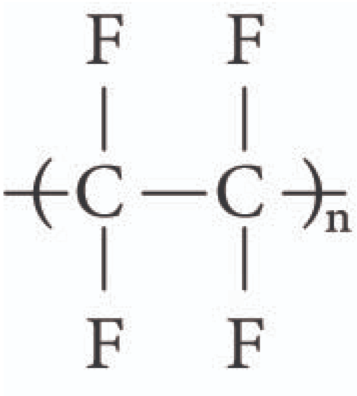
8.8

Fluoropolymers (PTFE, FEP, PFA)

The **fluoropolymers** differ from the other engineering thermoplastics because their usefulness is not primarily based on their mechanical properties but rather on the unique physical and chemical properties that result from the presence of fluorine in the polymer. In the most important of the fluoropolymers, **polytetrafluoroethylene (PTFE)**, which is represented in Figure 8.8, only carbon and fluorine atoms are present in the molecule. In general, for all polymers the higher the concentration of fluorine atoms to the total, the stronger are the unique properties associated with the presence of the fluorine. The discussion of fluoropolymer properties focuses on the polymer characteristics arising from the fluorine atom, and then on the relatively minor differences among the various **fluorocarbons**.



$$\left(-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right)_n$$

Figure 8.8 Polymer repeating unit for polytetrafluoroethylene (PTFE).

During the life of the original patents on fluoropolymers, the DuPont brand name of Teflon® was synonymous with the fluoropolymer class. DuPont has applied the Teflon® brand name to a variety of fluoropolymers beyond the simple PTFE. Today, several other companies make fluoropolymers; some of the most common brand names are Allied's Ultralon®, Whitford's Xylan®, and Hoechst's Hostaflon®. All these polymers are made by addition polymerization.

8.8.1. General Fluoropolymer Family Characteristics

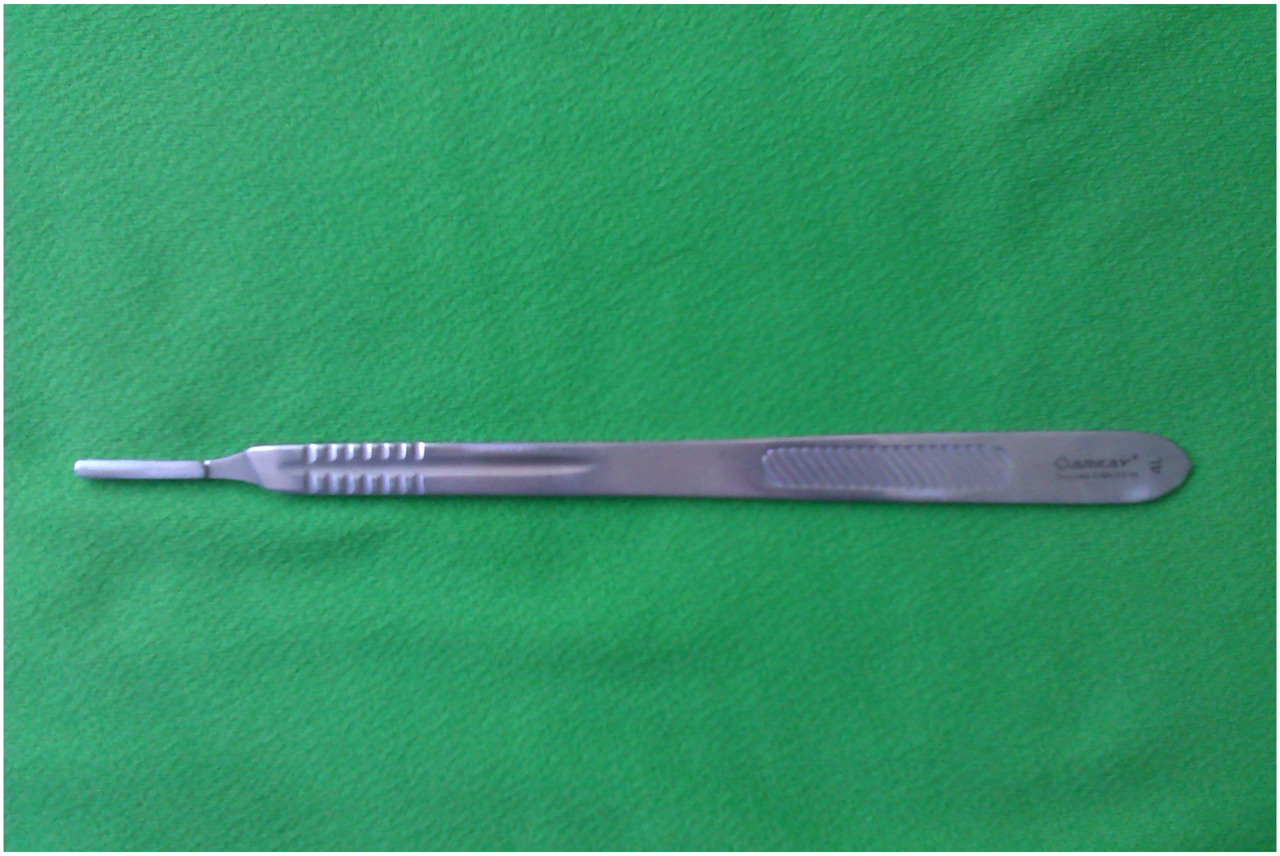
Fluorine is the most electronegative of the elements and strongly attracts electrons to it in any bond that it forms. The electrons around fluorine are held tightly, thus forming very stable bonds with low chemical reactivity. Therefore, an inherent property of fluoropolymers is that they do not bond readily with other materials, a property that is popularly called **nonstick**. This chemical inertness and lack of bonding was obvious in early nonstick coating applications on pans, where the fluoropolymer prevented cooked materials from sticking to the pan but was removed with only minor mechanical abrasion. No chemical bonding occurred between the coating and the pan. The coating was held in place by mechanical linkages (that is, the fluoropolymer flowed into cracks, crevices, and craters on the surface of the pan). These mechanical linkages were not strong and so even minor abrasion caused the coating to flake off. More recent grades of fluoropolymer coatings have improved bonding capability and fluoropolymers are widely used to give nonstick surfaces to pans, medical devices, industrial rollers of many types (such as rollers for printing, photocopying, and food applications), process guides and dies, and a myriad of other products for consumer and industry that need easy-release properties.

The chemical inertness of PTFE gives superior solvent resistance. It is not attacked by any known solvent under normal operating conditions and by only a few solvents under extreme conditions. This has led to applications such as linings for reaction tanks, valves, pipes and chemical storage containers, gaskets, packing, and thread sealants. Bonding of fluoropolymers is a problem because of the chemical inertness. No solvent bonding system will effectively bond these materials, and bonding by other methods such as melt bonding, ultrasonic welding, rf welding, and so on, is only partially successful.

The tightly held electrons in fluorocarbons result in very high electrical resistances and the lowest electrical permittivity of any plastic. Hence, fluoropolymers are used extensively as wire insulation, especially for high-value applications where the high cost of fluoropolymers can be accepted. **Lubricity** is closely related to the nonstick property and implies that the material will easily slide against other materials. The lubricity of fluoropolymers is very high. They are used for guide plates, rollers, and bearings, especially when external lubricants are not added. Powdered fluoropolymers are added to other materials to improve their lubricity. PTFE is also available as an externally applied lubricant, often in an aerosol spray.

The presence of fluorine atoms makes fluoropolymers inherently nonflammable. This property enhances the value of fluoropolymers in electrical insulation, bearing assemblies, and many electrical and mechanical devices in sensitive aerospace applications. However, the presence of fluorine atoms presents a problem if the fluoropolymer decomposes. The resulting products can be toxic. Fortunately, the service temperatures of fluoropolymers are quite high, ranging to 500°F (260°C) for continuous use. Various applications for PTFE are pictured in Photo 8.8.

Photo 8.8 Various applications using polytetrafluoroethylene (PTFE). (a) PTFE-coated electro-surgical blades. (b) PTFE-coated non-stick pan.



8.8.2. Properties of Specific Fluoropolymer Types

As already indicated, PTFE is the most widely used of the fluoropolymers, with perhaps as high as 90% of total fluoropolymer sales. Its repeating unit, shown in Figure 8.8, is very simple, having only carbons along the backbone and fluorine pendant atoms. PTFE was first discovered, by accident, at a DuPont laboratory when no gas would come out of a supposedly full cylinder of tetrafluoroethylene, sometimes called perfluoroethylene. The cylinder was cut open and found to contain a waxy solid in the bottom. The waxy solid was identified as PTFE, the properties were characterized, and DuPont began scale-up and marketing. The product was an instant success because of the unique nonstick, electrical insulation, chemical resistance, and lubricity properties.

PTFE molecules are long and straight with little branching, thus leading to structures that are over 90% crystallized. This high level of crystallinity gives PTFE the highest density of any plastic material, 2.0 to 2.3 g/cm^3. The denseness of the structure combines with the inherent chemical inertness to increase PTFE's resistance to chemical attack, increase the nonstick property, and decrease the coefficient of friction.

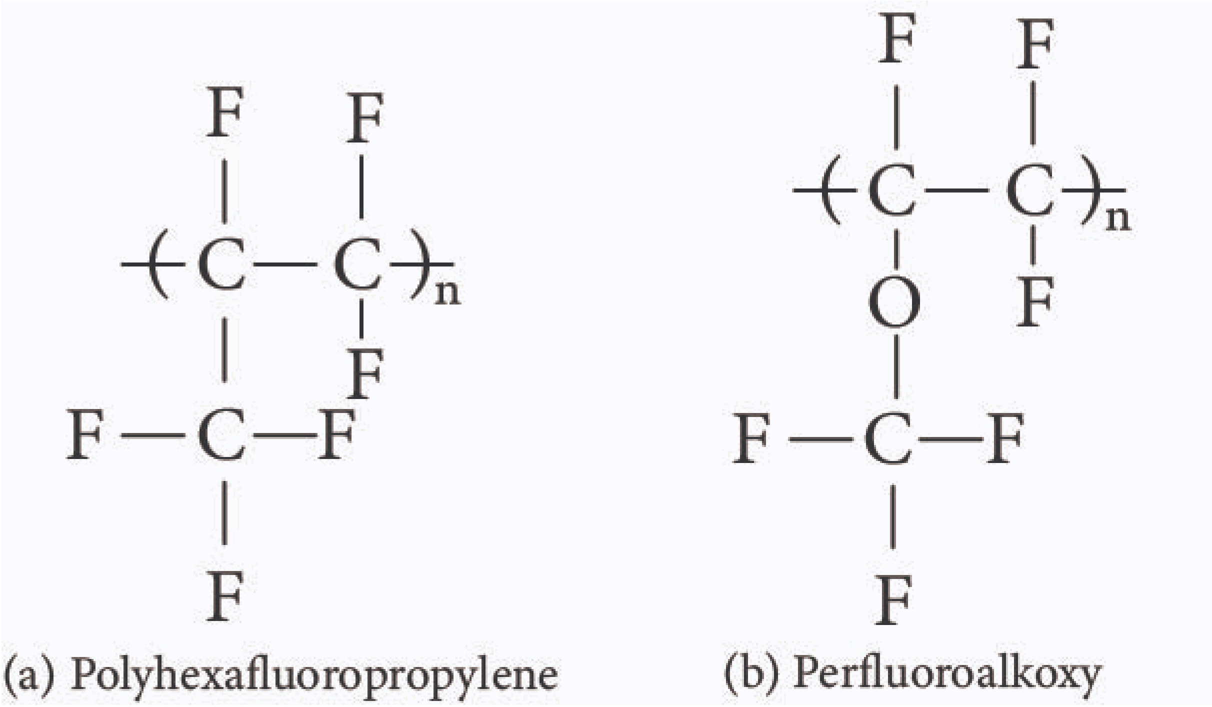
The high crystallinity also increases the mechanical properties of PTFE. Were it not for the bonds within the crystal structures, PTFE would have extremely low strength because the straight, unreactive molecules with small pendant groups would have little intermolecular interaction. As a result, the tensile strength of PTFE (2000 to 5000 psi, 14 to 36 MPa) is considerably lower than the strengths of any of the other engineering thermo-plastics and is closer to the range of commodity thermoplastics like polypropylene (3000 to 5500 psi, 21 to 39 MPa) or HDPE (3000 to 5400 psi, 21 to 38 MPa). Hardness is usually related closely to tensile strength and that is true of PTFE, where hardness is about the same as that of HDPE and is less than nylon.

The use of PTFE in abrasion pads is due more to the nonstick properties than to the inherent abrasion resistance. However, PTFE can be filled with fiber reinforcements and then has much improved abrasion resistance and still retains good nonstick properties. PTFE is quite tough, about the same as nylon, due to the relatively high elongation, and this also adds to its value for abrasion applications. A major application is coating surfaces with PTFE. Small polymer particles are usually dispersed in a solvent and then sprayed onto the surface of an item, which is then heated to drive off the solvent and fuse the PTFE.

In spite of the high crystallinity, PTFE creeps readily. The crystalline bonds do not seem to be sufficient to hold the molecules in place in the near absence of any polar bonding or pendant group interference.

PTFE is difficult to process because its melting point is close to or above the decomposition temperature. Hence, PTFE has no melt phase that can be used to mold the plastic. Consequently, forming techniques more closely associated with metals and ceramics are used. The most common of these is **sintering**. In this process a powder of the material is packed into a mold and held under pressure while the material is heated to near its melting point. At these temperatures and pressures, the powder **particles** fuse together—that is, they join along their edges—to produce a solid mass. Some voids between the particles inevitably remain and so the tensile strength of the part is less than that of a nonvoid material; however, for most applications not requiring strength, this molding method is satisfactory. Parts made by sintering can be machined and otherwise finished, but the shapes cannot be as complex as those possible with molding from a melt. Another method of forming PTFE is **ram extrusion**. In this process the powdered material is heated and pressed through a forming die to make a continuous, uniform cross-section part. Ram-extruded parts are simple in shape.

The inability to process PTFE in conventional plastics molding processes like injection molding, extrusion, and blow molding led to the development of a second type of fluoropolymer. What was desired was a lower melting point, less crystallinity, and more flexibility while still retaining the non-stick, chemical inertness and electrical resistance. The latter requirement suggested that a **perfluoro** monomer be used, that is, one in which only carbon and fluorine are in the molecule. For greater flexibility and lower melting point, the three-carbon monomer was chosen. The resulting polymer, shown in Figure 8.9a, is called polyhexafluoropropylene (PHFP).


(a) Polyhexafluoropropylene

(b) Perfluoroalkoxy

Figure 8.9 Repeating units for (a) polyhexafluoropropylene (PHFP) and (b) perfluoroalkoxy (PFA).

PHFP proved to have a melt temperature that made the polymer processible in conventional thermoplastic molding equipment, but the properties associated with the fluorine character were less like PTFE than anticipated. For many applications, the PHFP would not work. Perhaps a copolymer of perfluoroethylene and perfluoropropylene would give the desired fluorocarbon properties and still be melt processible. This supposition proved to be correct and the resulting copolymer, combining the TFE and HFP monomers, is called FEP, for fluorinated ethylene propylene. The relative amounts of perfluoroethylene and perfluoropropylene can be adjusted for specific applications.

FEP, the second-largest fluoropolymer in terms of sales, is used in applications such as tubing and pipes for chemical processes, gaskets, tubing for shrinkwrap electrical connections, shrink tubing for coating rollers and other long, thin parts (rather than coating by spraying on the PTFE), chemically resistant containers, and wire insulation. Many properties of FEP make it less advantageous than PTFE, however. Tensile strength is 10 to 15% lower, maximum use temperature is 20% lower, and solvent sensitivity is higher. However, some properties of FEP are improved over PTFE, such as toughness (10% higher) and dielectric strength (10 to 20% higher). Another derivative of PTFE shown in Figure 8.9b has a pendant group in which an oxygen links a perfluorinated carbon to the backbone. This polymer, perfluoroalkoxy (PFA), has the capability of being melt processible, but it bonds better to metals. Hence, PFA is widely used as a coating material. It has also been found to deform slightly when bonding to substrates and is, therefore, more rugged as a coating for pans and industrial products than is PTFE. PFA also retains most of the electrical, chemical inertness, and high-use-temperature characteristics of PTFE. To avoid internal stresses in the product, PFA should be processed at high temperatures (around 700°F, 370°C) and at slow rates.

Several other fluoropolymer products have been developed, largely for special applications and unique combinations of properties. These polymers include the following:

- Nafion® (DuPont), a PTFE derivative that has a sulfonated pendant group on the end. This sulfonated group allows the material to absorb and pass water. The product is used extensively in chemical cell membranes.
- Films made from monomers in which fluorine atoms do not replace all of the hydrogen atoms in ethylene. These films have excellent weatherability and are used for exterior coatings, packaging of corrosive materials, and flame retardance (Tedlar® from DuPont and Kynar® from Pennwalt). Related products are made from copolymers of ethylene and perfluoroethylene (Tefzel® from DuPont).