*Kirk-Othmer Encyclopedia of Chemical Technology.*

# FLUORINE-CONTAINING POLYMERS, TETRAFLUOROETHYLENE-ETHYLENE COPOLYMERS

Copolymers of ethylene [74-85-1] and tetrafluoroethylene [116-14-3] (ETFE) have been a laboratory curiosity for more than 40 years. These polymers were studied in connection with a search for a melt-fabricable PTFE resin (1–5); interest in them fell with the discovery of TFE–HFP (FEP) copolymers (6). 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 TFE–ethylene copolymers [11939-51-6] might have the right combination of properties. Subsequent research efforts (7) led to the introduction of modified ethylene–tetrafluoroethylene polymer [25038-71-5] (Tefzel) by E. I. du Pont de Nemours & Co., Inc. in 1970.

Modified ethylene–tetrafluoroethylene copolymers 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% tetrafluoroethylene (by weight) soften between 200 and 300°C, depending on composition (1). The tetrafluoroethylene 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 tetrafluoroethylene 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 Du Pont, Hoechst, Daikin, Asahi Glass, and Ausimont and sold under the trade names of Tefzel, Hostaflon ET, Neoflon EP, Aflon COP, and Halon ET, respectively.

## 1. Monomers

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

## 2. Manufacture

Tetrafluoroethylene–ethylene copolymers have tensile strengths two to three times as high as the tensile strength of polytetrafluoroethylene or of the ethylene homopolymer (1). 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 tetrafluoroethylene between 60:40 and 40:60 is required (8, 9).

Copolymerization is effected by suspension or emulsion techniques under such conditions that tetrafluoroethylene, 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 (10), free-radical sources (11), and ionizing radiation (12).

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 (13, 14).

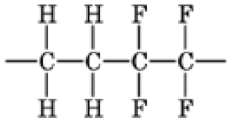
Reactivity ratios of ethylene and tetrafluoroethylene are

| Temperature, °C | $r_{\mathrm{TFE}}$ | $r_{\mathrm{E}}$ |
|---|---|---|
| −35 | $0.014 \pm 0.008$ | $0.010 \pm 0.02$ |
| 65 | $0.045 \pm 0.010$ | $0.14 \pm 0.03$ |

These values indicate strong alternation tendencies that decrease with increasing temperature. Computations show that 1:1 ETFE copolymers obtained at $-30$ and 65°C should have about 97 and 93%, respectively, of alternating sequences (15).

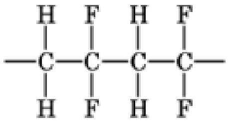
## 3. Properties

The equimolar copolymer of ethylene and tetrafluoroethylene is isomeric with poly(vinylidene fluoride) but has a higher melting point (16, 17) and a lower dielectric loss (18, 19) (see Fluorine compounds, organic–poly(vinylidene fluoride)). A copolymer with the degree of alternation of about 0.88 was used to study the structure (20). Its unit cell was determined by x-ray diffraction. 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



$$-CH_2-CF_2-CH_2-CF_2-$$

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 % tetrafluoroethylene; 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 (21).

This polymer can be dissolved in certain high boiling esters at temperatures above 230°C (22), 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 (23).

### 3.1. Transitions

Samples containing 50 mol % tetrafluoroethylene with ca 92% alternation were quenched in ice water or cooled slowly from the melt to minimize or maximize crystallinity, respectively (19). Internal motions were studied by dynamic mechanical and dielectric measurements, and by nuclear magnetic resonance. The dynamic mechanical behavior showed that the $\alpha$ relaxation occurs at 110°C in the quenched sample; in the slowly cooled sample it is shifted to 135°C. The $\beta$ relaxation appears near $-25^\circ C$. The $\gamma$ relaxation at $-120^\circ C$ in the quenched sample is reduced in peak height in the slowly cooled sample and shifted to a slightly higher temperature. The $\alpha$ and $\gamma$ relaxations reflect motions in the amorphous regions, whereas the $\beta$ relaxation occurs in the crystalline regions. The $\gamma$ relaxation at $-120^\circ C$ in dynamic mechanical measurements at 1 Hz appears at $-35^\circ C$ in dielectric measurements at $10^5$ Hz. The temperature of the $\alpha$ 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.

**Table 1. Typical Properties of Tefzel[a]**

| Property | 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 | 965 | 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[c] at 50°C, % | D621 | 4.11 | 0.68 |
| coefficient of linear expansion per °C × $10^{-5}$ | D696-70 |  |  |
| 20–30°C |  | 9 | 3 |
| 50–90°C |  | 9.3 | 1.7 |
| 104–180°C |  | 14 | 3.2 |
| specific gravity | D792 | 1.70 | 1.86 |
| refractive index, $n_D$ |  | 1.4028 |  |
| flammability | UL 94 | 94 V-0 | 94 V-0 |
|  | D635 | ATB[g] <5 s<br>ALB[g] 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 othewise 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. It is expected that its continuous-use temperature will be above 150°C.

[f] To convert J/m to ftlbf/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; 689 kPa = 100 psi.

The activation energy is 318.1 kJ/mol (76 kcal/mol) for the $\alpha$ relaxation and 44.3 kJ/mol (10.6 kcal/mol) for the $\gamma$ relaxation. These relaxations are attributed to the motion of long and short segments in the amorphous regions, respectively. As ETFE copolymer is isomeric with poly(vinylidene fluoride) (18), the $\gamma$ relaxations occur at about the same temperature. Activation energies are similar and are attributed to the motion of short amorphous segments. The $\beta$ relaxation in $PVF_2$ is considered to be the main-chain amorphous relaxation and is analogous to the $\alpha$ relaxation in the ethylene–tetrafluoroethylene copolymer. However, the arrangement of dipoles in the all-trans conformation is more symmetrical.

### 3.2. Physical and Mechanical Properties

Modified ethylene–tetrafluoroethylene copolymer 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 1 (24, 25). 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-$\mu$m 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.

### 3.3. Thermal Properties

Modified ETFE copolymer has a broad operating temperature range up to 150°C for continuous exposure (24). 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.

The thermodynamic properties of Tefzel 200 and 280 are shown in Table 2; 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.

**Table 2. Thermodynamic Properties of Modified ETFE**

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

[a] To convert J to cal, divide by 4.184.
[b] Little dependence on temperature.

### 3.4. 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 $>3\ \mathrm{m/min}$) for Tefzel 200 is 0.4, which drops to 0.3 for the 25% glass-reinforced product at these conditions (24). The wear factor also improves from $12 \times 10^{-14}$ to $32 \times 10^{-17} 1/\mathrm{Pa}$ ($6000 \times 10^{-10}$ to $16 \times 10^{-10}$ $\mathrm{in.^3 \cdot min/ftlbf \cdot h}$). 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 3 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.

**Table 3. Bearing Wear Rate[a] of Tefzel HT-2004**

| | | Wear factor, $K \times 10^{-17}$, 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 lubricants ambient air temperature, metal finish 406 nm.
[b] To convert kPa to psi, multiply by 0.145.
[c] To convert 1/Pa to $(\mathrm{in.^3 \cdot min})/(\mathrm{ftlbf \cdot h})$, divide by $2 \times 10^{-7}$.
[d] AISI 1018.
[e] LM24M (English).

### 3.5. Electrical Properties

Modified ethylene–tetrafluoroethylene is an excellent dielectric (Table 4). 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 tenfold. 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 $\mu$m 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 (26).

**Table 4. Electrical Properties of ETFE Resins**

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

### 3.6. Chemical Resistance and Hydrolytic Stability

Modified ethylene–tetrafluoroethylene copolymers are resistant to chemicals and solvents (Table 5) that often cause rapid degradation in other plastic materials. Performance is similar to that of perfluorinated polymers (27), 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.

**Table 5. Tefzel Resistance to Chemicals after Seven Days Exposure[a]**

| | | | Retained properties, % | | |
|---|---|---|---|---|---|
| Chemical | Bp, °C | Test temperature, °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*-dimethylaniline | 190 | 120 | 82 | 97 | |
| *n*-butylamine | 78 | 78 | 71 | 73 | 4.4 |
| di-*n*-butylamine | 159 | 120 | 81 | 96 | |
| di-*n*-butylamine | 159 | 159 | 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 |

**Table 5.** ***Continued***

| Chemical | Bp, °C | Test temperature, °C | Retained properties, % | | |
|---|---|---|---|---|---|
| | | | Tensile strength | Elongation | Weight gain |
| 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 | |
| *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% | 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-$\mu$m microtensile bars; tensile strength, elongation, and weight gain determined within 24 h after termination of exposure.

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% by weight), 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 (28, 29).

The ETFE copolymer can be cross-linked by radiation (30), despite the high content of tetrafluoroethylene units. 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 copolymer 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 due to their high transparency to both uv and visible light and excellent resistance to weathering (31).

### 3.7. Vacuum Outgassing and Permeability

Under vacuum, modified ethylene–tetrafluoroethylene copolymers give off little gas at elevated temperatures. The loss rate is about one-tenth of the acceptable maximum rates for spacecraft uses. Exposing 750-$\mu$m 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-$\mu$m, ASTM D1434) at 25°C (1 nmol/m·s·GPa = 0.5 cc·mil/100 in.$^2$d·atm):

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

## 4. Fabrication

Modified ethylene–tetrafluoroethylene copolymers are commercially available in a variety of physical forms (Table 6) 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. In the United States, the 1992 price was $27.9–44.2/kg, depending on volume and grade; color concentrates are also available.

Like other thermoplastics, they exhibit melt fracture (32) above certain critical shear rates. In extrusion, many variables control product quality and performance (33).

## 5. 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 (24). Because of high melt viscosity, ETFE resins are usually processed at high (300–340°C) temperatures.

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.

**Table 6. 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, heavy-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 kg) load.

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.

### 5.1. 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.

### 5.2. 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.

## 6. Assembly

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

#### *6.0.1. 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.

#### *6.0.2. 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.

#### *6.0.3. 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.

#### *6.0.4. 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.

#### *6.0.5. 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.

### 6.1. 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 pullout strengths of 111–155 N (25–35 lbf).

### 6.2. Bonding

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

Ethylene–tetrafluoroethylene copolymers 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 (34).

## 7. Health and Safety

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 (35).

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 Du Pont 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.

## 8. Testing and Standards

A description of modified ethylene–tetrafluoroethylene copolymers and their classification is given by the American Society for Testing and Materials under the designation D3159-83 (36). A comprehensive listing of industrial and military specifications is available (37).

## 9. 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 (38). 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 periods 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.

## BIBLIOGRAPHY

“Tetrafluoroethylene Copolymers With Ethylene” under “Fluorine Compounds, Organic” in *ECT* 3rd ed., Vol. 11, pp. 35–41, by R. L. Johnson, E. I. du Pont de Nemours & Co., Inc.

### Cited Publications

1. U.S. Pat. 2,468,664 (Apr. 26, 1949), W. E. Hanford and J. R. Roland (to E. I. du Pont de Nemours & Co., Inc.).
2. U.S. Pat. 2,479,367 (Aug. 16, 1949), (to E. I. du Pont de Nemours & Co., Inc.).
3. Brit. Pat. 1,166,020 (Oct. 1, 1969), M. Modena and co-workers (to Montecatini Edison, SpA).
4. Jpn. Kokai 64 22,586 (Sept. 12, 1964), K. Hirose and co-workers (to Nitto Chemical Industry, Co., Ltd.).
5. Belg. Pat 725,356 (Feb. 14, 1969), Z. Kenkyusho (to Asahi Glass, Ltd.).
6. 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.).
7. D. P. Carlson, *Development of Tefzel Fluoropolymer Resins,* unpublished paper.
8. U.S. Pat. 3,624,250 (Nov. 30, 1971), D. P. Carlson (to E. I. du Pont de Nemours & Co., Inc.).
9. U.S. Pat. 4,123,602 (Oct. 31, 1978), H. Ukihashi and M. Yamake (to Asahi Glass Co.).
10. Brit. Pat. 1,353,535 (May 22, 1974), R. Hartwimmer (to Farbwerke Hoechst, AG).
11. U.S. Pat. 3,401,155 (Sept. 10, 1986), G. Borsini and co-workers (to Montecatini Edison SpA).
12. Y. Tabata, H. Shibano, and H. Sobue, *J. Polym. Sci. Part A* **2**(4), 1977 (1964).
13. U.S. Pat. 3,960,825 (June 1, 1976), D. N. Robinson and co-workers (to Pennwalt Corporation).
14. U.S. Pat. 4,338,237 (July 1982), R. A. Sulzbach and co-workers (to Hoechst Aktiengesellschaft).
15. M. Modena, C. Garbuglio, and M. Ragazzini, *Polym. Lett.* **10**, 153 (1972).
16. M. Modena, C. Garbuglio, and M. Ragazzini, *J. Polym. Sci. Part B* **10**, 153 (1972).
17. F. S. Ingraham and D. F. Wooley, Jr., *Ind. Eng. Chem.* **56**(9), 53 (1964).
18. S. Yano, *J. Polym. Sci. Part A-2* **8**, 1057 (1970).
19. H. W. Starkweather, *J. Polym. Sci. Part A-2* **11**, 587 (1973).
20. F. C. Wilson and H. W. Starkweather, *J. Polym. Sci. Part A-2* **11**, 919 (1973).
21. B. Chu and Chi Wu, *Macromolecules* **20**, 93–98 (1987).
22. B. Chu, C. Wu, and W. Buck, *Macromolecules* **22**, 371 (1989).
23. Z. Wang, A. Tontisakis, W. Tuminello, W. Buck, and B. Chu, *Macromolecules* **23**, 1444 (1990).
24. *Tefzel Fluoropolymer, Design Handbook*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1973.

25. *Tefzel—Properties Handbook*, E-31301-3, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., Dec. 1991.
26. S. K. Randa, C. R. Frywald, and D. P. Reifschneider, *Proceedings of the 36th International Wire and Cable Symposium,* Arlington, Va., 1987, 14–22.
27. Can. Pat. 900,075 (May 9, 1972), D. P. Carlson, J. A. Effenberger, and M. B. Polk (to E. I. du Pont de Nemours & Co., Inc.).
28. M. Carpenter, S. Chillons, and R. Will, Society of Automobile Engineers (SAE) International Technical Paper Series 910103, presented at the *International Congress and Exposition,* Detroit, Mich., Feb. 25–Mar. 1, 1991.
29. D. Goldsberry, S. Chillons and R. Will, SAE Technical Paper Series 910104, presented at the *International Congress and Exposition,* Detroit, Mich., Feb. 25–Mar. 1, 1991.
30. U.S. Pat. 3,738,923 (June 12, 1973), D. P. Carlson and N. E. West (to I. du Pont de Nemours & Co., Inc.).
31. J. Emsley, *New Scientist*, **46** (April 22, 1989).
32. *Technical Information, Jacketing Rate Calculation*, Bulletin No. 10, Fluoropolymers Division Technical Service Laboratory, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., Aug. 1982.
33. *Extrusion Guide for Melt Processible Fluoropolymers*, Bulletin E-41337, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
34. S. Kaplan, O. Kolluri, G. Hansen, R. Rushing, and R. Warren, technical paper presented at Conference on Adhesives, Society of Manufacturing Engineers, Atlanta, Ga., Sept. 12, 1989.
35. *Tefzel Fluoropolymers, Safe Handling Guide*, Bulletin E-85785, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., May 1986.
36. *Modified ETFE-Fluorocarbon Molding and Extrusion Materials*, ASTM D3159-83, American Society for Testing and Materials, Philadelphia, 1987.
37. *J. Teflon* **15**(1), 1974.
38. *Tefzel Fluoropolymers, Product Information* (Du Pont Materials for Wire and Cable), Bulletin E-81467, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., May 1986.

## General Reference

39. S. V. Gangal, "Tetrafluoroethylene Polymers, Tetrafluoroethylene–Ethylene Copolymers," in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. **16**, Wiley-Interscience, New York, 1989, 626–642.

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