in the medium (276); a chain-transfer agent may be added for molecular weight control.

Temperatures range from 15 to 95°C, and the pressures from 0.45 to 3.55 MPa (65–515 psi). The temperatures used for the aqueous process are higher than those for the nonaqueous process.

Alkyl vinyl ethers tend to rearrange when exposed to free radicals (277). Temperatures must be kept low enough to prevent termination by free-radical coupling. In the aqueous process, temperatures below 80°C minimize the number of acid end groups derived from vinyl ether transfer. In the nonaqueous process, temperature must also be limited to avoid excessive vinyl ether transfer as well as reaction with the solvent. End groups are stabilized by treating the polymer (278) with methanol, ammonia, or amines (279–281). Treatment of PFA with elemental fluorine generates CF_3 end groups and a very low level of contamination (282), which is important for the semiconductor industry (283).

The polymer is separated from the medium and converted to useful forms such as melt-extruded cubes for melt-processible applications. Teflon PFA is also available as a dispersion, a fine powder, or in unmelted bead form.

Description and classification of PFA resins are given in Reference 284. Various specifications are given in Reference 285.

A family of copolymers containing TFE and perfluoromethyl vinyl ether modified with PPVE referred to as MFA is produced by Solvay-Solexis (286). The relatively small pendant group $-O-CF_3$ seems to have a similar effect on the crystallinity reduction as is exhibited by $-CF_3$ in FEP (perfluoropropylene–tetrafluoroethylene copolymer); however, the higher reactivity of perfluoromethyl vinyl ether than that of HFP makes the polymerization process more efficient. The performance characteristics are described in References 273 and 287.

A new family of copolymers called Teflon HP Plus has been introduced by DuPont using perfluoroethyl vinyl ether analogous to PPVE used to produce the standard PFA (288). A significantly higher reactivity of perfluoroethyl vinyl ether has made it possible to produce copolymers with widely different comonomer concentrations on a commercial scale while reducing the tendency to rearrange and form acid end groups from vinyl ether transfer. Even though perfluoroethyl group provides a somewhat shorter pendant group, its effect on the reduction of crystallinity is very similar to that of perfluoropropyl group. This makes the perfluoroethyl vinyl ether an optimum commonomer to produce a versatile family of products.

4.4. Properties. The melting point of commercial Teflon PFA is 305°C, ie, between those of PTFE and FEP. Second-order transitions are at −100, −30, and 90°C, as determined by a torsion pendulum (289). The crystallinity of the virgin resin is 65–75%. Specific gravity and crystallinity increase as the cooling rate is reduced. An ice-quenched sample with 48% crystallinity has a specific gravity of 2.123, whereas the press-cooled sample has a crystallinity of 58% and a specific gravity of 2.157.

Mechanical Properties. Table 19 shows the physical properties of Teflon PFA (290,291). At 20–25°C the mechanical properties of PFA, FEP, and PTFE are similar; differences between PFA and FEP become significant as the temperature is increased. The latter should not be used above 200°C, whereas PFA can be used up to 260°C. Tests at liquid nitrogen temperature indicate that PFA performs well in cryogenic applications (Table 20).

Unfilled Teflon PFA has been tested in mechanical applications, using Teflon FEP 100 as a control (292). Tests were run on molded thrust bearings at 689.5 kPa (100 psi) against AISI 1080, Rc 20, 16AA steel, and at ambient conditions in air without lubrication. A limiting PV value of 5000 was found. Wear factors and dynamic coefficients of friction are shown in Table 21.

Hardness is determined according to ASTM D2240 on 7.6 × 12.7 × 0.48 cm injection-molded panels (293). Results on the D scale are 63–65 for Teflon PFA and 63–66 for Teflon FEP.

Chemical Properties. A combination of excellent chemical and mechanical properties at elevated temperatures results in high performance service in the chemical processing industry. Teflon PFA resins have been exposed to a variety of organic and inorganic compounds commonly encountered in chemical service (294). They are not attacked by inorganic acids, bases, halogens, metal salt solutions, organic acids, and anhydrides. Aromatic and aliphatic hydrocarbons, alcohols, aldehydes, ketones, ethers, amines, esters, chlorinated compounds, and other polymer solvents have little effect. However, like other perfluorinated polymers, they react with alkali metals and elemental fluorine.

Thermal Stability. Teflon PFA resins are very stable and can be processed up to 425°C. Thermal degradation is a function of temperature and time. A significant increase in melt flow rate indicates degradation after a short time above 425°C; at lower temperatures degradation takes longer. Degradation is not significant if the change in melt flow rate of the resin during molding is below 20%. Degradation is also indicated by the formation of small bubbles or discoloration;

however, high stock temperatures may cause slight discoloration without adversely affecting properties.

Heat aging at 285°C, a temperature slightly below but near the melting point, increases the strength of Teflon PFA. Samples aged in a circulating air oven for 7500 h at 285°C show a decrease in melt flow number as defined by ASTM D2116. A decline in melt flow number indicates an increase in average molecular weight, which is also indicated by a 25% increase in tensile strength and enhanced ultimate elongation. Toughness is also measured by MIT flex life, which improves severalfold on heat aging at 285°C.

When exposed to fire, Teflon PFA contributes little in fuel value and is self-extinguishing when the flame is removed. The fuel value is approximately 5.4 MJ/kg (2324 Btu/lb). It passes the UL-83 vertical-flame test and is classified as 94VE-O according to UL-94. The limiting oxygen index (LOI) by ASTM D2863 is above 95%.

Electrical Properties. The electrical properties of Teflon PFA are given in Table 22. The dielectric constant of PFA resins is about 2.06 over a wide range of frequencies (10^2–2.4×10^{10} Hz), temperatures, and densities (ASTM D150). The values for PFA density vary only slightly, 2.13–2.17, and the dielectric constant varies only about 0.03 units over this range, among the lowest of all solid materials. Humidity has no measurable effect on the dielectric constant of PFA. The dielectric strength (short-term) of PFA resins is 80 kV/mm (0.25-mm films, ASTM D149); FEP films give similar results, whereas PTFE films are typically measured at 47 kV/mm. Like other fluoropolymer resins, PFA loses dielectric strength in the presence of corona discharge. The dissipation factor at low frequency (10^2–10^4 Hz) decreases with increasing frequency and decreasing temperature. Temperature and frequency have little influence on the dissipation factor over the frequency range 10^4–10^7 Hz. As frequencies increase to 10^{10} Hz, there is a steady increase in dissipation factor. Above 10^7 Hz, increases measured at room temperature are highest; a maximum at about 3×10^9 Hz is indicated. The higher dissipation factor with increasing frequency should be considered in electrical insulation applications at high frequencies. The volume and surface resistivities of fluorocarbon resins are high and are not affected by time or temperature. When tested with stainless steel electrodes (ASTM D495), no tracking was observed for the duration of the test (180 s), indicating that PFA resin does not form a carbonized conducting path (295,296).

Optical Properties and Radiation Effects. Within the range of wavelengths measured (uv, visible, and nir radiation), Teflon PFA fluorocarbon film transmits slightly less energy than FEP film (297) (Table 23). In thin sections, the resin is colorless and transparent; in thicker sections, it becomes translucent. It is highly transparent to ir radiation; uv aborption is low in thin sections. Weather-O-Meter tests indicate unlimited outdoor life.

Like other perfluoropolymers, Teflon PFA is not highly resistant to radiation (298). Radiation resistance is improved in vacuum, and strength and elongation are increased more after low dosages (up to 30 kGy or 3 Mrad) than with FEP or PTFE. Teflon PFA approaches the performance of PTFE between 30 and 100 kGy (3–10 Mrad) and embrittles above 100 kGy (10 Mrad). At 500 kGy (50 Mrad) PTFE, FEP, and PFA are degraded. The effect of radiation on tensile strength and elongation is shown in Table 24.

4.5. Fabrication. Teflon PFA resins are fabricated by the conventional melt-processing techniques used for thermoplastics (299). Processing equipment is constructed of corrosion-resistant materials and can be operated at 315–425°C. A general-purpose grade, PFA 340, is designed for a variety of molding and extrusion applications, including tubing, shapes, and molded components, in addition to insulation for electrical wire and cables. Because of the excellent thermal stability of PFA 350, a wide range of melt temperatures can be used for fabrication. Extrusion temperatures are 20–26°C above the melting point.

Teflon PFA 440 HP is a chemically modified form of PFA 340 that provides additional benefits such as enhanced purity and improved thermal stability. This product is suitable for producing tubing, pipe linings for production of ultrapure chemicals, semiconductor components, and fluid handling systems for high performance filters (300).

Extrusion. Like other thermoplastics, Teflon PFA resin exhibits melt fracture above certain critical shear rates. For example, samples at 372°C and 5-kg load show the following behavior:

Teflon PFA	Melt flow, g/10 min	Critical shear rate, s^{-1}
340	14	50
310	6	16
350	2	6

Because Teflon PFA melt is corrosive to most metals, special corrosion-resistant alloys must be used for the extrusion equipment, such as Hastelloy C, Monel 400, and Xaloy 306. Barrels, liners, screws, adapters, breaker plates, and dies are made of corrosion-resistant metals (301). Corrosion is promoted by resin degradation and high processing temperatures, long residence times, or dead spots. Extruders used with Teflon FEP are also suitable for PFA resins. Heaters and controllers capable of accurate operation in the range of 330–425°C are required. Extruder barrels should have three or four independently controlled heating zones, each equipped with its own thermocouple and temperature-indicating control.

The screw consists of a feed section, a rapid transition section, and a metering section; a rounded forward end prevents stagnation. The breaker plate that converts the rotary motion of the melt into smooth, straight flow should have as many holes as possible; both ends of each hole should be countersunk for streamlined flow.

The temperature of the melt downstream from the breaker plate may exceed the front barrel temperature because of the mechanical work transmitted to the resin by the screw; it varies with screw speed and flow rate. The melt temperature is measured by a thermocouple inserted into the melt downstream from the breaker plate. A hooded exhaust placed over the extruder die and feed hopper removes decomposition products when the extrudate is heated.

High melt strength of Teflon PFA 350 permits large reductions in the cross section of the extrudate by drawing the melt in air after it leaves the die orifice

(302). At a given temperature, the allowable flow rates are limited at the low end by resin degradation and at the high end by the onset of melt fracture. A broader range of specific gravities (2.13–2.17) may be obtained in articles fabricated from PFA 350 than from FEP 160. Unlike with PTFE, higher crystallinity in PFA seems to have little effect on flex life.

Injection Molding. Any standard design plunger or reciprocating screw injection machine can be used for PFA 340, although a reciprocating screw machine is preferred (303). Slow injection into mold cavities avoids surface or internal melt fracture, and control of ram speed is important at low speed. Corrosion-resistant metals are used for parts in continuous contact with molten resin; Hastelloy C and Xaloy 306 or 800 are recommended.

Because the mold is usually maintained at temperatures below the melting point of the resin, corrosion on the mold surface is less than in the molding machine. Nonreturn ball check valves and ring check valves are used; the latter is preferred for PFA. A streamlined flow must pass through the valve, preventing areas of stagnant flow or holdup and localized degradation.

A smear head causes less stagnation and overpacking than a nonreturn valve. A conventional-type reverse-tapered nozzle with the bore as large as possible without sudden changes in diameter is preferred. Independently controlled, zone-type heaters for heating the nozzle and at least two zones on the cylinder are used.

At a holdup time longer than 10–15 min at a high temperature, resin degradation is avoided by keeping the rear of the cylinder at a lower temperature than the front. At short holdup times (4–5 min), cylinder temperatures are the same in rear and front. If melt fracture occurs, the injection rate is reduced; pressures are in the range of 20.6–55.1 MPa (3000–8000 psi). Low back pressure and screw rotation rates should be used.

The cycle can usually be estimated on the basis of about 30 s/3 mm of thickness; most of it is devoted to ram-in-motion time (except for very thin sections). The mold temperature used with PFA 340 is often the highest temperature that allows the part to be ejected undamaged from the mold and retain its shape while cooling.

The resin must be of highest purity for optimum processing characteristics and properties. Degradation results in discoloration, bubbling, and change in melt flow rate.

Transfer Molding. Valve and fitting liners are made by a transfer-molding process (304), with the valve or fitting serving as the mold. Melted resin is forced into the fitting at a temperature above the melting point of the resin. The melt may be produced by an extruder or an injection molding machine or melted cubes contained in a melt pot and transferred by applying pressure to a piston in the pot. After the resin transfer is completed, the fitting is cooled under pressure. Stock temperatures of 350–380°C and fitting temperatures of 350–370°C are used to process PFA 350. A slight adjustment in the cooling cycles may be required for transfer molding PFA 350 because it has higher melting and freezing points than FEP.

Rotocasting Teflon PFA Beads. The resin has sufficient thermal stability for a commercial rotocasting operation; that is, TE-9738 has a melting point of about 303°C. In rotocasting trials, incoming flue gas temperatures of

355–365°C (305,306) and heat cycles of 90–180 min have been used. Conventional rotations for major and minor axes can be applied without modifications; Freecote 33 performs adequately as a mold release agent. Mold release instructions can be followed without modification. Heating cylces, including a preheat and a fusion stage, give consistent rotocasting. Preheating at 15–30°C below the fusion temperature takes 10–25 min. Heat-cycled Teflon PFA rotocastings are translucent white, often with bluish tinge. Rotocastings that have been heated too long may darken to a translucent brown. Uniform cooling is essential for undistorted, stress-free products; combinations of air and water are employed. The rotocasting is cooled below the resin melting temperature with air at ambient temperature and then with a water spray, and finally with a stream of air.

Dispersion Processing. A commercial aqueous dispersion of Teflon PFA 335 contains more than 50 wt% PFA particles, about 5 wt% surfactants and fillers. This dispersion is processed by the same technique as for PTFE dispersion. It is used for coating various surfaces, including metal, glass, and glass fabrics. A thin layer of Teflon PFA coating can also serve as an adhesive layer for PTFE topcoat.

Powder Coating. Teflon PFA is also available in a finely divided powder form. It can be used to produce thin layers on various surfaces by heating these surfaces above the melting point of PFA and then bringing the powder in contact with them. This allows a thin layer of the powder to melt on the surface of the substrate.

For some applications the powder is suspended in an aqueous medium or a solvent with the help of emulsifying agents and then sprayed onto the substrate. The powder is also used as a filler to prepare sprayable compositions of PTFE dispersions, which then can be used to coat various substrates (307).

Pigmentation. Commercial color concentrates of Teflon PFA containing approximately 2% pigment can be easily dispersed in clear extruded cubes. The resin can also be dry-blended with stable inorganic pigments. At 0.1–1% of concentration, the pigment has no appreciable effect on the dielectric strength and constant or mechanical properties. The dissipation factor of pigmented resin varies with the type and concentration of the pigment.

Pigment used for dry blending is dried overnight at 150°C in a vacuum oven to remove absorbed gases and moisture. It is screened through a 149-μm (100-mesh) screen directly onto the cubes, which are rolled or tumbled for at least 15 min. The pigmented resin is stored in an airtight container to prevent absorption of moisture.

4.6. Applications and Economic Aspects. The perfluorovinyl ether comonomer used for PFA is expensive, as is PFA. Most PFA grades are sold as extruded, translucent cubes in various colors at $50.00–65.00/kg. Some PFA types are also marketed in nonextruded forms.

4.7. Health and Safety Factors. Safe practices employed for handling PTFE and FEP resins are adequate for Teflon PFA (117); adequate ventilation is required for processing above 330–355°C. In rotoprocessing, a vacuum (250–750 Pa or 1.8–5.6 mm Hg) in the oven ensures exhaust to the outside (307). Removal of end caps or opening of sealed parts in a well-ventilated area ensures ventilation of decomposition fumes. During rotoprocessing, molds should be vented.

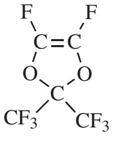
4.8. Applications. Teflon PFA can be fabricated into high temperature electrical insulation and components and materials for mechanical parts requiring long flex life. Teflon PFA 350 is used as liner for chemical process equipment, specialty tubing, and molded articles for a variety of applications. Teflon PFA 340 is a general-purpose resin for tubing, shapes, primary insulation, wire and cable jacketing, injection- and blow-molded components, and compression-molded articles. Teflon PFA 440 HP is a chemically modified form of PFA 340 with enhanced purity and improved thermal stability while processing. This resin is suitable in semiconductor manufacturing, fluid handling systems for industry or life sciences, and instrumentation for precise measurements of fluid systems.

5. Tetrafluoroethylene–Perfluorodioxole Copolymers

5.1. Introduction. Copolymers of tetrafluoroethylene and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) are perfluorinated amorphous polymers and possess unusual combination of properties. They retain the outstanding chemical, thermal, and surface properties of perfluorinated polymers in addition to having excellent electrical and optical properties; and have solubility at ambient temperature in a normal fluorosolvent. This family of copolymers is manufactured by DuPont and sold under the trade name of Teflon AF, amorphous fluoropolymers.

All tetrafluoroethylene-based homo- and copolymers, described in earlier papers, are semicrystalline with distinct melting points. On the other hand, tetrafluoroethylene–PDD copolymers are totally amorphous and can be tailored for specific glass-transition temperatures by altering the polymer composition (308). So these perfluorinated amorphous polymers exhibit properties derived from their amorphous structure and perfluorinated chains.

5.2. Monomer. *Preparation.* 2,2-Bistrifluoromethyl difluoro-1,3-dioxole (PDD) monomer is synthesized in four steps (309). In the first step, hexafluoroacetone and ethylene oxide are reacted to form 2,2-bistrifluoromethyl-4,5-dichloro-4,5-difluoro-1,3-dioxolane. This product is then fully chlorinated and subsequently partially fluorinated to difluoro-1,3-dioxolane. In the last step, the fluorinated product is dechlorinated to obtain the final product, PDD.



PDD Monomer

(**2**)

Properties. PDD is a colorless liquid with the boiling point of 33°C (310). It is very reactive and can homopolymerize, and therefore, needs to be stored at low temperature with a small amount of free-radical inhibitor. PDD can copolymerize with tetrafluoroethylene or other fluorinated monomers, such as vinylidene fluoride, vinyl fluoride, or chlorotrifluoroethylene.

5.3. Copolymerization. Copolymers of tetrafluoroethylene and PDD can be synthesized by free-radical initiators in either aqueous or nonaqueous medium (308). The homopolymer of PDD results in an amorphous polymer with the glass-transition temperature T_g of 335°C. This polymer is difficult to melt process because of the narrow processing window below its decomposition temperature. Copolymers can be prepared with any proportion of tetrafluoroethylene and PDD. Polymers containing less than 20 mol% PDD tend to be partially crystalline. At 20 mol% PDD, the T_g of the copolymer is about 80°C. The glass-transition temperature increases with an increase in PDD. The commercial Teflon AF products are copolymers of tetrafluoroethylene and PDD, and have glass-transition temperatures of 160 and 240°C for Teflon AF-1600 and Teflon AF-2400, respectively (311). During aqueous polymerization small amounts of acid fluoride or carboxylic acid end groups may be produced by ring-opening. For many applications these unstable ends are removed and converted to perfluorinated end groups by first treating the polymer with ammonia, followed by fluorination (312).

Properties. Teflon AF copolymers have many characteristics similar to those of other copolymers of tetrafluoroethylene, such as high-temperature stability, excellent chemical resistance, low surface energy, low water absorption, and high limiting oxygen index (LOI). On the other hand, many properties are different because of their amorphous structure. These polymers are soluble at ambient temperature in fluorinated solvents. They are transparent and have low refractive index. They are significantly stiffer and have high gas permeability. The glass-transition temperature of tetrafluoroethylene–PDD copolymers is sensitive to the structure of the dioxide monomer. It is likely that steric interactions involving the two trifluoromethyl groups lead to a highly congested chain structure with limited mobility (313). The structural study of these polymers indicate that there are microvoids in their structure and probably cause lower than expected polymer density, low dielectric constant, low refractive index, high gas permeability, and low thermal conductivity. Most likely the origin of these microvoids is loose chain packing caused by the high energy for rotation and reorientation of the dioxole ring containing polymer chain (314).

Table 25 summarizes mechanical, electrical, optical, and thermal properties of Teflon AF-1600 and AF-2400 (10). The dielectric constant for Teflon AF is lower than that for PTFE and is unaffected by humidity.

The low temperature dielectric properties invetigation (318) revealed that the γ relaxation found at −186°C for PTFE is only one-third the intensity for AF-1600 and AF-2400. This relaxation is attributed to the cooperative motion of the four carbon atoms of a TFE dimer unit. The low concentration of such units in AF explains the difference in the intensity of γ relaxation.

The refractive index of Teflon AF is the lowest known for any solid organic polymer (319). One of the key properties of AF is its solubility in fluorinated solvents, such as "Fluorinert" FC-72, -75, and -40, perfluorobenzene, perfluoromethylcyclohexane, perfluorodimethylcyclohexane, perfluoroctane, or perfluorodecalin.

The thermal stability of Teflon AF approaches that of other perfluorinated polymers. At 260°C after 4 h of exposure no weight loss was observed. The weight losses after the exposure at 360, 380, 400, and 420°C were 0.3, 0.5, 1.9, and 8.8%, respectively.

Copolymers of PDD with other fluoromonomers are discussed in Reference (310).

5.4. Fabrication. Teflon AF is processed by a wide variety of techniques. AF solutions can be used for spin coating, dip coating, spraying, or casting. Melt-processing techniques such as extrusion and injection molding are used. Compression molding has also been used effectively. Spin coating is used to produce very thin and uniform coatings on flat substrates. The film thickness is influenced by the nature of the substrate, the spin speed, and the concentration of the solution. Dip coating is suitable for nonplanar surfaces (320). Compression molding is done about 100°C above T_g and may require longer heat-up time than other polymers because of its lower thermal conductivity. Laser ablation and vacuum pyrolysis techniques are also used (321,322).

5.5. Economic Aspects. The PDD monomer used for AF is very expensive, which results in making AF products very costly. These polymers in solid form are sold in 25 and 500 g packages at prices $500 and $5000, respectively. The solutions are available in 100 mL and 1 L packages. They contain 1–18% solids, depending on the grade. The prices for solutions range from $70 for 1% solids of AF-2400 in 100 mL to $7810 for 18% solids of AF-16015-18 in 1 L package.

5.6. Health and Safety Factors. Safe practices employed for handling PTFE and PFA resins are adequate for Teflon AF (117). Adequate ventilation is required for processing above 330°C.

5.7. Applications. Teflon AF is used to provide antireflective coatings (323), low dielectric coatings, pellicles used in electronic chips (324), cladding in plastic optical fiber (325), as a low dielectric insulator, to coat gas separation membranes (326).

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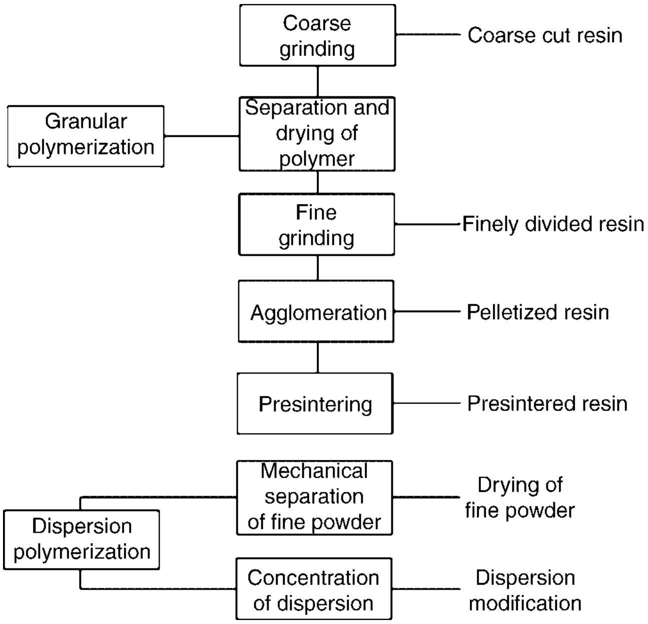

Fig. 1. Granular, fine powder, and dispersion PTFE products.

Table 1. **Physical Properties of Tetrafluoroethylene**[a]

Property	Value
boiling point at 101.3 kPa,[b] °C	−76.3
freezing point, °C	−142.5
liquid density at t°C, g/mL	
$-100 < t < -40$	$= 1.202 - 0.0041t$
$-40 < t < 8$	$= 1.1507 - 0.0069t - 0.000037t^2$
$8 < t < 30$	$= 1.1325 - 0.0029t - 0.00025t^2$
vapor pressure at T K, kPa[c]	
$196.85 < T < 273.15$	$\log_{10} P_{\mathrm{kPa}} = 6.4593 - 875.14/T$
$273.15 < T < 306.45$	$\log_{10} P_{\mathrm{kPa}} = 6.4289 - 866.84/T$
critical temperature, °C	33.3
critical pressure, MPa[d]	39.2
critical density, g/mL	0.58
dielectric constant at 28°C	
at 101.3 kPa[b]	1.0017
at 858 kPa[b]	1.015
thermal conductivity at 30°C, m W/(m·K)	15.5
heat of formation for ideal gas at 25°C, ΔH, kJ/mol[e,f]	−635.5
heat of polymerizationof 25°C to solid polymer ΔH, kJ/mol[e],[f]	−172.0
flammability limits in air at 101.3 kPa[c], vol%	14–43

[a] From Ref. 22, unless otherwise stated.
[b] To convert kPa to atm, multiply by 0.01.
[c] To convert kPa to psi, multiply by 0.145.
[d] To convert MPa to atm, divide by 0.101.
[e] To convert J to cal, divide by 4.184.
[f] Ref. 23.
[g] Ref. 24.

Table 2. **Transitions in Polytetrafluoroethylene**

Temperature, °C	Region affected	Technique	Reference
1st order			
19	crystalline, angular, displacement causing, disorder	thermal methods, x ray, nmr	75
30	crystalline, crystal disordering	thermal methods, x ray, nmr	75
90 (80 to 110)	crystalline	stress relaxation, Young's modulus, dynamic methods	78
2nd order			
−90 (−110 to −73)	amorphous, onset of rotational motion around C—C bond	thermal methods, dynamic methods	79
−30 (−40 to −15)	amorphous	stress relaxation, thermal expansion, dynamic methods	78
130 (120 to 140)	amorphous	stress relaxtion, Young's modulus, dynamic methods	78

Table 3. **Typical Mechanical Properties of Molded and Sintered PTFE Resins**[a]

Property	Granular resin	Fine powder	ASTM method
tensile strength at 23°C, MPa[b]	7–28	17.5–24.5	D638-61T
elongation at 23°C, %	100–200	300–600	D628-61T
flexural strength at 23°C, MPa[b]	does not break		D790-61
Flexural modulus at 23°C, MPa[b]	350–630	280–630	D747-61T
impact strength, J/m[c]			
at 21°C	106.7		D256–56
at 24°C	160		
at 77°C	>320		
hardness durometer, D	50–65	50–65	D1706-59T
compression stress, MPa[b]			
at 1% deformation at 23°C	4.2		D695-52T
at 1% offset at 23°C	7.0		D695-52T
coefficient of linear thermal expansion 12×10^{-5} per °C, 23–60°C	12×10^{-5}		D696-44
thermal conductivity, 4.6-mm thickness, W/(m·K)	0.24		Cenco-Fitch
deformation under load, at 26°C, 24 h, %			D621-59
6.86 MPa[b]		2.4	
13.72 MPa[b]	15		
water absorption, %	< 0.01	< 0.01	D570-54T
flammability	nonflammable		D635-56T
static coefficient of friction with polished, steel	0.05–0.08		

[a] Ref. 83.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to ft·lbf/in., divide by 53.38.

Table 4. **Properties of Filled PTFE Compounds**[a]

		Glass fiber, wt%			
Property	Unfilled	15	25	Graphite, 15 wt%	Bronze, 60 wt%
specific gravity	2.18	2.21	2.24	2.16	3.74
tensile strength, MPa[b]	28	25	17.5	21	14
elongation, %	350	300	250	250	150
stress at 10% elongation, MPa[b]	11	8.5	8.5	11	14
thermal conductivity, mW/(m·K)	0.244	0.37	0.45	0.45	0.46
creep modulus, kN/m[c]	2	2.21	2.1	3.4	6.2
hardness durometer, Shore D	51	54	57	61	70
izod impact, J/m[d]	152	146	119		
PV[e] for 0.13-mm radial wear in 1000 h, unlubricated, (kPa·m)/s[f]	0.70	106	177	52	281
wear factor, 1/Pa[g]	5×10^{-14}	28×10^{-17}	26×10^{-17}	100×10^{-17}	12×10^{-17}
coefficient of friction					
static, 3.4 MPa[b] load	0.08	0.13	0.13	0.10	0.10
dynamic at PV[e] = 172 (kPa.m)/s[f]		0.15–0.24	0.17	0.15	0.15
V = 900 m/s	0.01	−0.24		−0.18	−0.22

[a] Ref. 88.

[b] To convert MPa to psi, multiply by 145.

[c] To convert kN/m to lbf/in., divide by 0.175.

[d] To convert J/m to ftlbf/in., divide by 53.38.

[e] PV = pressure × velocity.

[f] To convert kPa to psi, multiply by 0.145.

[g] To convert 1/Pa to $(\text{in.}^3\cdot\text{min})/(\text{ft}\cdot\text{lbf}\cdot\text{h})$, divide by 2×10^{-7}.

Table 5. **Permeability of PTFE Resin to Vapors**

	Permeability constant [a,b], × 10^{15} mol/(m·s·Pa)	
Permeant	23°C	30°C
benzene	1.81	2.93
carbon tetrachloride	0.13	
ethanol	1.88	
HCl, 20%	<0.71	
piperidine	0.96	
H_2SO_4, 98%	54.20	
water		20.70

[a] Ref. 95. Test method ASTM E96-35T (at vapor pressure; for 25.4-μm film thickness). Values are averages only and not for specification purposes.
[b] Original data converted to SI units using vapor pressure data from Ref. 98.

Table 6. **Electrical Properties of Polytetrafluoroethylene**[a]

Property	Granular	Fine powder	ASTM method
dielectric strength, short time, 2-mm thickness, V/mm	23,600	23,600	D149-55T
surface arc-resistance, s	>300	>300	D495-55T
volume resistivity, Ω·cm	$>10^{18}$	$>10^{18}$	D257-57T
surface resistivity at 100% Rh, Ω/sq	$>10^{16}$		D257-57T
dielectric constant, at 60 to 2×10^9 Hz	2.1	2.1	D150-59T
dissipation factor, at 60 to 2×10^9 Hz	0.0003		D150-59T

[a] Ref. 83.

Table 7. **Applications of Polytetrafluoroethylene Resins**

Resin grade	Processing	Description	Main uses
Granular			
agglomerates	molding, preforming, sintering, ram extrusion	free-flowing powder	gaskets, packing, seals, electronic componenets, bearings, sheet, rod, heavy-wall tubing; tape and molded shapes for nonadhesive applications
coarse	molding, preforming, sintering	granulated powder	tape, molded shapes, nonadhesive applications
finely divided	molding, preforming, sintering	powder for highest quality, void-free moldings	molded sheets, tape wire wrapping, tubing, gaskets
presintered	ram extrusion	granular, free-flowing powder	rods and tubes
Fine powder			
high reduction ratio	paste extrusion	agglomerated powder	wire coating, thin-walled tubing
medium reduction ratio	paste extrusion	agglomerated powder	tubing, pipe, overbraided hose, spaghetti tubing
low reduction ratio	paste extrusion	agglomerated powder	thread-sealant tape, pipe liners, tubing, porous structures
Dispersion			
general purpose	dip coating	aqueous dispersion	impregnation, coating, packing
coating	dip coating	aqueous dispersion	film, coating
stabilized	coagulation	aqueous dispersion	bearings

Table 8. **Properties of Hexafluoropropylene**[a]

Properties	Value
molecular weight	150.021
boiling point at 101 kPa[a], °C	−29.4
freezing point, °C	−156.2
critical temperature, °C	85
critical pressure, kPa[b]	3254
critical density, g/cm^3	0.60
vapor pressure at K, kPa[b]	
$243.75 < T < 358.15$	$\log P\ (\text{kPa}) = 6.6938 - 1139.156/T$
liquid density, g/cm^3	
60°C	1.105
20°C	1.332
0°C	1.419
−20°C	1.498
heat of formation for ideal gas at, 25°C, ΔH, kJ/mol[c],[d]	−1078.6
flammability limits in air at 101 kPa[a]	nonflammable for all mixtures of air and hexafluoropropylene
heat of combustion, kJ/mol[c],[d]	879
toxicity, LC_{50} (rat), 4 h, ppm[e]	3000

[a] Ref. 122.
[b] To convert kPa to mm Hg, multiply by 7.5.
[c] To convert kJ to kcal, divide by 4.184.
[d] Ref. 137.
[e] Ref. 138.

Table 9. **Properties of Teflon FEP Fluorocarbon Resin**[a]

Mechanical property	ASTM method	Teflon 110	Teflon 100	Teflon 140	Teflon 160
melt flow number, g/10 min	D2116		7.0	3.0	1.5
specific gravity	D792	2.13–2.17	2.13–2.17	2.13–2.17	2.13–2.17
tensile strength at 23°C, MPa	D1708	20	23	30	31
elongation at 23°C, %	D1708	300	325	325	305
compressive strength, MPa	D695		21	21	23
flexural strength at 23°C, MPa	D790		18	18	18
impact strength at 23°C, J/m	D256		no break	no break	no break
flexural modulus at 23°C, MPa	D790	655	620	620	586
hardness durometer, Shore D	D2240	55	56	56	57
coefficient of friction, metal/film	D1894		0.27	0.27	0.235
deformation under load at 23°C, 6.9 MPa, 23 h, %	D621	1.8	0.5	0.5	0.5
water absorption, 24 h, %	D570	<0.01	0.004	0.004	0.004
linear coefficient of expansion °C	E831				
0–100°C			13.5×10^{-5}	13.9×10^{-5}	7.6×10^{-5}
100–150°C			20.8×10^{-5}	21.2×10^{-5}	11.5×10^{-5}
150–200°C			26.6×10^{-5}	27.0×10^{-5}	14.2×10^{-5}

[a] Compression-molded specimens; property data on extruded wire specimens are similar.

Table 10. **Mechanical Properties of FEP**[a]

Property	Value	ASTM method
specific gravity	2.14–2.17	D792-50
thermal conductivity, W/(m·K)		Cenco-Fitch
−129–182°C	2.4	
−253°C	1.4	
water absorption in 24 h, 3.175-mm-thick sample,		D570-547
% wt increase	<0.1	
dimensional change at 23°C	none	
coefficient of thermal expansion per °C		D696-44
>23°C	9.3×10^{-5}	
<23°C	5.7×10^{-5}	
specific heat, kJ/(kg·K)[b]		
20°C	1.09	
100°C	1.17	
260°C	1.30	
heat distortion, °C		D648-56
455 kPa[c]	70	
1820 kPa[c]	51	
tensile yield strength, av, MPa[d]		D638-527
−251°C	165	
−73°C	62	
23°C	12	
121°C	3.5	
tensile modulus, Pa[e]		
−251°C	57	
−73°C	24	
23°C	4	
100°C	1	
tensile elongation, %		D638-527
−251°C	4	
−73°C	200	
23°C	350	
flexural modulus, Pa[e]		D747-50
−251°C	53	
−101°C	32	
23°C	6.6	
55°C	3.4	
compressive strength, MPa[d]		D695
−251°C	251	
23°C	15	
100°C	3.4	
Izod impact strength, notched, J/m[f]		D256-56
23°C	no break	
hardness durometer, Shore D		D2240-T
23°C	59	
taber abrasion, g/MHz, 100-g load CS−17 wheel	7.5	

[a] Measured on Teflon FEP T−100.
[b] To convert kJ to kcal, divide by 4.184.
[c] To convert kPa to atm, multiply by 0.01.
[d] To convert MPa to psi, multiply by 145.
[e] To convert Pa to mm Hg, multiply by 7.5×10^{-3}.
[f] To convert J/m to ft·lbf/in., divide by 53.38 (see ASTM D256).

Table 11. **Permeability of FEP Fluorocarbon Resins to Liquid Vapors and Gases**

	Permeability constant,[a,b] 10^{15} mol/(m·s·Pa)		
Vapor	23°C	35°C	50°C
acetic acid		9.07	
acetone	0.37		3.23
benzene	0.75		
carbon tetrachloride	0.24	0.41	
decane	112.18		33.48
dipentene	23.50		10.67
ethyl acetate	0.27	2.06	4.09
ethanol	1.61	4.66	
H_2SO_4, 98%	21.70		
toluene	5.38		
water	8.14	20.32	18.26

[a] Ref. 183 Test method ASTM E96-35T (at vapor pressure; for 25.4-μm film thickness). Values are averages only and not for specification purposes.

[b] Original data converted to SI units using vapor pressure data from Ref. 195.

Table 12. **Typical Properties of Tefzel**[a]

	ASTM method	Tefzel 200, 280	Tefzel[b] HT-2004
ultimate tensile strength, MPa[c]	D638	44.8	82.7
ultimate elongation	D887-64T	200[d]	8
compressive strength, MPa[c]	D695	48.9	68.9
shear strength, MPa[c]		41.3	44.8
Heat deflection temp., °C	D648		
at 0.45 MPa		104	265
at 1.8 MPa		74	210
max continuous use temp., no load, °C		150[e]	200
low temp. embrittlement	D746	below -100°C	
tensile modulus, MPa[c]	D638	827	8270
flexural modulus, MPa[c]	D790	96.5	6550
impact strength notched Izod	D256		
at -54°C, J/m[f]		>1067	373
at 23°C		no break	485
deformation under load, 13.7 MPa at 50°C, %	D621	4.11	0.68
coefficient of linear expansion per °C	D696-70		
20–30°C		9×10^{-5}	3×10^{-5}
50–90°C		9.3×10^{-5}	1.7×10^{-5}
140–180°C		14×10^{-5}	3.2×10^{-5}
specific gravity	D792	1.70	1.86
refractive index n_D		1.4028	
flammability	UL 94	94V-O	94V-O
	D635	ATB[g] <5 s; ALB 10 mm	
melting point, dta peak, °C		270	270
water absorption at saturation, %	D570	0.029	0.022
hardness			
Rockwell	D785	R50	R74
Durometer D		D75	
coefficient of friction[h]			
dynamic, 689 kPa (at >3 m/min)		0.4	0.3
static, 689 kPa			0.3

[a] At 23°C and 50% Rh, unless otherwise specified.

[b] Reinforced with 25 wt% glass fiber.

[c] To convert MPa to psi, multiply by 145.

[d] Elongations between 100 and 300% are achieved with varying methods of sample fabrication.

[e] Long-term heat-aging tests on Tefzel 280 are in progress. Early data indicate that initial properties are retained after more than 2000 h at 200°C. It is expected that the continuous use temperature of Tefzel 280 will be above 150°C.

[f] To convert J/m to ft·lbf/in., divide by 53.38.

[g] ATB; average time of burning to nearest 5 s; ALB: average length of burn to nearest 5 mm. Test bar thickness = 2.9 mm.

[h] Mating material AISI 1018 Steel, Rc20, 16AA.

Table 13. **Thermodynamic Properties of Modified ETFE**

Property	Tefzel 200 and 280
melting point, °C	270
specific heat	0.46–0.47
heat of sublimation, kJ/mol	50.2
heat of fusion[a], J/g	46.0
heat of combustion, kJ/g	13.72
thermal conductivity, W/(m·K)	0.238
critical surface tension of molten resin, mN/m (=dyn/cm)	22

[a] Little dependence on temperature.

Table 14. **Bearing Wear Rate**[a]

		Wear factor K, 10^{17} 1/Pa[c]	
Pressure, kPa[b]	Velocity, cm/s	Tefzel	Metal
on steel[d]			
6.8	2.5	32	8
6.8	5.1	28	12
6.8	7.6	38	26
6.8	8.9	60	32
6.8	10.2	fail	
on aluminum[e]			
2.0	5.1	2400	2400
0.68	25.4	960	780

[a] Thrust-bearing tester, no lubricant, ambient air temperature, metal finish 406 nm.

[b] To convert kPa to psi, multiply by 0.145.

[c] To convert 1/Pa to $(\text{in.}^3\cdot\text{min})/(\text{ft}\cdot\text{lbf}\cdot\text{h})$, divide by 2×10^{-7}.

[d] AISI 1018.

[e] LM24M (English).

Table 15. **Electrical Properties of ETFE Resins**

	ASTM test	ETFE	Reinforced
dissipation factor	D150		
10^2 Hz		0.0006	0.004
10^3 Hz		0.0008	0.002
10^4 Hz			0.002
10^5 Hz			0.003
10^6 Hz		0.005	0.005
10^9 Hz		0.005	
10^{10} Hz		0.010	0.012
volume resistivity, $\Omega\cdot$cm	D257	$>10^{16}$	10^{16}
surface resistivity, Ω/sq	D257	$>10^{16}$	10^{15}
arc resistance, s	D495	75	110

Table 16. **Tefzel Resistance to Chemicals after 7 Days of Exposure**[a]

			Retained properties, %		
Chemical	Boiling point, °C	Test temp., °C	Tensile strength	Elongation	Weight, gain
organic acids and anhydrides					
acetic acid (glacial)	118	118	82	80	3.4
acetic anhydride	139	139	100	100	0
trichloroacetic acid	196	100	90	70	0
hydrocarbons					
mineral oil		180	90	60	0
naphtha		100	100	100	0.5
benzene	80	80	100	100	0
toluene	110	110			
amines					
aniline	185	120	81	99	2.7
aniline	185	180	95	90	
N-methylaniline	195	120	85	95	
N,*N*-dimethyl aniline	190	120	82	97	
n-butylamine	78	78	71	73	4.4
di-*n*-butylamine	159	120	81	96	
di-*n*-butylamine	159	160	55	75	
tri-*n* butylamine	216	120	81	80	
pyridine	116	116	100	100	1.5
solvents					
carbon tetrachloride	78	78	90	80	4.5
chloroform	62	61	85	100	4.0
dichloroethylene	77	32	95	100	2.8
methylene chloride	40	40	85	85	0
Freon 113	46	46	100	100	0.8
dimethylformamide	154	90	100	100	1.5
dimethyl sulfoxide	189	90	95	95	1.5
Skydrol		149	100	95	3.0
Aerosafe		149	92	93	3.9
A-20 stripper solution		140	90	90	
ethers, ketones, esters					
tetrahydrofuran	66	66	86	93	3.5
acetone	56	56	80	83	4.1
acetophenone	201	180	80	80	1.5
cyclohexanone	156	156	90	85	0
methyl ethyl ketone	80	80	100	100	0
n-butyl acetate	127	127	80	60	0
ethyl acetate	77	77	85	60	0
other organic compounds					
benzyl alcohol	205	120	97	90	
benzoyl chloride	197	120	94	95	

Table 16. (*Continued*)

			Retained properties, %		
Chemical	Boiling point, °C	Test temp., °C	Tensile strength	Elongation	Weight, gain
o-cresol	191	180	100	100	
decalin	190	120	89	95	
phthaloyl chloride	276	120	100	100	
inorganic acids					
hydrochloric (conc)	106	23	100	90	0
hydrobromic (conc)	125	125	100	100	
hydrofluoric (conc)		23	97	95	0.1
sulfuric (conc)		100	100	100	0
nitric, 70% (conc)	120	120	0	0	
chromic	125	125	66	25	
phosphoric (conc)		100			
halogens					
bromine (anhy)	59	23	90	90	1.2
chlorine (anhy)		120	85	84	7
bases, peroxides					
ammonium hydroxide		66	97	97	0
potassium hydroxide, 20%		100	100	100	0
sodium hydroxide, 50%		120	94	80	0.2
hydrogen peroxide, 30%		23	99	98	0
other inorganic compounds					
ferric chloride, 25%	104	100	95	95	0
zinc chloride, 25%	104	100	100	100	0
sulfuryl chloride	68	68	86	100	8
phosphoric trichloride	75	75	100	98	
phosphoric oxychloride	104	104	100	100	
silicon tetrachloride	60	60	100	100	

[a] Changes in properties <15% are considered insignificant; test performed on 250–1250 μm microtensile bars; tensile strength, elongation, and weight gain determined within 24 h after termination of exposure.

Table 17. **Forms of Modified ETFE Resins**

Tefzel grade	Form	Melt flow,[a] g/10 min	Application
210	extruded cubes	45	injection molding, thin coating
200	extruded cubes	8	general purpose, insulation, tubing, fasteners
280	extruded cubes	3	chemical resistance, jacketing, havy-wall, logging cables
HT-2000	compacted powder	8	compounded products
HT-2010	compacted powder	3	compounded products, coating lining
HT-2010	compacted powder	45	coating

[a] At 297°C and 45 N (5 kgf) load.

Table 18. **Properties of Perfluoropropyl Vinyl Ether, $F_3C{-}CF_2{-}CF_2{-}O{-}CF{=}CF_2$**

Property	Value
critical temperature, K	423.58
critical pressure, MPa[a]	1.9
critical volume, $cm^3/(g{\cdot}mol)$	435
surface tension, mN/m(=dyn/cm)	9.9
boiling point, °C	36
specific gravity at 23°C	1.53
vapor density at 75°C, g/cm^3	0.2
vapor pressure at 25°C, kPa[b]	70.3
solubility in water	0
odor	none
color	colorless
flash point, °C	−20
flammable limits in air,[c] vol.%	1

[a] To convert MPa to atm, divide by 0.1013.

[b] To convert kPa to psi (psia), multiply by 0.145.

[c] Extremely flammable.

Table 19. **Properties of Teflon PFA**

Property	ASTM method	Teflon 340	Teflon 350
nominal melting point, °C		302–306	302–306
specific gravity	D3307	10.6	1.8
continuous use temp., °C		260	260
tensile strength, MPa[a]			
at 23°C	D1708	28	31
at 250°C		12	14
tensile yield, MPa[a]			
at 23°C	D1708	14	15
at 250°C		3.5	4.1
ultimate elongation, %			
at 23°C		300	300
at 250°C	D1708	480	500
flexural modulus, MPa[a]			
at 23°C	D790	655	690
at 250°C		55	69
creep resistance[b] tensile, modulus, MPa[a]			
at 20°C	D695	270	270
at 250°C	D695	41	41
hardness durometer	D2240	D60	D60
MIT folding endurance, 775–200 μm film thickness, cycles		50,000	500,000
water absorption, %	D570	0.03	0.03
coefficient of linear thermal expansion per °C	D696		
20–100°C		12×10^{-5}	12×10^{-5}
100–150°C		17×10^{-5}	17×10^{-5}
150–210°C		20×10^{-5}	20×10^{-5}

[a] To convert MPa to psi, multiply by 145.

[b] Apparent modulus after 10 h: stress = 6.89 MPa at 20°C, 6.89 kPa at 250°C.

Table 20. **Cryogenic Properties of Teflon PFA Resins**

Property	ASTM method	At 23°C	At −196°C
yield strength, MPa[a]	D1708[b]	15	
ultimate tensile strength, MPa[a]	D1708[b]	18	129
elongation, %	D1708[b]	260	8
flexural modulus, MPa[a]	D790-71[c]	558	5790
impact strength, notched Izod, J/m[d]	D256-72a[e]	No break	64
compressive strength, MPa[a]	D695		414
compressive strain, %	D695		35
modulus of elasticity, MPa[a]	D695		4690

[a] To convert MPa to psi, multiply by 145.

[b] Crosshead speed B, 1.3 mm/min; used at both temperatures for more direct comparison.

[c] Method 1, Procedure B.

[d] To convert J/m to ft·lbf/in., divide by 53.38.

[e] Method A, head weight is 4.5 kg at 23°C and 0.9 kg at 160°C.

Table 21. **Teflon PFA Fluorocarbon Resin Thrust-Bearing Wear-Test Results**[a]

Velocity, m/min	Wear factor *K*, 10^{17}, 1/Pa[b]	Dynamic coefficient of friction	Test duration, h
Teflon PFA			
TE-9704			
0.91	3.12	0.210	103
3.05	3.67	0.214	103
9.1	1.96	0.229	103
15.24	1.38	0.289	103
Teflon FEP 100			
0.91	3.71	0.341	104
3.05	2.19	0.330	104
9.1	3.16	0.364	104
15.24	1.60	0.296	103

[a] Mating surface: AISA 1018 steel, R*c* 20, 16AA; contact pressure: 689 kPa; at 20°C in air; no lurbricant.

[b] To convert 1/Pa to (in.^{3}·min)/(ft·lbf·h), divide by 2×10^{-7}.

Table 22. **Electrical Properties of Teflon PFA**

Property	ASTM method	Value
dielectric strength,[a] kV/m		79
volume resistivity, Ω·cm	D257	10^{18}
surface resistivity, Ω/sq	D257	10^{18}
dissipation factor	D150	
at 10^2 Hz		0.000027
at 10^6 Hz		0.000080
at 10^7 Hz		0.000145
at 10^9 Hz		0.00115
at 3×10^9 Hz		0.00144
at 1.4×10^{10} Hz		0.00131
at 2.4×10^{10} Hz		0.00124

[a] Short term, 250-μm-thick sample.

Table 23. **Optical Properties of Teflon PFA Film**

Property	ASTM method	Value
refractive index[a]	D542-50	1.350 ± 0.002
haze, %	D10003-52	4
light transmission, %		
ultraviolet[b] 0.25–0.40 μm		55–80
visible, 0.40–0.70 μm		80–87
infrared, 0.70–2.1 μm		87–93

[a] Measured at 546 nm and 20°C.

[b] Cary Model Spectrophotometer.

Table 24. **Effects of Radiation on Tensile Strength of PFA**[a]

	ASTM D1708	
Exposure, kGy	Tensile strength, MPa[b]	Elongation, %
0	30.27	358
5	28.20	366
10	24.96	333
20	21.24	302
50	14.55	35
200		<5
500		<5

[a] *Sample:* 250-µm compression-molded films of Teflon PFA 340. *Source:* G.E. resonance transformer, 2 MeV capacity, at a current of 1 mA.

[b] To convert MPa to psi, multiply by 145.

Table 25. **Properties of Teflon AF-1600 and AF-2400**

Property	AF-1600	AF-2400	ASTM method	Refs
melt viscosity, Pa·s[a]			D3835	315
at 250°C	2650			
at 350°C		540		
density, g/cm^3	1.78	1.67	D792	311
water absorptivity; 1	<0.01	<0.01	D570	316
contact angle, water, deg	104	105		315
critical surface energy, mN/m(=dyn/cm)	15.6–15.7	15.6–15.7		315
electrical properties				
dielectric strength, kV(0.1 mm)$^{-1}$	2.1	1.9	D149	315
dielectric constant				
1 MHz	1.934	1.904	D150	315
1 GHz	1.93	1.897		
13.6 GHz	1.927	1.89		
dissipation factor				
1 MHz	0.00012	0.00012	D150	311
1 GHz	0.00018	0.00024		
13.6 GHz	0.00020	0.00035		
flammability, LOI %O_2	95	95		316
hardness, Rockwell	103	97.5	D785	315
refractive index	1.31	1.29	D542	316
optical transmissions	>95	>95	D1003	316
tensile strength at break, MPa[a]			D638	316
23°C	27	26		
150°C	8			
220°C		4		
elongation at break, %				
23°C	17	8	D638	316
150°C	89			
220°C		8		

[a] To convert MPa to psi, multiply by 145.

[b] To convert Pa·s to P, multiply by 10.