

The Miracle Nonstick Polymer—"Teflon"

Of all the polymers created in the last half century or so, polytetrafluoroethylene (PTFE)—popularly known under the trade name of Teflon—has found enough diverse uses to qualify as a "miracle polymer." Almost totally chemically inert, PTFE has good flammability resistance. It is one of the best electrical insulators and one of the most solvent-resistant plastics available. With its extremely low coefficient of friction, nothing adheres to PTFE, most familiar as the nonstick coating on frying pans or razor blades.

In 1933, tetrafluoroethylene (C_2F_4 or TFE) was first isolated by Ruff and Bretschneider as the product of decomposition of carbon tetrafluoride in an electric arc. TFE, an odorless, colorless gas with a boiling point of $-76.6^\circ C$, can be stored under pressure with various stabilizers in the absence of oxygen.

In 1938, Roy Plunkett and Jack Rebok at the Du Pont Company accidentally discovered the first polymerized TFE as a powdery white residue that had formed in a cylinder of TFE gas. They soon realized that this strange residue had some remarkable material properties.

Three years later, Plunkett reported the first successful intentional polymerization of TFE, using superatmospheric conditions while storing TFE gas in a cylinder. Full-scale commercial production of PTFE began in 1948, ten years after its discovery.

A waxy, dense, crystalline, and highly linear polymer, PTFE has a high molecular weight, ranging from 400,000 to as high as 9,000,000. It is chemically inert to most ordinary chemicals except molten alkali. About half the PTFE currently produced is used in electrical applications. PTFE exhibits high dielectric strengths, volume resistivity, and arc resistance, and also unusually low dissipation factors and dielectric constants, even over wide frequency ranges. All this makes PTFE closer to an ideal electrical insulator than any other known solid.

PTFE's most well-known material characteristic is its extremely low coefficient of friction, about one-fifth that of an analogous hydrocarbon plastic. PTFE has a coefficient of friction, μ , of 0.04 against polished steel; by comparison, plastics such as polyethylene or nylon have $\mu = 0.3-0.6$. And so PTFE has been used for corrosion-resistant gaskets, seals, and hoses, and for compos-

ite metal bearings that reduce friction even when only one surface is coated. Of course, the most widely recognized use for PTFE and its trade name Teflon is as a coating for cooking utensils because its nonstick nature allows easy cleanup of cooked-on food.

Originally, PTFE and other fluorocarbon polymers such as trifluorochloroethylene and fluorinated ethylene-propylene could not be extruded or vulcanized, so they were used primarily as solid plastic materials. However, fluorinated diolefin brought about heat-resistant, rubbery PTFE polymers that could be worked into fibers or coatings.

PTFE is a highly crystalline thermoplastic polymer with a melting temperature higher than most plastics (about $330^\circ C$) and a very low glass transition temperature (about $-110^\circ C$). By comparison, polyvinyl chloride has a glass transition temperature of $20^\circ C$, and polystyrene $90^\circ C$. PTFE can be used even above $260^\circ C$ and does not become brittle at temperatures down to about $-200^\circ C$. Unfortunately, high melting temperatures make it impossible to form fluorocarbon plastics through the normal manufacturing methods used for melt processible resins.

While fluorinated ethylene-propylene can be injection molded and extruded in a thin film, PTFE must be preformed and sintered at a very high pressure, using techniques similar to those used in powder metallurgy and in processing ceramics. Even then, the manufactured object may require further refinement to obtain an accurate form.

Granular PTFE powder is compressed at room temperature to 2,000-10,000 psi and then sintered in an oven or fluid bath kept at $370-390^\circ C$ until the entire preformed piece becomes amorphous. From here, depending on the dimensional accuracy required, the piece is either removed from the mold and baked freely or placed in a cold coining die and formed under pressure (2,000 psi). If more accurate dimensions are required, the piece can be machined when it has cooled.

In 1954 Du Pont introduced PTFE fibers under the trade name of Teflon. PTFE fibers are now produced around the world, including in the former Soviet Union, where it is known as Ftorlon or Polifen.

To create Teflon fibers, TFE gas is purified

and polymerized with the help of a peroxide catalyst in stainless-steel autoclaves under heat and pressure. The polymerized dispersion is then extruded through a spinneret into a dilute solution of hydrochloric acid, which acts as an aqueous coagulating bath. Once coagulated, the PTFE particles hold together as weak filaments in which the particles remain separate. When the filaments are rapidly heated to about $385^\circ C$ for several seconds, the weak polymer particles fuse into a coherent filament. The fluorine atoms surround the carbon chain as a sheath, making it strong, chemically inert, and relatively dense, held together with strong carbon-fluorine bonds. This coherent filament is cooled quickly and then drawn to three or four times its original length at room temperature.

Teflon fibers combine the flexibility and toughness typical of organic fibers while keeping the temperature, chemical, and solvent resistance of inorganic or mineral fibers (such as asbestos). PTFE fibers, however, are expensive to manufacture, and some of the very material properties that make them advantageous for other purposes make them unsuitable for general use in textiles. Fabric made of Teflon fiber has a greasy feel, high density, no moisture absorption, and a low modulus. However, these fibers are ideal for such uses as filter fabrics and felts, electrical tapes, and low-friction backings.

PTFE and several other fluorocarbon polymers and fluorinated hydrocarbon resins have found specialized applications in weaponry, medicine, and the aerospace industry.

Bullets coated with Teflon or similar nonstick coatings have been developed to penetrate certain types of bulletproof vests. In vascular surgery, expanded PTFE is used to create artificial veins. In the 1960s, many intracardiac septal defects (a breach between the right and left sides of the heart) were repaired by directly suturing or inserting Teflon patches. Because of their complete and low coefficient of friction, Teflon coatings have been used in medical prostheses, including artificial joints. In aircraft and spacecraft, PTFE and fluorinated ethylene-propylene are standard insulation materials.

Fluorine chemistry is relatively new; the element was not isolated until 1886. But since their commercial development half a century ago, fluorocarbon polymers have found an enormous range of uses for their unusual material properties. New polymer refinements will certainly lead to continued growth in applications for PTFE.

KEVIN J. ANDERSON

□