BRIEFING

REVIEW OF THERMOPLASTIC FLUOROPOLYMERS USED IN HIGH-PURITY WATER APPLICATIONS

A fluoropolymer by definition is any polymer with a fluorine atom in the molecular structure. Thermoplastic fluoropolymers are one of the many niche families of specialty polymers that can be used in molding, extrusion, coating, solvent casting or foaming to make final components for handling chemicals, including various qualities of water. The range of this discussion will be oriented to present data and documented uses on the most common melt processable fluoropolymers that make up more than 95% of the commercial market (1).

For the purposes of setting limits related to polymer discussion, polytetrafluoroethylene (PTFE) will not be included. While melt-processable versions of PTFE are being developed, they are not yet used in chemical handling equipment at the volumes of the other melt processable fluoropolymers like polyvinylidene fluoride (PVDF), polyvinylidene fluoride copolymer (VF2/HFP), fluorinated ethylene-propylene copolymer (FEP), perfluoroalkoxy copolymer (PFA and MFA), poly ethylene-tetrafluoroethylene (ETFE), and poly ethylene chlorotrifluoroethylene (ECTFE).

Additionally, for the purposes of setting limits to the discussion, the fluoropolymers described here will be those that are typically sold at prices below \$65 per kilogram (/kg) to the manufacturers that make the original processed components (2).

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Fluoropolymers used in Water Systems

In most comparisons of polymer families, fluoropolymers are considered to be on the high end of the engineering family of polymers. For ease of understanding the performance ranges of fluoropolymers they are often categorized as "soft" or "hard". While there are exceptions, soft fluoropolymers tend to be made up mostly of carbon and fluorine and hard fluoropolymers have significant amounts of carbon and fluorine, but also hydrogen in the polymer backbone. Soft fluoropolymers tend to have very high melting points and hard fluoropolymers tend to have higher tensile strength values up to 140^{o}C.

Here is a list of the most commonly used fluoropolymers:

Soft fluoropolymers: FEP, MFA, PFA
Hard fluoropolymers: ECTFE, ETFE, PVDF, VF2/HFP

Fluoropolymers become attractive in the high-purity water process because they can possess many properties not found in alternative materials of construction. Each fluoropolymer has important properties that vary compared to others in this family, but selected properly, fluoropolymers can give excellent performance that cannot always be achieved by other polymer types or metals.

Advantages

Depending on the choice of soft or hard fluoropolymers, these materials can offer the following advantages:

- No rusting or rouging throughout the life of the system in contact with water.
- Limited extraction of ionic or organic species.
- High resistance to cleaning agents of all sorts (bleach, acid, ozone, and peroxide, among others).
- The ability to autoclave and no loss of performance after steam cleaning (3).
- Very smooth inner surface of process components.
- Low friction surface.
- High impact resistance at ambient and colder temperatures.
- High resistance to burning (FM 4910 compliance; ASTM E84 25/50 rating).
- Improved resistance to biofilm buildup (4).
- Low permeation to water and oxygen (5).
- Easily thermoformed, welded or machined.
- High abrasion resistance (specific to hard fluoropolymers).
- Regulatory listings and/or compliance (FDA, USP Class 6, NSF—dependent on manufacturer).
- Powder or liquid coating versions available for application to metal.
- Soluble in common solvents for casting of micro-porous membranes (specific to hard fluoropolymers).
- Extrudable into fine fibers for nonwoven filtration products (specific to hard fluoropolymers).

In comparing the common thermoplastic fluoropolymers, it may be best to point out some comments followed by a description of the most popular uses of these materials in the high-purity water handling applications such as the semiconductor and biopharma industries.

Characteristics

From the engineering cost performance standpoint, it is well known that PVDF is the least expensive fluoropolymer based on density and price per pound (2).

TABLE A
Physical, Thermal, and Mechanical Properties of Fluoropolymers

Property	*Test Method and (Units)*	*FEP*	*PFA*	*ECTFE*	*ETFE*	*PVDF*	*VF2/HFP Copolymer Range**
Melting Point	ASTM D3418 – (°C)	260	305	240	245	168	95-167
Specific Gravity		2.15	2.15	1.69	1.70	1.76	1.77 – 1.81
Tensile Yield	ASTM D638 – (MPa)	17	17	34	34	52	6 - 41
Hardness	ASTM D2240 – (Shore D)	55	60	75	75	78	45 - 75
Flexural Modulus	ASTM D790 – (MPa)	600	600	1660	1200	2070	69 - 1240
Tabor Abrasion	CS-17 1000g – (mg/1,000 cycles)	75	25	7	60	7	6 - 70
Limiting Oxygen Index (LOI)	ASTM D2868 – (%)	95	95	64	30	42 - 65	42

**This is a series of resins that can exhibit the ranges given and can be specifically selected to meet a requirement at either end of the data listed.*

This lower cost makes PVDF often the first fluoropolymer considered in design when the high performance is needed. PVDF is also able to be processed on standard molding and extrusion equipment without exotic design because of its lower melting point and processing temperatures. PVDF homopolymer has the highest heat deflection temperature as well as the highest abrasion resistance, which is about the same low material loss as ECTFE and some forms of VF2/HFP copolymer. Finally, PVDF homopolymer grades that have been subjected to a rigorous 20,000 hour test are given a UL® RTI rating of 150°C.

PVDF copolymer (VF2/HFP) covers a very broad set of properties, depending on the level of HFP in the molecular structure. In general, this copolymer is more flexible and impact resistant than PVDF homopolymer. PVDF copolymer broadens the range of PVDF by essentially having the opposite properties when it comes to flexibility. Also, PVDF copolymer is able to be blended with PVDF homopolymer to tailor make products or, to make welded structures that require both a rigid and a flexible product in the same design.

ECTFE and ETFE round out the common hard fluoropolymers. These fluoropolymers have higher melt points than PVDF but lower deflection temperatures (6), so care must be taken to understand any actual advantages. Under low pressure, these materials have useful properties above 160°C. They can be post welded and fabricated in similar manners to PVDF or PVDF copolymer.

FEP is well known as a fluoropolymer with adequate flexibility for tubing, and a high melting point. It has almost universal chemical resistance, but because of it being soft, it is not often used as a self-supporting structural material. In the high-purity industry, FEP is often over-shadowed by PFA, which is more expensive, but has a higher temperature rating and is more universal for very high-end performance needs (7). FEP, PFA, or MFA would be considered for tubing or bonded structures where very high temperatures or extremely aggressive cleaning agents are involved in pure water processing. Figure 1 shows pipes, fittings, wetted pump components, and composite tank structures used for high purity water.

While there are more than one manufacturer of each version of fluoropolymer, Table A makes an effort to compare "general" properties of each of the fluoropolymers mentioned. It is highly recommended that a design professional do a more involved search of each manufacturer's typical property ranges before making a decision on a fluoropolymer type (especially for the soft fluoropolymers that show the greatest variation in literature).

Based on the chemical resistance and the physical, thermal, and mechanical properties, the manufacturers of the fluoropolymers list the following general applications in the high-purity water industry (shown in Table B) (8).

Final Thought

Thermoplastic Fluoropolymers have

Figure 1. Examples of molded, extruded, and formed fluoropolymer parts.

Figure 2. Fluoropolymer composite tubing designed for high flexibility in biotech applications.
Photo courtesy of Eldon James, Denver, CO.

Figure 3. Hard fluoropolymers such as found in hollow fiber membranes.

TABLE B
Common Fluid Handling Components Made with Thermoplastic Fluoropolymers

Fluoropolymer	*Applications*
FEP (TFE/HFP)	Tubing, Sheets, Rods & Blocks, Film, Vessel lining, Pipe Lining
ECTFE	Solid & Lined Pipe, Pumps, Valves, Tanks, Vessel Lining, Housings, Fabrics, Coatings, Sheets, Rods & Blocks, Fittings, Films
ETFE	Tanks, Pumps, Valve & Pipe Linings, Coatings, Fittings, Sheets, Rods & Blocks, Films, Tower Packing, Vessel Lining, Rotomolding
PFA	Tubing, Piping, Wafer Carriers, Vessel Linings, Tanks, Sheets, Rods & Blocks, Pumps, Filter Housings, Tower Packing, Seals, Films, Filtration Systems, Fittings, Valves, Rotomolding
PVDF	Piping, Pumps, Tanks, Sheets, Rods & Blocks, Nozzles, Instrumentation, Tubing, Tower Packing, Filtration Systems, Membranes, Vessel Linings, Tanks, Pipe Lining, Films, Fittings, Valves, Housings, Fabrics, Coatings, ASTM E84 25/50 components
PVDF Copolymer	Piping, Pumps, Tanks, Sheets, Rods & Blocks, Nozzles, Instrumentation, Tubing, Filtration Systems, Membranes, Vessel Linings, Tanks, Pipe Lining, Films, Fittings, Valves, Housings, Fabrics, Coatings, Composite Tubing Structures, Rotomolding

been a highly developing field of polymers over the last 10 years and for the next 3 years are projected to grow at about 5% globally across all markets (9). Some of the new things to look for that are becoming available are:

1. PVDF resins composites with tensile yield properties of 70 megapascal (MPa) for structural applications.
2. PVDF copolymer/polyurethane composite tubing for biotech applications that combine the purity and chemical resistance of PVDF with the high flexibility of polyurethane. Figure 2 shows an example of a highly flexible two-layer polymer tube with an inner layer of PVDF copolymer used for food processing and pharmaceutical pure water.
3. PVDF homopolymer fibers of very low diameter for filtration fabrics. Figure 3 shows hard fluoropolymers such as found used in hollow-fiber membranes.

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