Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE-CONTAINING POLYMERS, POLYTETRAFLUOROETHYLENE

Polytetrafluoroethylene [9002-84-0] (PTFE), more commonly known as Teflon (Du Pont), a perfluorinated straight-chain high polymer, has a most unique position in the plastics industry due to its chemical inertness, heat resistance, excellent electrical insulation properties, and low coefficient of friction over a wide temperature range. Polymerization of tetrafluoroethylene (TFE) 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 to 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 Du Pont 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), Du Pont (Teflon), Hoechst (Hostaflon), ICI (Fluon), Ausimont (Algoflon and Halon), and the CIS (Fluoroplast). India and The People's Republic of China also manufacture some PTFE products.

1. Monomer

1.1. Preparation

The manufacture of tetrafluoroethylene [116-14-3] (TFE) involves the following steps (2–9). The pyrolysis is often conducted at a PTFE manufacturing site because of the difficulty of handling TFE.

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

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

$$CHCl_3 + 2\,HF \xrightarrow{SbF_3} CHClF_2 + 2\,HCl$$

$$2\,CHClF_2 \xrightarrow{\Delta} CF_2{=}CF_2 + 2\,HCl$$

Pyrolysis of chlorodifluoromethane is a noncatalytic gas-phase reaction carried out in a flow reactor at atmospheric or 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 (10).

Tetrafluoroethylene was first synthesized in 1933 from tetrafluoromethane, CF_4, in an electric arc furnace (11). Since then, a number of routes have been developed (12–18). 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 (19, 20). Depolymerization products contain highly toxic perfluoroisobutylene and should be handled with care.

1.2. Properties

Tetrafluoroethylene (mol wt 100.02) is a colorless, tasteless, odorless, nontoxic gas (Table 1). It is stored as a liquid; vapor pressure at $-20^\circ C = 1\ MPa$ (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 (24). Under controlled conditions, oxygenation produces an epoxide (25) or an explosive polymeric peroxide (24). Trifluorovinyl ethers, $RO{-}CF{=}CF_2$, are obtained by reaction with sodium salts of alcohols (26). An ozone–TFE reaction is accompanied by chemiluminescence (27). Dimerization at 600°C gives perfluorocyclobutane, C_4F_8; further heating gives hexafluoropropylene, $CF_2{=}CFCF_3$, and eventually perfluoroisobutylene, $CF_2{=}C(CF_3)_2$ (28). Purity is determined by both gas–liquid and gas–solid chromatography; the ir spectrum is complex and therefore of no value.

1.3. Uses

Besides polymerizing TFE to various types of high PTFE homopolymer, TFE is copolymerized with hexafluoropropylene (29), ethylene (30), perfluorinated ether (31), isobutylene (32), propylene (33), and in some cases it is used as a termonomer (34). It is used to prepare low molecular weight polyfluorocarbons (35) and carbonyl

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	
$-100 < t < -40$	$1.202–0.0041\ t$
$-40 < t < 8$	$1.1507–0.0069\ t\text{-}0.000037\ t^2$
$8 < t < 30$	$1.1325–0.0029\ t\text{-}0.00025\ t^2$
vapor pressure at T K, kPa[c]	
$196.85 < T < 273.15$	$\log_{10} P_{kPa} = 6.4593 - 875.14/T$
$273.15 < T < 306.45$	$\log_{10} P_{kPa} = 6.4289 - 866.84/T$
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, mW/(m·K)	15.5
heat of formation for ideal gas at 25°C, ΔH, kJ/mol[e, f]	−635.5
heat of polymerization at 25°C to solid polymer ΔH, kJ/mol[e,g]	−172.0
flammability limits in air at 101.3 kPa,[c] vol %	14–43

[a] From Ref. 21, 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. 22.
[g] Ref. 23.

fluoride (36), as well as to form PTFE *in situ* on metal surfaces (37). Hexafluoropropylene [116-15-4] (38, 39), 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.

2. Manufacture of PTFE

Engineering problems involved in the production of TFE seem simple 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 also are available in various grades. Differences in fine powder grades correspond to their usefulness in specific applications and to the ease of fabrication. Aqueous

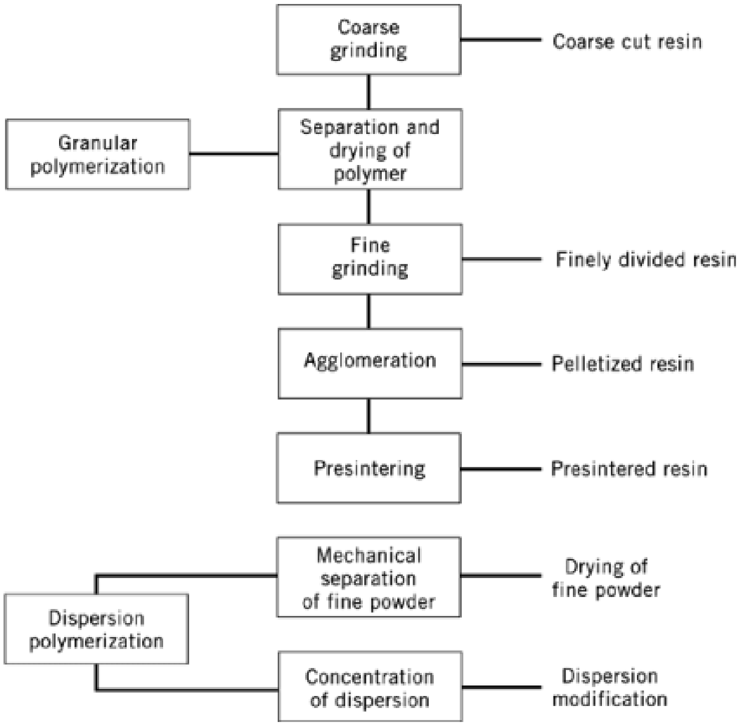

Fig. 1. Granular, fine powder, and dispersion PTFE products.

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.

2.1. 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.

2.2. Granular Resins

Granular PTFE is made by polymerizing TFE alone or in the presence of trace amounts of comonomers (40, 41). An initiator, a small amount of dispersing agent, and other additives (42) may be present; an alkaline buffer is occasionally used (43). 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 (44). For ram extrusion of granular resin into long tubes and rods, a partially presintered resin is preferred. Granular PTFE resin is nonflammable.

2.3. Fine Powder Resins

Fine powder resins are made by polymerizing TFE in an aqueous medium with an initiator and emulsifying agents (45). 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 (46), 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 (47–50). 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 (51–57).

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.

2.4. Aqueous Dispersions

The dispersion is made by the polymerization process used to produce fine powders of different average particle sizes (58). 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 (59). The concentrated dispersion can be modified further with chemical additives. The fabrication characteristics of these dispersions depend on polymerization conditions and additives.

2.5. 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.

3. Properties

The properties described herein are related to the basic structure of polytetrafluoroethylene 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 389×10^3 to 8900×10^3 (60, 61). 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 (62). The correlation between number-average molecular weight (M_n) based on end group estimations, and standard specific gravity (SSG) is given by

$$\mathrm{SSG} = 2.612 - 0.058\log_{10} M_n$$

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 (63).

Melting and recrystallization behavior of virgin PTFE has been studied by dsc (64). A quantitative relationship was found between M_n and the heat of crystallization (ΔH_c) in the molecular weight range of 5.2×10^5 to 4.5×10^7, where H_c is heat of crystallization in J/g, which is independent of cooling rates of 4–32°C/min.

$$M_n = 2.1 \times 10^{10} \cdot \Delta H_c^{-5.16}$$

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 $10\ \mathrm{GPa \cdot s}$ (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) (65).

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 (66). Electron micrographs and diffraction patterns (67) 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 $\gamma : \tau = K\gamma^{1/4}$. 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 toward 0.5 at the final melting point (68).

3.1. Transitions

Transitions observed by various investigators (69–74), 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

Table 2. Transitions in Polytetrafluoroethylene

Temperature, °C	Region affected	Technique	Reference
	1st order		
19	crystalline, angular displacement causing disorder	thermal methods, x-ray, nmr	70
30	crystalline, crystal disordering	thermal methods, x-ray, nmr	70
90 (80 to 110)	crystalline	stress relaxation, Young's modulus, dynamic methods	73
	2nd order		
−90(− 110 to −73)	amorphous, onset of rotational motion around C—C bond	thermal methods, dynamic methods	74
−30(− 40 to −15)	amorphous	stress relaxation, thermal expansion, dynamic methods	73
130 (120 to 140)	amorphous	stress relaxation, Young's modulus, dynamic methods	73

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 (69). 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 (70, 71).

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 (75). 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.

Polytetrafluoroethylene 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.

3.2. 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 (72, 76, 77) (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.

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]			
21°C	106.7		D256-56
24°C	160		
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 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. 77.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J/m to ft·lbf/in., divide by 53.38.

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 (78). Treatment with alkali metals promotes the adhesion between PTFE and other substances (79) but increases the coefficient of friction (80).

3.3. 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 (81).

3.4. Chemical Properties

Vacuum thermal degradation of PTFE results in monomer formation. The degradation is a first-order reaction (82). Mass spectroscopic analysis shows that degradation begins at ca 440°C, peaks at 540°C, and continues until 590°C (83).

3.5. Radiation Effects

Polytetrafluoroethylene is attacked by radiation. In the absence of oxygen, stable secondary radicals are produced. An increase in stiffness in material irradiated in vacuum indicates cross-linking (84). 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 (85). 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

Table 4. Properties of Filled PTFE Compounds[a]

Property	Unfilled	Glass fiber, wt %		Graphite, 15 wt %	Bronze, 60 wt %
		15	25		
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, Shore durometer, *D*	51	54	57	61	70
Izod impact, J/m[d]	152	146	119		
PV,[e] (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 = 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. 81.

[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 ft·lbf/in., divide by 53.38.

[e] PV = pressure × velocity. For 0.13-mm radial wear in 1000 h, unlubricated.

[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}.

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 ($2 \times 10^4 - 7 \times 10^4$ 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 (86).

3.6. Absorption, Permeation, and Interactions

Polytetrafluoroethylene is chemically inert to industrial chemicals and solvents even at elevated temperatures and pressures (87). 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 (87).

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

Table 5. Permeability of PTFE Resin to Vapors

	Permeability constant,[a,b] mol/(m·s·Pa) × 10^{15}	
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. 87. 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. 90.

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 (87).

Dynamic mechanical measurements were made on PTFE samples saturated with various halocarbons (88). The peaks in loss modulus associated with the amorphous relaxation near $-90°\mathrm{C}$ and the crystalline relaxation near room temperature were not affected by these additives. An additional loss peak appeared near $-30°\mathrm{C}$, 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 for nonpolar partially crystalline polymers (89). 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 30deg;C (in mol/(m·s·Pa) × 10^{15}) are as follows: CO_2, 0.93; N_2, 0.18; He, 2.47; anhydrous HCl, <0.01 (89).

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.

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. 77.

3.7. 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 Hz to 10 GHz.

Articles fabricated according to standard practice should have dielectric constants in the range of 2.05 ± 0.5 when tested at 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 (91). 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.

4. Fabrication

4.1. 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.

4.2. Molding

Many PTFE manufacturers give detailed descriptions of molding equipment and procedures (92–98). 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. For large-area, thin-walled moldings of unfilled polymer, a short-stroke press with a working capacity of 19.6–34.3 MPa (194–339 atm) mold pressure is sufficient; for tall moldings of filled compounds with a small cross-sectional area, a long-stroke press with a low thrust is required. The powder should be evenly distributed and leveled in the mold (92). 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; it is preferable to machining finished material. 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.

4.3. 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 homogeneity, 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.

4.4. 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 (92, 99–101). 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.

4.5. 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 Reference (102–108).

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 above. The preform is extruded in the form of rods, which are calendered on hot rolls to the desired width and thickness (109, 110).

Different resins have been developed for use in different reduction–ratio application ranges (111, 112). 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 (113–115).

4.6. 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.

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 (116, 117) 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.

4.7. 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 five 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

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 components, 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

slow cooling. The stress–crack resistance of various PTFE insulations is correlated with the crystallinity and change in density due to thermal mechanical stress (118).

5. 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.

5.1. 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.

5.2. 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.

5.3. 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 (113).

5.4. Micropowders

The PTFE micropowders, also called waxes, are tetrafluoroethylene homopolymers with molecular weights significantly lower than that of normal PTFE. 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 to 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.

6. Economic Aspects

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 1992 list prices from primary producers were between 16.3 and 23.5 $/kg, depending on the resin type. For example, granular PTFE resins cost 16.3–18.0 $/kg supplied in 22.5-kg containers. The coagulated fine powders cost 19.10–22.10 $/kg packaged in 22.5-kg containers. Formulated dispersions are 20.00–23.5 $/kg in 19-L 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. Most of the resin is consumed in the United States (ca 9000 t in 1991), followed by Europe and Japan.

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 119.

8. Health and Safety

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 (120).

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 (120). 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 hours; 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. 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 finishes 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.

BIBLIOGRAPHY

"Tetrafluorethylene Resins" in *ECT* 1st ed., Vol. 11, pp. 687–691, by B. E. Ely, E.I. du Pont de Nemours & Co., Inc.,; "Polytetrafluoroethylene" under "Fluorine Compounds, Organic" in *ECT* 2nd ed., Vol. 9, pp. 805–831, by S. Sherratt, Imperial Chemical Industries, Ltd., Plastics Division; in *ECT* 3rd ed., Vol. 11, pp. 1–24, by S. V. Gangal, E.I. du Pont de Nemours & Co., Inc.

Cited Publications

1. U.S. Pat. 2,230,654 (Feb. 4, 1941), R. J. Plunkett (to Kinetic Chemicals, Inc.).

2. J. D. Park and co-workers, *Ind. Eng. Chem.* **39**, 354 (1947).
3. J. M. Hamilton, in M. Stacey, J. C. Tatlow, and A. G. Sharpe, eds., *Advances in Fluorine Chemistry*, Vol. **3**, Butterworth & Co., Ltd., Kent, U.K., 1963, p. 117.
4. J. W. Edwards and P. A. Small, *Nature* **202**, 1329 (1964); J. W. Edwards and P. A. Small, *Ind. Eng. Chem. Fundam.* **4**, 396 (1965).
5. F. Gozzo and C. R. Patrick, *Nature* **202**, 80 (1964).
6. Jpn. Pat. 60 15,353 (Oct. 14, 1960), M. Hisazumi and H. Shingu.
7. U.S. Pat. 2,994,723 (Aug. 1, 1961), O. Scherer and co-workers (to Farbewerke Hoechst).
8. Brit. Pat. 960,309 (June 10, 1964), J. W. Edwards, S. Sherratt, and P. A. Small (to ICI).
9. U.S. Pat. 3,459,818 (Aug. 5, 1969), H. Ukahashi and M. Hisasne (to Asahi Glass Co.).
10. U.S. Pat. 2,407,405 (Sept. 10, 1946), M. A. Dietrich and R. M. Joyce (to E.I. du Pont de Nemours & Co., Inc.).
11. O. Ruff and O. Bretschneider, *Z. Anorg. Allg. Chem.* **210**, 173 (1933).
12. E. G. Locke, W. R. Brode, and A. L. Henne, *J. Am. Chem. Soc.* **56**, 1726 (1934).
13. O. Ruff and W. Willenberg, *Chem. Ber.* **73**, 724 (1940).
14. L. T. Hals, T. S. Reid, and G. H. Smith, *J. Am. Chem. Soc.* **73**, 4054 (1951) U.S. Pat. 2,668,864 (Feb. 9, 1954), (to Minnesota Mining and Manufacturing Co.).
15. U.S. Pat. 3,009,966 (Nov. 21, 1961), M. Hauptschein and A. H. Fainberg (to Pennsalt Chemical Corp.).
16. U.S. Pat. 3,471,546 (Oct. 7, 1969), G. Bjornson (to Phillips Petroleum Co.).
17. U.S. Pat. 3,662,009 (May 9, 1972), W. M. Hutchinson (to Phillips Petroleum Co.).
18. U.S. Pat. 3,799,996 (Mar. 26, 1974), H. S. Bloch (to Universal Oil Products).
19. E. E. Lewis and M. A. Naylor, *J. Am. Chem. Soc.* **69**, 1968 (1947).
20. U.S. Pat. 3,832,411 (Aug. 27, 1974), B. C. Arkles and R. N. Bonnett (to Liquid Nitrogen Processing Co.).
21. M. M. Renfrew and E. E. Lewis, *Ind. Eng. Chem.* **38**, 870 (1946).
22. H. C. Duus, *Ind. Eng. Chem.* **47**, 1445 (1955).
23. W. M. D. Bryant, *J. Polym. Sci.* **56**, 277 (1962).
24. A. Pajaczkowski and J. W. Spoors, *Chem. Ind.* **16**, 659 (1964).
25. Brit. Pat. 931,587 (July 17, 1963), H. H. Gibbs and J. L. Warnell (to E.I. du Pont de Nemours & Co., Inc.).
26. U.S. Pat. 3,159,609 (Dec. 1, 1964), J. F. Harris, Jr., and D. I. McCane (to E.I. du Pont de Nemours & Co., Inc.).
27. F. S. Toby and S. Toby, *J. Phys. Chem.* **80**, 2313 (1976).
28. B. Atkinson and V. A. Atkinson, *J. Chem. Soc. Part II*, 2086 (1957).
29. U.S. Pat. 2,946,763 (July 26, 1960), M. I. Bro and B. W. Sandt (to E.I. du Pont de Nemours & Co., Inc.).
30. U.S. Pat. 3,847,881 (Nov. 12, 1974), M. Mueller and S. Chandrasekaran (to Allied Chemicals Co.).
31. U.S. Pat. 3,528,954 (Sept. 15, 1970), D. P. Carlson (to E.I. du Pont de Nemours & Co., Inc.).
32. U.S. Pat. 3,475,391 (Oct. 28, 1969), J. N. Coker (to E.I. du Pont de Nemours & Co., Inc.).
33. U.S. Pat. 3,846,267 (Nov. 5, 1974), Y. Tabata and G. Kojima (to Japan Atomic Energy Research Institute).
34. U.S. Pat. 3,467,636 (Sept. 16, 1969), A. Nersasian (to E.I. du Pont de Nemours & Co., Inc.).
35. U.S. Pat. 3,403,191 (Sept. 24, 1968), D. P. Graham (to E.I. du Pont de Nemours & Co., Inc.).
36. U.S. Pat. 3,404,180 (Oct. 1, 1969), K. L. Cordes (to E.I. du Pont de Nemours & Co., Inc.).
37. U.S. Pat. 3,567,521 (Mar. 2, 1971), M. S. Toy and N. A. Tiner (to McDonnell Douglas).
38. U.S. Pat. 3,446,858 (May 27, 1969), H. Shingu and co-workers (to Daikin Kogyo Co.).
39. U.S. Pat. 3,873,630 (Mar. 25, 1975), N. E. West (to E.I. du Pont de Nemours & Co., Inc.).
40. U.S. Pat. 3,855,191 (Dec. 17, 1974), T. R. Doughty, C. A. Sperati, and H. Un (to E.I. du Pont de Memours & Co., Inc.).
41. U.S. Pat. 3,655,611 (Apr. 11, 1972), M. B. Mueller, P. O. Salatiello, and H. S. Kaufman (to Allied Chemicals Co.).
42. U.S. Pat 4,189,551 (Feb. 19, 1980), S. V. Gangal (to E.I. du Pont de Nemours & Co., Inc.).
43. U.S. Pat. 3,419,522 (Dec. 31, 1968), P. N. Plimmer (to E.I. du Pont de Nemours & Co., Inc.).
44. U.S. Pat. 3,766,133 (Oct. 16, 1973) R. Roberts and R. F. Anderson (to E.I. du Pont de Nemours & Co., Inc.).
45. U.S. Pat. 2,612,484 (Sept. 30, 1952), S. G. Bankoff (to E.I. du Pont de Nemours & Co., Inc.).
46. U.S. Pat 4,186,121 (Jan. 29, 1980), S. V. Gangal (to E.I. du Pont de Nemours & Co., Inc.).
47. U.S. Pat. 4,725,644 (1988), S. Malhotra (to E.I. du Pont de Nemours & Co., Inc.).
48. T. Folda and co-workers, *Nature* **333**, 55 (1988).
49. B. Luhmann and A. E. Feiring, *Polymer* **30**, 1723 (1989).
50. B. Chu, C. Wu, and W. Buck, *Macromolecules* **22**, 831 (1989).

51. U.S. Pat. 4,576,869 (Mar. 18, 1986), S. C. Malhotra (to E.I. du Pont de Nemours & Co., Inc.).
52. U.S. Pat. 4,363,900 (Dec. 14, 1982), T. Shimizu and S. Koizumi (to Daikin Kogyo Co.).
53. U.S. Pat. 4,766,188 (Aug. 23, 1988), T. E. Attwood and R. F. Bridges (to ICI).
54. U.S. Pat. 4,036,802 (July 19, 1977), R. V. Poirier (to E.I. du Pont de Nemours & Co., Inc.).
55. U.S. Pat. 4,129,618 (Dec. 12, 1978), J. M. Downer, W. G. Rodway, and L. S. J. Shipp (to ICI).
56. U.S. Pat. 4,840,998 (June 6, 1989), T. Shimizu and K. Hosokawa (to Daikin Kogyo Co.).
57. U.S. Pat. 4,879,362 (Nov. 7, 1979), R. A. Morgan (to E.I. du Pont de Nemours & Co., Inc.).
58. U.S. Pat. 4,342,675 (Aug. 3, 1982), S. V. Gangal (to E.I. du Pont de Nemours & Co., Inc.).
59. U.S. Pat. 2,478,229 (Aug. 9, 1949), K. L. Berry (to E.I. du Pont de Nemours & Co., Inc.).
60. K. L. Berry and J. H. Peterson, *J. Am. Chem. Soc.* **73**, 5195 (1951).
61. R. C. Doban and co-workers, paper presented at *130th Meeting of the American Chemical Society,* Atlantic City, N. J., Sept. 1956.
62. C. A. Sperati and H. W. Starkweather, *Fortschr. Hochpolym. Forsch.* **2**, 465 (1961).
63. R. E. Moynihan, *J. Am. Chem. Soc.* **81**, 1045 (1959).
64. T. Suwa, M. Takehisa, and S. Machi, *J. Appl. Polym. Sci.* **17**, 3253 (1973).
65. P. L. McGeer and H. C. Duus, *J. Chem. Phys.* **20**, 1813 (1952).
66. C. W. Bunn, *J. Polym. Sci.* **16**, 332 (1955).
67. H. D. Chanzy, P. Smith, and J. Revol, *J. of Polym. Sci. Polym. Lett. Ed.* **24**, 557 (1986).
68. H. W. Starkweather, Jr., *J. Polym. Sci. Polym. Phys. Ed.* **17**, 73–79 (1979).
69. R. H. H. Pierce and co-workers, in Ref. 61.
70. E. S. Clark and L. T. Muus, paper presented at *133rd Meeting of the American Chemical Society,* New York, Sept. 1957.
71. E. S. Clark, paper presented at *Symposium on Helices in Macromolecular Systems*, Polytechnic Institute of Brooklyn, Brooklyn, N.Y., May 16, 1959.
72. C. A. Sperati, in J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 2nd ed., John Wiley & Sons, Inc., New York, 1975 pp. V-29–36.
73. Y. Araki, *J. Appl. Polym. Sci.* **9**, 3585 (1965).
74. N. G. McCrum, *J. Polym. Sci.* **34**, 355 (1959).
75. H. W. Starkweather, Jr., *Macromolecules* **19**, 2541 (1986).
76. J. T. Milek, *A Survey Materials Report on PTFE Plastics*, AD 607798, U.S. Dept. of Commerce, Washington, D.C., Sept. 1964.
77. *Mechanical Design Data, Teflon Fluorocarbon Resins*, bulletin, E.I. du Pont de Nemours & Co., Inc. Wilmington, Del. Sept. 1964.
78. M. K. Bernett and W. A. Zisman, *J. Phys. Chem.* **63**, 1911 (1959).
79. U.S. Pat. 2,871,144 (Jan. 27, 1959), R. C. Doban (to E.I. du Pont de Nemours & Co., Inc.).
80. A. J. G. Allan and R. Roberts, *J. Polym. Sci.* **39**, 1 (1959).
81. *J. Teflon (Du Pont)* **13**(2), 3 (1972).
82. J. C. Siegle and co-workers, *J. Polym. Sci.* **Part A2**, 391 (1964).
83. G. P. Shulman, *Polym. Lett.* **3**, 911 (1965).
84. L. A. Wall and R. E. Florin, *J. Appl. Polym. Sci.* **2**, 251 (1959).
85. W. M. Peffley, V. R. Honnold, and D. Binder, *J. Polym. Sci.* **4**, 977 (1966).
86. *J. Teflon (Du Pont)* **10**(1), (Jan.–Feb. 1969).
87. *J. Teflon (Du Pont)* **11**(1), (Jan.–Feb. 1970).
88. H. W. Starkweather, Jr., *Macromolecules* **17**, 1178 (1984).
89. *Ibid.*, **10**, 1161 (1977).
90. D. W. Green, ed., *Perry's Chemical Engineers' Handbook*, 6th ed., McGraw-Hill Book Co., Inc., New York, 1984.
91. J. C. Reed, E. J. McMahon, and J. R. Perkins, *Insulation (Libertyville, Ill.)* **10**, 35 (1964).
92. *Hostaflon*, TF product information booklet, American Hoechst Corp., Somerville, N.J., 1970.
93. *Soreflon,* products information booklet, Ugine Kuhlmann, France.
94. *Teflon TFE-Fluorocarbon Resins Molding Techniques*, 2nd ed., bulletin, E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1966.
95. *The Moulding of Granular Polymers*, technical service note, ICI, Wilmington, Del., 1966.

96. J. A. Ross, *High Speed Molding of Teflon Tetrafluoroethylene Resins*, technical release, E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1963.
97. *Automatic Molding with "Halon" TFE*, Allied Chemical Corp., Morristown, N.J., 1967.
98. *Isostatic Molding of Teflon TFE-Fluorocarbon Resins*, preliminary information bulletin, E.I. du Pont de Nemours & Co., Wilmington, Del., 1969.
99. R. J. Dahlen, *The Ram Extrusion of Teflon*, technical release, E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1969.
100. *The Granular Extrusion of "Halon" TFE*, Allied Chemical Corp., Morristown, N.J., 1968.
101. *The Extrusion of Granular Polymers*, 2nd ed., technical service note, ICI, Wilmington, Del., 1966.
102. V. Adamec, *Nature* **200**, 1196 (1963).
103. Technical brochure, *Teflon 62 Hose and Tubing*, H-11959, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., Feb. 1991.
104. J. F. Lontz and co-workers, *Ind. Eng. Chem.* **44**, 1805 (1952).
105. *TFE-Fluorocarbon Resins Paste Extrusion of Wire Insulations*, bulletin, E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1961.
106. *The Extrusion Coating of Wire*, 2nd ed., technical service note, Wilmington, Del., 1969.
107. *Teflon TFE-Fluorocarbon Resins Extrusion of Thin-Walled Tubing*, bulletin, E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1957.
108. *The Extrusion of Thin Sections*, 3rd ed., technical service note, ICI, Wilmington, Del., 1969.
109. R. C. Ribbans, *Unsintered Tape Manufactured Calendering Round Rods*, technical release, E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1966.
110. *The Manufacture of Unsintered Tape*, 2nd ed., technical data, ICI, Wilmington, Del., 1966.
111. U.S. Pat. 3,142,665 (July 28, 1964), A. J. Cardinal, W. L. Edens, and J. W. Van Dyk (to E.I. du Pont de Nemours & Co., Inc.).
112. U.S. Pat. 4,038,231 (July 26, 1977), J. M. Douner, W. G. Rodway, and L. S. J. Shipp (to ICI).
113. U.S. Pat. 3,962,153 (June 8, 1976), R. W. Gore (to W. L. Gore and Assoc.).
114. U.S. Pat. 3,993,584 (Nov. 23, 1976), J. E. Owen and J. W. Vogt (to Kewanee Oil Co.).
115. U.S. Pat. 3,704,171 (Nov. 28, 1972), H. P. Landi (to American Cyanamid Co.).
116. U.S. Pat. 3,051,545 (Aug. 28, 1962), W. Steuber (to E.I. du Pont de Nemours & Co., Inc.).
117. P. E. Frankenburg, in P. E. Frankenburg, *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. **A-10**, 5th ed., VCH Publishing, Inc., New York, 1987, 649–650.
118. R. L. Baillie, J. J. Bednarczyk, and P. M. Mehta, paper presented at *35th International Wire and Cable Symposium,* Nov. 18–20, 1986.
119. *J. Teflon (Du Pont)* **8**, 6 (Nov. 1967).
120. *Teflon Occupational Health Bull.* **17**(2), (1962) (published by Information Service Division, Dept. of National Health and Welfare, Ottawa, Canada).

SUBHASH V. GANGAL
E.I. du Pont de Nemours & Co., Inc.

Related Articles

Fluorine compounds, Organic, Introduction; Fluorine compounds, organic; perfluorinated ethylene-propylene copolymers