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FLUORINE-CONTAINING POLYMERS, POLYCHLOROTRIFLUOROETHYLENE

Many challenging industrial and military applications utilize polychlorotrifluoroethylene [9002-83-9] (PCTFE) where, in addition to thermal and chemical resistance, other unique properties are required in a thermoplastic polymer. Such has been the destiny of the polymer since PCTFE was initially synthesized and disclosed in 1937 (1). The synthesis and characterization of this high molecular weight thermoplastic were researched and utilized during the Manhattan Project (2). The unique combination of chemical inertness, radiation resistance, low vapor permeability, electrical insulation properties, and thermal stability of this polymer filled an urgent need for a thermoplastic material for use in the gaseous UF_6 diffusion process for the separation of uranium isotopes (see Diffusion separation methods).

1. Properties

The physical properties of PCTFE are primarily determined by a combination of molecular weight and percent crystallinity. Because of the lack of suitable solvents, a correlation between the number average molecular weight and zero-strength time (ZST: typical values of 200 to 400 s) has been developed (3, 4). The high molecular weight thermoplastic has a melt temperature (T_m) of 211–216°C, a glass-transition temperature (T_g) of 71–99°C (5), and is thermally stable up to 250°C. The useful operational temperature range is considered to be from -240 to 200°C although an increase in service temperature can be achieved through selected fiber filling of the polymer (fiber glass, from 1 to 20% weight of the fiber).

The theoretical specific gravity of PCTFE for the amorphous and crystalline polymers has been calculated to range from 2.075 to 2.185, respectively (6–12). In reality, PCTFE molded parts have exhibited ranges of crystallinity from approximately 45% (specific gravity of 2.10) for quick-quenched parts to 65% (specific gravity of 2.13) for slow-cooled parts. The use of the terms amorphous and crystalline are relative but can be significant in the application. Basically, two types of crystallinity, micro and macro, exist in the polymer as a result of the synthesis and processing. The higher crystalline forms are less transparent, have higher tensile modulus, lower elongation, and have more resistance to liquids and vapors. The less crystalline form is optically clear, tough, and ductile, exhibiting higher elongation and lower modulus.

The typical mechanical properties that qualify PCTFE as a unique engineering thermoplastic are provided in Table 1; the cryogenic mechanical properties are recorded in Table 2. Other unique aspects of PCTFE are resistance to cold flow due to high compressive strength, and low coefficient of thermal expansion over a wide temperature range.

The high fluorine content contributes to resistance to attack by essentially all chemicals and oxidizing agents; however, PCTFE does swell slightly in halogenated compounds, ethers, esters, and selected aromatic solvents. Specific solvents should be tested. PCTFE has the lowest water-vapor transmission rate of any plastic (14, 15), is impermeable to gases (see also Barrier polymers), and does not carbonize or support combustion.

Table 1. Mechanical Properties of Polychlorotrifluoroethylene

Property	Value
tensile strength, MPa[a]	32–39
compressive strength, MPa[a]	38
modulus of elasticity, MPa[a]	1400
hardness, Shore D	76
deformation under load, at 25°C, 24 h, 7 MPa[a], %	0.3
heat deflection temperature, at 0.46 MPa[a], °C	126

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

Table 2. Cryogenic Mechanical Properties of Polychlorotrifluoroethylene[a]

Property	PCTFE, % crystallinity	Temperature, °C	Value[a]
tensile: ultimate strength, MPa[b]	40	25	38.6
		−129	150
		−252	200
elongation, %	40	25	140
		−129	9
		−252	5
modulus of elasticity, MPa[b]	40	25	1520
		−129	5500
		−252	8700
impact strength notched Izod, J/m[c]	60	25	13.7
		−196	12.8
		−252	13.7

[a]ASTM D1430—89 Type 1, Grade 2 (13).
[b]To convert MPa to psi, multiply by 145.
[c]To convert J/m to ft·lbf/in., divide by 53.38 (see ASTM D256).

Table 3. Electrical Properties of PCTFE

Property	ASTM method	Value
dielectric strength,[a] V/μm	D149	20
arc resistance, s	D495	360
volume resistivity,[b] ohm cm^2/cm	D257	10^{18}
surface resistivity,[b] ohm	D257	10^{15}

[a]Short time. To convert to V/mil, multiply by 25.
[b]Fifty percent rh at 25°C.

PCTFE plastic is compatible with liquid oxygen, remains ductile at cryogenic temperatures (16–22), and retains its properties when exposed to either uv or gamma radiation. PCTFE exhibits a refractive index of 1.43 (ASTM D542) and an amorphous sheet can provide over 90% transmittance.

PCTFE exhibits very good electrical properties in terms of high insulation resistance, minimal tracking, corona formation, and surface flashover due to the polymer's nonwettable surface and ultralow moisture absorption (Table 3).

Table 4. PCTFE Manufacturers and Products

Trademark	Manufacturer	Product forms
homopolymers		
Daiflon	Daikin Koygo, Osaka, Japan	molding powder, pellets, dispersion oils, and greases
Kel-F 81	3M Co., St. Paul, Minn.	molding powders and pellets
Voltalef	Ugine Kuhlmann, Pierre-Benite, France	molding powders and pellets
Halocarbon oil	Halocarbon Products Corp., River Edge, N.J.	oils, waxes, and greases
copolymers		
Aclon, Aclar	Allied-Signal Chemical, Morristown, N.J.	molding powders, pellets, and film
Kel-F 800	3M Co., St. Paul, Minn.	molding powders

2. Manufacture and Processing

The synthesis of the high molecular weight polymer from chlorotrifluoroethylene [79-38-9] has been carried out in bulk (23–27), solution (28–30), suspension (31–36), and emulsion (37–41) polymerization systems using free-radical initiators, uv, and gamma radiation. Emulsion and suspension polymers are more thermally stable than bulk-produced polymers. Polymerizations can be carried out in glass or stainless steel agitated reactors under conditions (pressure 0.34–1.03 MPa (50–150 psi) and temperature 21–53°C) that require no unique equipment.

After polymerization, the polymer is isolated from the latex or suspension. The suspension polymer, already in powder form, is washed to remove initiator residues and then dried. The emulsion polymer is coagulated from the latex by freezing or by the addition of salts, acids, and solvents (see Latex technology) and separated from the aqueous phase. The isolated powder is then washed and dried. The dried powder from either process additionally can be chemically treated to remove trace impurities that can result in chain degradation during further processing. Treatment with carboxylic acids (42), ozone in air (43), or chlorine (44) improves thermal stability, color, and light transmission of the final polymer. The polymer product can then be processed by plastic fabrication techniques in powder or melt-extruded pellet forms.

The lower molecular weight oils, waxes, and greases of PCTFE can be prepared directly by telomerization of the monomer or by pyrolysis of the higher molecular weight polymer (45–54).

PCTFE plastics can be processed by the standard thermoplastic fabrication techniques, eg, extrusion, injection, compression, and transfer molding. Specific corrosion-resistant alloys or chrome or nickel plating are recommended for equipment parts in contact with the polymer melt, such as molds, barrels, screws, etc (see Pplastics technology). The control of processing temperatures is paramount since prolonged overheating (above 260°C) can result in degradation of the polymer causing discoloration, voids, blisters, and loss of properties. The plastic can be easily machined from billets or rod stock on standard machining equipment to fabricate more precise part geometries, but sharp tools should be employed.

3. Economic Aspects

Several worldwide commercial manufacturers of PCTFE and vinylidene fluoride-modified copolymers [9010-75-7] offer a variety of products as shown in Table 4. PCTFE plastics have selling prices in the range of $40–100/kg, depending on the molecular weight, grade, product form, and supplier. As a result, PCTFE thermoplastics are used in high technology, specialty engineering areas where the unique combination of properties and part reliability demands a high performance thermoplastic polymer.

4. Specifications and Test Methods

PCTFE plastic is available in products that conform to ASTM 1430-89 Type I (Grades 1 and 2) and is suitable for processing into parts that meet MIL-P 46036 (Federal Specification LP-385C was canceled 1988). Standards for fabricated forms are available for compression molded heavy sections (AMS-3645 Class C), thin-walled tubing, rod, sheet, and molded shapes (AMS-3650). PCTFE plastics have been approved for use in contact with food by the FDA (55).

The test methods employed are the determination of molecular weight as measured by ZST (ASTM D1430); specific gravity (ASTM D792); tensile strength, elongation, and modulus (ASTM D638); compressive strength and modulus (ASTM D621); heat deflection (ASTM D648); impact strength (ASTM D256); flammability (ASTM D2863); hardness (ASTM D2240 and D785); and coefficient of linear expansion (ASTM D696).

5. Health and Safety Factors

In general, the PCTFE resins have been found to be low in toxicity and irritation potential under normal handling conditions. Specific toxicological information and safe handling procedures are provided by the manufacturer of specified PCTFE products upon request.

6. Uses

The principal uses of PCTFE plastics remain in the areas of aeronautical and space, electrical/electronics, cryogenic, chemical, and medical instrumentation industries. Applications include chemically resistant electrical insulation and components; cryogenic seals, gaskets, valve seats (56, 57) and liners; instrument parts for medical and chemical equipment (58), and medical packaging; fiber optic applications (see Fiber optics); seals for the petrochemical/oil industry; and electrodes, sample containers, and column packing in analytical chemistry and equipment (59).

The lower molecular weight PCTFE oils, waxes, and greases are used as inert sealants and lubricants for equipment handling oxygen and other oxidative or corrosive media. Other uses include gyroscope flotation fluids and plasticizers for thermoplastics.

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