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PVDF: A Fluoropolymer for Chemical Challenges

When it comes to selecting materials of construction, keep in mind the favorable properties of fluoropolymers for corrosive service

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IN BRIEF

PVDF AND THE FLUOROPOLYMER FAMILY

COPOLYMERS CHANGE FLEXURAL PROPERTIES

PVDF COMPONENTS

Since its commercialization in the mid-1960s, polyvinylidene fluoride (PVDF) has been used across a variety of chemical process industries (CPI) sectors due to its versatility and broad attributes. With flagship applications in architectural coatings and the CPI, the breadth of industries where PVDF is utilized today is expansive. PVDF components (Figures 1 and 2) are utilized and installed where engineers are looking to maximize longevity and reliability of process parts in many CPI sectors, including semiconductor, pharmaceutical, food and beverage, petrochemical, wire and cable, and general chemicals.

FIGURE 1. A variety of fluoropolymer components are shown here

PVDF and the fluoropolymer family

PVDF is a high-performance plastic that falls into the family of materials called fluoropolymers. Known for robust chemical resistance, fluoropolymers are often utilized in areas where high-temperature corrosion barriers are crucial. In addition to being chemically resistant and non-rusting, this family of polymers is also considered to have high purity, non-stick surfaces, good flame and smoke resistance, excellent weathering and ultraviolet (UV) stability.

Fluoropolymers have carbon and fluorine as the main components of their chemical backbone. Small changes in percent fluorination or addition of other elements may change the performance properties. Fluoropolymers are divided into two main categories: perfluorinated and partially fluorinated [*1*]. The partially fluorinated polymers contain hydrogen or other elements, while the perfluorinated (fully fluorinated) polymers are derivatives or copolymers of the tetrafluoroethylene (C_2F_4) monomer. Commonly used commercial fluoropolymers include polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer (PFA), fluorinated ethylene propylene (FEP), polyvinylidene fluoride (PVDF), ethylene tetrafluoroethylene (ETFE), and ethylene chlorotrifluoroethylene (ECTFE).

PVDF is a partially fluorinated polymer consisting of repeated units of the vinylidene

FIGURE 2. These fluoropolymer tower packings are used in distillation columns

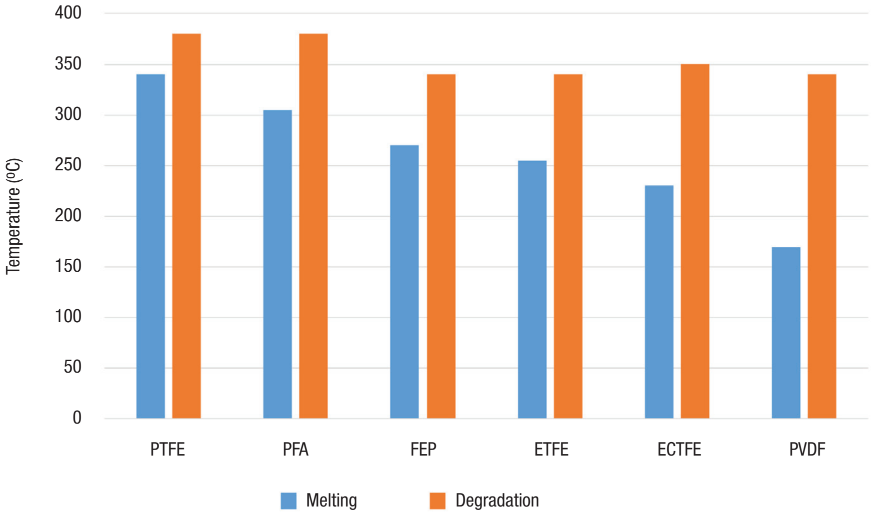

FIGURE 3. The processing temperature window for several fluoropolymers is shown here

fluoride (VF2) monomer [($C_2H_2F_2$)]. Standard PVDF homopolymer is 59.4% fluorinated and PVDF copolymers (described in later sections) can reach up to 65% fluorination. Generally, the higher the fluorine content, the higher the chemical resistance, as the carbon-fluorine bond is one of the strongest known in chemistry. PVDF homopolymers can tolerate chemistries from a pH of less than 1 up to 12 and PVDF copolymers can extend that range from much less than 1 up to 13.5.

While PTFE, with its high melting point of 325°C, is well known as a liner for high temperature applications, PVDF homopolymer has a melt point between 165 and 172°C and maintains a Underwriters Laboratories (UL) relative thermal index (RTI) rating of 150°C [*2*]. Table 1 shows the heat deflection temperature of fluoropolymers with PVDF holding mechanical integrity under pressure up to its usage certification temperature.

Aside from PTFE, which is most often processed by sintering, most other commercial fluoropolymers are melt processable, and require high heat to process in a molten state [*4*]. Equipment used to make most fluoropolymer components must be therefore equipped to handle the associated thermal stresses. Special considerations related to temperature requirements must be taken into account when processing most fluoropolymers.

Unlike its fluoropolymer counterparts, PVDF is the most benign to process. PVDF has the widest gap between its melt temperature and its degradation temperature, as shown in Figure 3. In fact, PVDF does not require special equipment and can be processed on standard equipment used to process polyolefins, such as polyethylene (PE) and polypropylene (PP).

Copolymers flexural properties

While PVDF is the strongest of the fluoropolymers up to 140°C, PVDF copolymers can bring added degrees of flexibility. Copolymerization is a true chemical reaction. It does not involve additives or stabilizers that can leach out over time. Some of most common comonomers are hexafluoropropylene (HFP), tetrafluoroethylene (TFE), and chlorotrifluoroethylene (CTFE). HFP is a fully fluorinated monomer that disrupts the crystallinity of PVDF, resulting in added ductility and increased elongation [*5*]. Varying amounts of HFP can be reacted with VF2 to yield broad ranges of flexibility. Table 2 gives an example of the range of flexural moduli of PVDF, both homopolymer and copolymer, compared to other fluoropolymers.

Variations in material flexibility result in a wider range of components available in PVDF materials. While PVDF homopolymer has a long legacy of use in piping, valves, pumps and other applications that require high mechanical rigidity, the PVDF copolymer range has a variety of melt-processed components, such as wire and cable jacketing (Figure 4), tubing, hoses and gaskets, to name a few.

PVDF components

As previously described, the properties of PVDF make it useful across a variety of applications. The following are just a few highlighted components

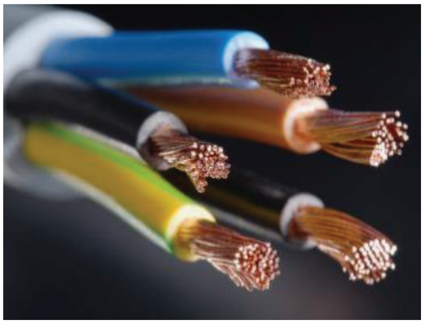

FIGURE 4. Wire and cable components are commonly made of fluoropolymers

FIGURE 5. PVDF piping systems come in a various forms

FIGURE 6. Electrofusion is one joining method of PVDF systems

where PVDF materials are specified to bring long-lasting solutions.

Piping systems. PVDF piping systems (Figure 5) have a UL RTI rating of 150°C (302°F) and are available in various forms: solid piping, lined metal piping and fiberglass-reinforced dual laminate piping. Unlike metals, PVDF is non-rusting and lightweight, making installation easier.

PVDF piping systems can be joined by various welding techniques. Socket fusion is a recommended method in the CPI, as the strong weld creates a lap joint that can resist harsh chemistries, such as hydrochloric, sulfuric, and nitric acids. Butt fusion, one of the easiest types of joining methods, is a choice in areas where the chemistries are more benign. Beadless and smooth inner bore systems leave no welding bump, which make them ideal methods for the pharmaceutical and semiconductor industries. Both of these industries need a smooth surface to minimize bacterial hang-ups and ensure the highest levels of purity. Mechanically joined and threaded systems are utilized for applications where systems are taken apart to be cleaned. PVDF piping can withstand sterilization with saturated steam at temperatures [6] up to 150°C depending on the joining method and design.

Flexible tubing. Flame and smoke additives can be added to PVDF resins to meet the stringent standards of ASTM International E84 (UL723) 25/50 [7] and at least one formulation of PVDF holds a 0/5 ASTM E84 rating using no additives at all, and is compliant with U.S. Food and Drug Administration (FDA) and National Sanitation Foundation (NSF) stan-

FIGURE 7. This flexible tubing is made from PVDF copolymers

dards [8]. Piping systems for waste drainage applications along with wire and cables made with PVDF are widely specified in the plenum areas of buildings. Electrofusion is a specialized pipe-joining technique for that industry, where built-in electric heating elements are used to weld the joint together, thereby minimizing human error in fabrication.

While PVDF piping systems are used in areas where high mechanical rigidity is crucial, flexible tubing options are also available that take advantage of PVDF copolymer technology (Figure 7). With flexural moduli down to 10,000 psi, tubing is important in applications like beverage and fuel lines that can be utilized in many market segments. The beverage industry appreciates minimal cross-contamination of taste, making PVDF tubing a long-lasting choice. Several PVDF copolymers are FDA compliant per Title 21 CFR 177.2600 and are listed to NSF 51 for food contact. For fuel applications, the barrier properties of PVDF are used for low permeation of hydrocarbons in flexible fuel pipes, such as applications compliant with UL 971 Nonmetallic Underground Piping for Flammable Liquids. Fluid handling systems with PVDF can also be created in multilayer constructions, where a tie layer is used

FIGURE 9. Glass-reinforced PVDF resin can be used for bolts

FIGURE 8. PVDF fittings are one example of injection-molded pieces

to bind the PVDF to another material, such as polyurethane or polyethylene. With PVDF as the fluid contact layer on the inside and an engineering polymer material on the outside, the cost of the multilayer construction may be more economical for some applications.

Injection molded components. Piping systems and flexible tubing are usually created via profile extrusion but injection molding is another method to create components in specialized shapes and dimensions. From pumps, nozzles, and valves, PVDF components can be mass injection molded (Figure 8). Recently, PVDF components are being molded for conveyor belting for food-processing facilities.

Traditional materials used in plastic modular belting have faced scrutiny recently due to plastic bits contaminating food [9]. With PVDF, the higher mechanical and abrasion resistance combined with outstanding chemical resistance have proven to be a longer-lasting solution. Both rigid and copolymer grades of PVDF

FIGURE 10. PVDF rods can be machined into specialized components

TABLE 1. DEFLECTION TEMPERATURE OF FLUOROPOLYMERS* [3]			
Material	**Melt point, °F**	**Def. temp. at 66 psi,°F**	**At 264 psi,°F**
PTFE	620	250	132
PFA	590	164	118
FEP	554	158	124
ETFE	518	220	165
ECTFE	464	240	170
PVDF	352	298	235

* ASTM D648

TABLE 2. FLEXURAL PROPERTIES OF PLASTICS*	
Material	Flex modulus, psi
PVDF homopolymer 740	300,000
ECTFE	240,000
PVDF copolymer 2850	170,000
ETFE	170,000
PVDF copolymer 3120	110,000
PVDF copolymer 2800	100,000
FEP	85,000
PFA	85,000
PTFE	72,000
PVDF copolymer 2750	60,000
PVDF copolymer 2500	35,000
PVDF copolymer Ultraflex	10,000

*ASTM D790 at 73°F

can be molded into a variety of parts. Unmodified PVDF resins have a shrink rate of about 2–3% depending on part geometry and thickness. Engineers must take these values into account when designing molds for part production.

Recently, innovations in modifying PVDF resins have produced products that have reduced shrink values. By adding a carbon filler to the PVDF resin, shrink rates similar to polypropylene or polyethylene are obtained. Thus, PVDF can be substituted into those molds with minimal process adjustments. Additionally, glass-reinforced PVDF resins (Figure 9) strengthen PVDF to yield a flexural modulus (ASTM D790) over 1 million psi, similar to that of PEEK (polyether ether ketone) for a fraction of the cost. This glass-reinforced PVDF resin has a very low shrink rate of less than 1%.

Stock shapes. Rods and sheets are produced with PVDF resins for making stock shapes (Figure 10). These components can be utilized by component fabricators to create specialized parts. Rods and sheets can be cut, formed and machined into components that have tight tolerances. Additionally, stock shapes make PVDF components available to original equipment manufacturers (OEMs) that need the material properties of PVDF without having to invest in injection molding equipment.

PVDF sheets are commonly used in the tank industry. Tanks can be fabricated using a variety of techniques from solid PVDF, to linings on metal or fiberglass-reinforced tanks. Facilities that have corroding or rusting metal tanks may find PVDF sheet linings a viable solution to retrofit in the existing structure. ■

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