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Material Matters

Fluoropolymer Selection For Corrosive Pump & Valve Applications

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Power and Pollution Control, ITT Engineered Valves

Process engineers are faced with the decision of choosing the correct pump or valve material for corrosive applications. Decision criteria are sometimes based on cost, availability, reliability, durability, and performance history. Fluoropolymers are often times the preferred materials choice for pumps and valves in corrosive services due to their relative cost position compared to high alloy materials and due to their availability. Many times the proof test to determine if a fluoropolymer lined valve will work or not is if the process temperature if below 400°F (204°C). If the temperature remains below 400°F (204°C) it is assumed that the fluoropolymer lined products will work as expected. One pitfall of this approach is that fluoropolymer lined pumps or valves can be specified in certain applications resulting in unexpected performance due to other process conditions such as permeation, steam exposure, and abrasive media.

Without a proper knowledge of fluoropolymer materials they are often times over specified. Fluoropolymers are used extensively in the construction of pumps and valves for the Chemical Process Industry. From their use as seats, packing, seals, diaphragms, and liners it is important to have a good understanding of these materials in order to properly specify the correct materials for your application. The best place to start in order to understand fluoropolymers is to start with a definition.

Fluoropolymers

What is a fluoropolymer? A fluoropolymer is an organic compound consisting of fluorine and carbon atoms but can also contain oxygen or hydrogen. The atoms are held together by bonds to form monomers such as tetrafluorethylene (TFE). When the monomer is polymerized they form into long chains to which TFE becomes polytetrafluoroethylene (PTFE), also known as Teflon®. Fluoropolymers can be either fully fluorinated or partially fluorinated. Fully fluorinated simply means that fluorine atoms completely surround the carbon atoms while partially fluorinated means that fluorine atoms partially surround some of the carbon atoms. The strong chemical resistance of fluoropolymers is directly linked to the strong bond

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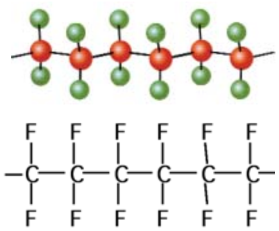
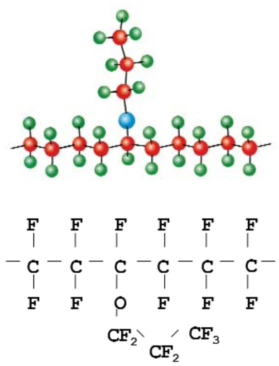
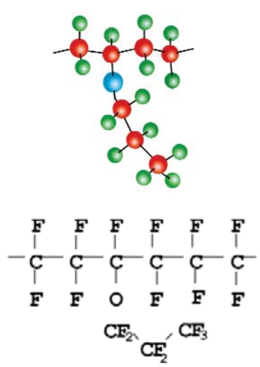


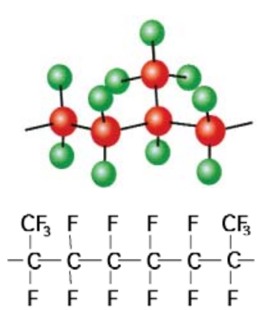
Polytetrafluoroethylene (PTFE)



Modified Polytetrafluoroethylene (PTFE)



Perfluoroalkoxy (PFA)



Perfluoroethylenepropylene (FEP)

between the carbon and fluorine atom within the polymer. Therefore, fully fluorinated fluoropolymers are typically more resistant to more chemicals and have higher temperature resistance than partially fluorinated fluoropolymers.

At left are some examples of fully fluorinated polymers along with select physical data, manufacturing processes and common product applications.

As you can see by the picture, all the carbon atoms are surrounded by fluorine atoms. Again, the strong carbon-fluorine bond leads to the high chemical resistance of this material. The picture above represents one monomer of TFE which when polymerize becomes PTFE.

PTFE [or Teflon®] is probably one of the most widely used fluoropolymers within the valve industry for components. It uses include seats, packing material, and diaphragms. The reason it is used for these components is due to its high molecular weight leading to its high strength compared to other fluoropolymers and its resistance to wear from cycling applications. PTFE provides excellent chemical resistance and also excellent mechanical strength.

Fabrication of PTFE is accomplished by a press and sintering process. PTFE cannot be melt processed, also known as injection molded or rotomolded. Therefore its application is limited mostly to pump or valve components. Occasionally, PTFE is used to line pump and valve bodies but it is mostly found in large diameter components or components with large volumes. It differs in appearance to PFA (described later) in that it is more of a solid white color as compared to the translucent white of PFA [another grade of Teflon®].

Modified PTFE [another grade of Teflon®] is simply PTFE with the addition of less than 1-% perfluoropropylvinylether (PPVE). This is represented above by the chain coming off the third fluorine atom. The addition of PPVE has no effect on the chemical compatibility or temperature capabilities of the PTFE but does change the mechanical properties of the base PTFE. Modified PTFE is a stronger and more durable material than PTFE. Benefits in pump and valve applications are less deformation under load and less permeability providing for longer service life in cycling applications and better creep resistance. Modified PTFE is still limited to fabrication by sintering and therefore we see seats, sleeves, seals, packing material, and diaphragms being the most common components from these materials.

Perfluoroalkoxy, or PFA [which is another grade of Teflon®], is probably the most commonly applied pump and valve liner. PFA is very similar to modified PTFE in that is has an additive of PPVE except the amount is increased from 1% to 4%. Chemical compatibility and temperature capabilities are unchanged but mechanical properties are changed. The most significant change results in this material now being able to be melt-processed. This change enables the use of molding technologies such as injection molding and transfer molding. Injection and transfer molding allow for intricate parts to be completely lined in PFA. Parts include valve bodies, bonnets, balls and stems.

Perfluoroethylenepropylene, or FEP [which is yet another grade of Teflon®], is another commonly applied pump and valve liner material. FEP is made from tetrafluorethylene and approximately 15 - 20 % hexafluoropropylene. Its chemical resistance is nearly the same as PTFE, Modified PTFE and PFA, however it's thermal resistance is less than PTFE, TFM or PFA. Typically you can see a reduction in valve temperature capabilities of 120°F (49°C). The decision to use FEP instead of PFA as a product liner is primarily driven by cost. FEP is a lower cost resin material than PFA. However, one should use caution when giving up temperature capabilities for a slightly lower cost and truly weigh out the two factors against each other. In fact the amount of FEP used in smaller pump or valve sizes can sometimes be so small

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that there is practically no price difference between a FEP and PFA lined products. For this reason FEP is more commonly specified on large diameter vessels where the cost of the material has more of an effect on the overall price. FEP can be melt processed in a similar manor as PFA and also is a translucent white color. There is no apparent visual difference when comparing the two materials.

Polyvinylidenefluoride, or PVDF [also known as Kynar®] is a partially fluorinated fluoropolymer. Meaning that not all of the carbon atoms are surrounded by fluorine atoms resulting in a lower chemical resistance then the fully fluorinated fluoropolymers. Hydrogen atoms have replaced some of the fluorine atoms, which have a weaker bond and are more suspect to chemical attack. Ketones, esters and organic amines can attack PVDF. The benefit of PVDF to pump and valve users is in its high mechanical strength at its permeation resistance. PVDF has good cold flow resistance and high impact strength resulting in great abrasion resistance. PVDF can be melt processed and therefore is found more commonly as a pump or valve liner. PVDF is also used to line large parts such as vessels due to its ability to resist stress cracking when cooling.

More than 15 years ago Ethylene-tetrafluoroethylene (ETFE) [also known as Tefzel®] and Ethylene-chlorotrifluoroethylene (ECTFE) [also known as Halar®] were widely used as product liner materials. At the time they provided the best in chemical and temperature resistance that the industry had to offer. Today these materials are being replaced with PFA which provides higher chemical and temperature capabilities. ETFE or Tefzel® is widely used in pumps today and also more commonly found as a liner in diaphragm valves and to a lesser extent some niche ball valve applications. ETFE provides a lower cost alternative to PFA while providing better abrasion resistance. Fillers materials such as glass are occasionally added to ETFE to enhance the abrasion resistance. Chemical and temperature resistance are somewhat limited as compared to the fully fluorinated fluoropolymers but ofer superior wear advantages.

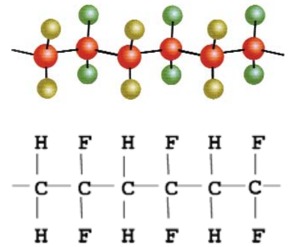
Lastly, there is polypropylene (PP). As evident in the picture, polypropylene is neither partially or full fluorinated resulting in a material that has less chemical and temperature resistance than all the fluorinated polymers. Its typical application range is up to 200°F (102°C) and is found most commonly used in mildly corrosive services. It is probably best known for its use as a liner for diaphragm valves, vessels, and other products used in demineralizers.

Application Decisions

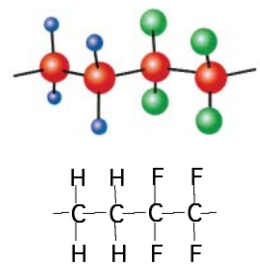
So with all the available lining and component materials how is an engineer to choose the correct material for their corrosive application? Fortunately many pump or valve manufacturers have already chosen the material combinations that best fit most applications. Also, pump or valve manufacturers are able to provide you with guidance and direction as to proper selection of materials to limit the factors influencing product performance. More times than not, PFA as a valve liner and PTFE or Modified PTFE as seats and packing, will work for your corrosive applications. For pumps requiring superior erosion and corrosion resistance ETFE (TEFZEL®) is often recommended as the preferred material. Below are the factors that might effect performance and possibly cause you to look for other alternatives. Or at least plan on a shorter life expectancy.

Abrasive and Corrosive media

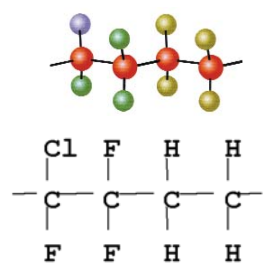
Solids or particulate have a negative effect on fluoropolymer lined products. Especially, when a valve element such as a ball, plug or disk are being turned into the body/seat; or solids impinge upon rotating pump components. The presence of abrasive material can drastically affect the life of a fluoropolymer lined pump or



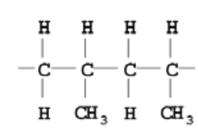
Polyvinylidenefluoride (PVDF)



Ethylene-Tetrafluoroethylene (ETFE)



Ethylene-Chlorotrifluoroethylene (ECTFE)



Polypropylene (PP)

Halar® - Registered Trademark of Solvay Solexes
Dyneon™ - Trademark of 3M
Teflon® - Registered Trademark of DuPont
Kynar® - Registered Trademark of Elf Atochem
Tefzel® - Registered Trademark of DuPont

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valve causing them to leak past the seat or seals prematurely, or experience accelerated localized wear. To counter this effect one can specify a ceramic ball or metal plug in a valve; and ceramic or metal wear rings, sleeves and seals in pumps to eliminate the wear point of these plastic components. However, the turning and/or rotational motion of the product element is still present and will continue to have a negative effect on the life of the PTFE components. Other alternatives would be to use a stronger material such as PVDF or reinforced ETFE. Or, one could use a valve that does not have a turning element such as a diaphragm pump or valve.

Permeating media

Fluoropolymer lined products provide for excellent chemical resistance to aggressive media. However, one of the downfalls of these materials is that certain chemicals can permeate the fluoropolymer and reach the base metal components causing product failure. Media to be concerned with are those that contain chlorine, fluorine, or bromine. These could be hydrochloric acid, hydrofluoric acid or hydrobromic acid.

Factors effecting permeation are concentration of the media, temperature of the media, time of exposure and product liner thickness.

Effects of process parameters on permeation

Higher concentration results in	Increased Permeation
Higher temperature results in	Increased Permeation
Longer exposure time results in	Increased Permeation
Thicker liner results in	Slower permeation to base material

Permeation is something that is best left to experience and direct consultation with pump and valve engineers, as all of the factors listed above need to be taken into consideration when selecting the correct material. For example PFA can be the correct choice for applications that are at ambient temperature while PFA with the same chemical at 350°F (177°C) may not be the correct choice. Fillers are another common solution to permeation but some fillers may be aggressively attacked by certain chemicals or not acceptable due to FDA requirements. Again, the best place to start is with a consultation with a knowledgeable pump and valve engineer.

Steam

Lastly, steam cleaning of process piping is a common procedure in some industries. Steam can also have a negative effect on the life of fluoropolymer lined pumps and valves. Unfortunately there are not a great deal of alternatives other than to carefully monitor the pressure and length of time for steam cleaning. The common recommendation is 30-psi steam for no longer than 60 minutes a day. The failure mode for fluoropolymer lined products that have failed from steam cleaning is deformation of the fluoropolymer or delamination from the base metal. Steam is a small molecule and can permeate the surface of the fluoropolymer similar to chlorine, fluorine, or bromine. When a pump or valve is cooled the steam can then condense in the liner. When the valve is steamed again the condensed liquid will vaporize and expand causing the liner to deform or delaminate from the base metal.

Summary

FEP (fluorinated ethylene propylene) Teflon and PFA (perfluoroalkoxy) Teflon are both melt processable polymers unlike PTFE (polytetrafluorethylene) Teflon. This gives FEP and PFA a processing advantage over PTFE. For example, FEP and PFA are both extrudable. They both "flow" and behave as liquids in the molten state.

While both FEP and PFA Teflon have all of the chemical inertness characteristics of Teflon, they may be processed like most thermoplastics. Ex. Extrusion, injection molding, and weldable.

These manufacturing techniques offer significant advantages over PTFE. Typically, when FEP and PFA Teflon are extruded or molded there is no void or micro porosity in the manufactured part. This means that FEP and PFA Teflon parts are much less prone to permeation effects because they have no voids into which permeants may collect.

FEP Teflon has a lower temperature capability than PTFE, 400°F (204°C) vs. 500°F (260°C). However, PFA has the same temperature capability as PTFE and PFA Teflon has mechanical properties that are superior to PTFE and FEP at elevated temperatures.

Within the last twenty years, several new fluorine-containing polymers have been invented. The most notable feature of these polymers is that they are not fully fluorinated. Without a fully fluorinated structure; these polymers lack both the temperature and chemical resistance capability of the Teflons. Because the carbon-tocarbon backbone of the polymer chain is not fully protected by fluorine atoms (the most electro-negative element) they are subject to degradation and polymer scission (cutting) by many different com-

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pounds. Teflons do not possess this liability. Some of these less than fully fluorinated polymers are Kynar (PVDF) poly vinylidene fluoride, Halar (ECTFE) and Tefzel (ETFE).

While these may not offer the superior chemical resistance of the fully fluorinated polymers they do offer significant improvements in strength, impact toughness and wear resistance.

While these partially fluorinated polymers possess excellent chemical and physical properties, they do have serious liabilities. Perhaps the most serious chemical and physical liability is that partially fluorinatedpolymers possess a high degree of crystallinity.

As a generalization, it is true to say that the more crystalline a polymer, the more prone it is to environmental stress cracking. A good example of this is Kynar (PVDF) lined piping and vessels. The Kynar liner is extruded uniformly, producing a uniform crystallinity. While Teflon as a fully fluorinated polymer is much less sensitive to the subtle manufacturing differences because it is more amorphous than the partially fluorinated polymers.

Polypropylene is an excellent polymer with proven chemical resistance in a wide variety of pump and valve service applications. It offers relatively good mechanical properties and relatively good cold temperature impact resistance.

Kynar® PVDF is a fluoropolymer with excellent resistance to most chemicals. It offers good stability and is resistant to radiation, abrasion, erosion, cold temperature and stress cracking.

Halar® ECTFE is a fluoropolymer that offers outstanding chemical resistance with good physical properties. It is a superior material choice where permeation, stress, and abrasion are problematic.

Tefzel® ETFE is another fluoropolymer offering superior chemical and physical properties. It is recommended in high pressure pump and valve applications, vacuum, or corrosive systems where cold flow and joint creep are a problem. Tefzel® is often regarded as the problem solver for many of the most demanding services.

Teflon® PTFE is an excellent fluoropolymer, virtually inert to all chemicals and offers superior corrosion resistance. It possesses high temperature corrosion resistance to almost all chemicals except fluorine and alkali metals. Its non-stick properties minimize or eliminate residue build-up on pump, valve and vessel walls.

Teflon® PFA is a newer melt-processible resin with the same chemical resistance, but with mechanical strength and high temperature resistance superior to PTFE Teflon®. It can be used at somewhat higher temperatures than PTFE under the same conditions.

The correct decision on what fluoropolymer material to use for your corrosive pump or valve application begins with truly understanding all the parameters of your application. Next, it involves an understanding of the capabilities of the materials you are considering. Lastly, it is always good to consult with pump and valve engineers, as chances are your application is not unique and they may be able to provide recommendations for the most appropriate solution.

Biography

The author is Manager of Markets and Products, ITT Engineered Valves, Lancaster, PA;
www.engvalves.com

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Atofina Kynar Performance Characteristics & Data ADV 010108 7.5M C&Q 9/01

Typical Fluoropolymer Resin Properties

Property	ASTM	Units	PTFE	FEP	PFA	TEFZEL ETFE	CTFE	HALAR ECTFE	KYNAR PVDF
Specific Gravity	D 792		2.13-2.14	2.13-2.15	2.15	1.71 - 178	2.12	1.68	1.75 – 1.78
Tensile Strength	D 1708	PSI	2,500-4,000	3,400	3,600	7,500	5,000	4,300	5,000 – 7,0000
Elongation	D 1708	%	200-400	3,400	300	100-300	150	250	50 - 250
Hardness-Durometer	D 2240	Shore D	50-65	56	60	63-72	80	75	75-80
Water Absorbtion	D 570	%	<0.01	<0.01	<0.03	<0.03	<0.00	<0.1	<0.05
Melting Point	D 3418	F	635-650	495-505	575-590	490-535	410	464	330
Upper Service Temp. (20,000 h)	UL 746B	F		400	500	302	248	300	300
Flammability	ANSI/UL 94		VO	VO	VO	VO	VO	VO	VO

All properties presented in this table should be considered typical values. These properties should not be used to establish specification limits nor used alone as a basis for design.