Overview of Fluoropolymer Materials

A fluoropolymer is a fluorocarbon based polymer with multiple strong carbon–fluorine bonds. It is characterized by a high resistance to solvents, acids, and bases.

In 1938, polytetrafluoroethylene (DuPont brand name Teflon) was discovered by accident by a recently hired DuPont Ph.D., Roy J. Plunkett. While working with tetrafluoroethylene gas, he noticed that a previously-pressurized cylinder had no pressure remaining. In dissecting the cylinder, he found a mass of white solid in a quantity similar to that of the tetrafluoroethylene gas. It was determined that this material was a new-to-the-world polymer. Tests showed the substance was resistant to corrosion from most substances and had better high temperature stability than any other plastic. By early 1941, a crash program was making commercial quantities.

Fluoropolymers share the properties of fluorocarbons in that they are not as susceptible to the van der Waals force as hydrocarbons. This contributes to their non-stick and friction reducing properties. Also, they are stable due to the stability multiple carbon–fluorine bonds add to a chemical compound. Fluoropolymers may be mechanically characterized as thermosets or thermoplastics. Fluoropolymers can be homopolymers or copolymers.

<table>
<thead>
<tr>
<th>Fluoropolymer</th>
<th>Trade names</th>
<th>Monomers</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVF (polyvinylfluoride)</td>
<td>Tedlar®</td>
<td>VF1</td>
<td>200</td>
</tr>
<tr>
<td>PVDF (polyvinylidene fluoride)</td>
<td>Kynar®, Solef®, Hylar®, Symalit®</td>
<td>VF2</td>
<td>175</td>
</tr>
<tr>
<td>PTFE (polytetrafluoroethylene)</td>
<td>Teflon®, Algoflon®, Hyflon®, Neoflon®</td>
<td>TFE</td>
<td>327</td>
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<tr>
<td>PCTFE (polychlorotrifluoroethylene)</td>
<td>Kel-F®, Neoflon®</td>
<td>CTFE</td>
<td>220</td>
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<tr>
<td>PFA (perfluoroalkoxy polymer)</td>
<td>Teflon®, Neoflon®, Hyflon®</td>
<td>PPVE + TFE</td>
<td>305</td>
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<tr>
<td>FEP (fluorinated ethylene-propylene)</td>
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<td>HFP + TFE</td>
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<tr>
<td>ETFE (polyethylenetetrafluoroethylene)</td>
<td>Tefzel®, Fluon®</td>
<td>TFE + E</td>
<td>265</td>
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<tr>
<td>ECTFE (polyethylenepentafluoroethylene)</td>
<td>Halar®</td>
<td>CTFE + E</td>
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</table>
**Typical Properties of Fluropolymers**

<table>
<thead>
<tr>
<th>Property</th>
<th>Method No.</th>
<th>Units</th>
<th>PTFE</th>
<th>FEP</th>
<th>PFA</th>
<th>ETFE</th>
<th>ECTFE</th>
<th>PCTFE</th>
<th>PVDF</th>
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<tbody>
<tr>
<td>Specific Gravity</td>
<td>D792</td>
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<td>2.17</td>
<td>2.15</td>
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<td>1.7</td>
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<td>1.78</td>
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<tr>
<td>Yield Strength</td>
<td>D638</td>
<td>psi</td>
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<td>1,740</td>
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<td>3,480</td>
<td>4,500</td>
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<td>Elongation</td>
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<td>%</td>
<td>200-500</td>
<td>250-350</td>
<td>300</td>
<td>200-500</td>
<td>200-300</td>
<td>80-250</td>
<td>20-150</td>
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<td>Tensile Modulus</td>
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<td>ksi</td>
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<td>57</td>
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<td>75</td>
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<td>HDT, @ 66 psi</td>
<td>D648</td>
<td>deg F</td>
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<td>Limiting Oxygen Index</td>
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<td>Dielectric Constant</td>
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<td>2.6</td>
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</table>

**Types of Fluoropolymers**

**PTFE (polytetrafluoroethylene)** is a high-molecular-weight fluoropolymer that consists entirely of carbon and fluorine atoms. PTFE is best known by the brand name Teflon®.

**PTFE / Teflon® Properties**

- Unsurpassed chemical resistance, only molten alkali metals and a few fluorine-containing compounds at elevated pressures and temperatures will attack its surface
- Not affected by any solvents
- Ultra-high purity
- Exceptional flame resistance, rated UL 94 V-0
- Extremely low coefficient of friction
- Excellent insulator
- Low dielectric constant over a wide frequency range
- May be used in food contact applications in compliance with FDA 21 CFR 177.1550
- Fillers can enhance PTFE’s mechanical properties
- Suitable for outdoor use with no degradation from exposure to the elements

**PTFE / Teflon® Applications**

When the ability to withstand high temperatures is required, compression-molded and machined PTFE is often used to make seals and other parts for aircraft, rockets and missiles. PTFE is also used to make seals that can withstand cryogenic temperatures.

Because PTFE is chemically inert from cryogenic temperatures to very high temperatures, PTFE is used in components for transferring ultrapure, aggressive fluids, such as seals, valves, laboratory equipment, pipes, liners, fittings, connectors, and pumps. Contaminants will not adhere to the surface of PTFE.

- The semiconductor industry uses ultra-pure PTFE for its extreme inertness and wide operating temperature range.

PTFE is one of the best insulating materials and is often used in electrical applications. Because it is non-wettable and absorbs only negligible amounts of water, it retains its high resistivity in damp, polluted environments. Its superior nonstick properties prevent the accumulation of conductive deposits. The construction industry uses PTFE bearing pads because they resist weather-related degradation.

Virgin PTFE complies with FDA regulations for use in the food, beverage, cosmetics and pharmaceutical industries.
**PFA (polyfluoroalkoxy)** is a fully fluorinated, semi-crystalline copolymer of TFE and a minor amount of a PAVE (perfluoroalkyl vinyl ether), such as PMVE (perfluoromethyl vinyl ether), PEVE (perfluoroethyl vinyl ether), or PPVE (perfluoropropyl vinyl ether).

The type and number of side chains provided by the co-monomers determine the thermomechanical properties of the PFA polymer. Generally, a high number of side chains will lower the thermal rating, melting point and creep resistance but will increase the tenacity (stress/strain at break) and the flex-life.

The bigger the side chains, the less co-monomer is needed to modify the polymer backbone to the same degree, which allows the design of resins with higher thermal ratings. Higher molecular weight leads to higher viscosity and a correspondingly lower melt flow index (MFI). Lower MFI resins exhibit higher tenacity and higher flex-life. Co-monomers with bigger side chains can be used to offset the negative effect of low molecular weight (high MFI) on resins that would otherwise have lower tenacity and flex life.

**PFA Properties**
PFA combines the processing ease of conventional thermoplastic resins with the superior properties of PTFE. The melt viscosity of PFA is over a million times lower than that of PTFE.

PFA offers the highest temperature rating and broadest chemical resistance of any melt-processible fluoropolymer, making it ideal for extreme chemical and thermal environments. PFA is similar to FEP in many ways but in general has better mechanical properties at higher temperatures.

PFA is one of the few plastics that is suitable for use in high-temperature and low-temperature applications. Products made from PFA can operate at continuous service temperatures from -260 °C (-436 °F) to 260°C (500°F), similar to the range for PTFE.

- Excellent universal resistance to chemicals and solvents
- Superior creep resistance at upper service temperature
- Excellent stress crack resistance
- Low coefficient of friction
- More than 10 times the flex-life of FEP
- Excellent flexibility
- Smoother surface that PTFE or FEP
- Low gas permeability
- Available in high-purity grades with extremely low levels of extractable trace elements, fluoride ions and other anions
- Available in grades with increased permeation resistance
- Available in anti-static industrial grades
- Exceptional flame resistance, rated UL 94 V-0
- Resists ignition, has a limiting oxygen index (LOI) of greater than 95
- Some grades may be used in food contact applications in compliance with FDA 21 CFR 177.1550
- Excellent low-temperature toughness
- Extremely high weathering resistance and UV stability
- Exceptionally low dielectric constant and dissipation factor, like those of PTFE, but with dielectric strength more than four times higher than that of PTFE
**PFA Applications**
PFA is used for many applications that are similar to those in which PTFE and FEP are used, but PFA is particularly preferred for applications that require extended service in hostile environments with high chemical, thermal and mechanical stresses:
- Semiconductor processing equipment (due to superb chemical resistance and high purity/low extractables), where purity in the parts-per-billion range is needed
- Chemical processing industry (CPI) components
- Bulk chemical distribution
- Fluid-handling components
- Laboratory components

**FEP (fluorinated ethylene propylene)** is a copolymer of TFE (tetrafluoroethylene) and HFP (hexafluoropropylene). Because FEP is fully fluorinated and the bonds between its carbon and fluorine atoms are so strong, it has excellent chemical, thermal and electrical stability.

**FEP Properties**
- Resistant to nearly all chemicals except for alkali metals, fluorine gas and some halogen complexes
- Very high stress crack resistance
- Low coefficient of friction
- Lowest critical surface energy of any plastic
- Excellent nonstick properties
- Non-wetting, hydrophobic, high contact angle with water, oleophobic
- Excellent insulator
- Low dielectric constant and dissipation and high dielectric strength over a wide range of frequencies and temperatures
- Retention of properties at temperatures as high as 204 °C (400 °F)
- Useful properties at temperatures as low as -270 °C (-454 °F)
- Outstanding low-temperature toughness
- UL 94 V-0 flame resistance
- Limiting Oxygen Index (LOI) greater than 95
- Lowest refractive index of any thermoplastic (about the same as water)
- Good transmittance of UV and visible rays
- Very low light reflection
- Good long-term weatherability with excellent resistance to sunlight and ozone
- May be used in food contact applications in compliance with FDA 21 CFR 177.1550
- Excellent toughness
- Relatively soft
- Generally low mechanical strength, lower tensile strength and creep and wear resistance than other high-end plastics
- Inferior to PTFE in some mechanical properties, such as cut-through and abrasion resistance

**FEP Applications**
When high stress-crack resistance is required, FEP is used to line vessels that contain highly corrosive chemicals.
**PCTFE (polychlorotrifluoroethylene)** is formed by the polymerization of the homopolymer of chlorotrifluoroethylene.

PCTFE / Kel-F® / NEOFLON™ - PCTFE is often still referred to as Kel-F®, even though 3M quit manufacturing Kel-F® PCTFE in 1995 and sold the rights to Daikin, who now produces the resin under the NEOFLON™ PCTFE brand name.

PCTFE is a crystalline polymer whose degree and type of crystallinity can be controlled by its thermal history, especially by how fast it is cooled. This makes PCTFE a versatile material whose properties can be modified over a wide range depending on manufacturing conditions. When molded with high crystallinity, PCTFE is dense and has high mechanical strength and low elongation. However, amorphous molded PCTFE has a lower density, is more elastic and optically clear.

Because PCTFE is not well suited for injection molding certain kinds of parts, compression molding followed by machining is used instead.

PCTFE objects made by compression molding are stronger than those made by injection molding or extrusion. Because PCTFE isn’t very stable in its molten state, injection molding or extrusion of PCTFE, which require elevated temperatures, can lead to molecular degradation (loss of molecular weight) and reduced properties as revealed by zero-strength-time (ZST) tests (ASTM D1430). However, expertly performed compression molding doesn’t cause the material to overheat and doesn’t induce a preferential orientation to the material.

**PCTFE / Kel-F® / NEOFLON™ Properties**

- Near-zero moisture absorption
- Extremely low gas permeability
- Fantastic barrier material toward air, water, steam and many fluids, including liquid gases
- Very low outgassing
- Nonflammable, even in the presence of a high oxygen concentration
- Exceptional chemical resistance to all mineral reactants and most organic reactants
- Excellent corrosion resistance
- High optical transparency
- Excellent electrical insulator (even with high humidity and thermal cycling)
- Resistance to strong UV radiation
- Retains its properties upon exposure to gamma radiation
- High compressive strength
- Low deformation under load, superior rigidity
- Lower cold flow than other fluoropolymers
- Useful temperature range of -400 °F to +400 °F
- Superior cryogenic properties
- Expensive relative to many other materials
- PCTFE is attacked by many organic solvents
- Low coefficient of thermal expansion
- High dimensional stability
- Can be machined to precise dimensions

**PCTFE / Kel-F® / NEOFLON™ Applications**

Because PCTFE has high dimensional stability and compressive strength, it is a good structural material to use when the high temperature resistance and chemical resistance of fluoropolymers are required. Although PCTFE has somewhat less heat resistance and chemical resistance than PFA and FEP, its mechanical properties are superior, especially its hardness.

Low outgassing and permeability make PCTFE ideal for laboratory and aerospace applications.
PCTFE is used for cryogenic applications such as liquid oxygen and liquid nitrogen handling. Because PCTFE retains its mechanical properties over a wide temperature range down to almost absolute zero, it is used in refrigeration engineering.

Because PCTFE absorbs essentially no moisture, direct contact with water or high humidity do not affect its dimensional stability, allowing it to remain an excellent electrical insulator even in adverse climates such as the tropics and marine environments.

PCTFE has good resistance to ionizing radiation. It is used in nuclear engineering components and uranium enrichment equipment.

**ETFE (ethylene-tetrafluoroethylene)** is a rugged thermoplastic with an outstanding balance of desirable properties. No other plastic approaches the chemical and electrical properties of fluoropolymers while providing mechanical ruggedness and economical processing.

- ASTM D3159 is the material specification that covers ETFE.

**ETFE / Tefzel® Properties**

- Superior mechanical toughness
- Impact resistant
- Good resistance to most chemicals but is attacked by chlorinated solvents and strong oxidizing agents
- Hydrolytically stable, tensile strength and elongation is essentially unaffected by long exposures to boiling water
- Water absorption of less than 0.03%
- No-load maximum continuous use temperature of 302 °F (150 °C)
- Upper service temperature in excess of 392 °F (230 °C) for certain specific applications
- Excellent abrasion resistance from -300 °F (-184 °C) to 300°F (149 °C)
- High purity
- Little outgassing at recommended maximum use temperature
- Unpigmented resins are rated UL94 V-0 down to 0.062” thick
- Limiting Oxygen Index (LOI) of 30
- Much better radiation resistance than PTFE but is not immune to gamma radiation, especially at higher temperatures and in the presence of oxygen
- Excellent resistance to outdoor weathering with few detrimental effects from long-term exposure
- Is an excellent low-loss dielectric, with a uniformity of electrical properties not usually found in other thermoplastics

**ETFE / Tefzel® Applications**

ETFE is often specified for applications where other materials lack mechanical toughness, broad thermal capabilities or the ability to withstand severe environmental conditions. ETFE is used to line components used in the chemical processing industry (CPI). Because of its high-energy radiation resistance and ability to withstand elevated temperatures, ETFE is used in the nuclear industry.

Unlike for many other polymers, adding glass reinforcement to ETFE improves its frictional and wear properties. Because ETFE also has outstanding creep resistance, the glass-reinforced resin is favored for bearing applications in abusive environments. Some grades can less abrasive on mating surfaces than most glass-reinforced polymers. Glass-filled ETFE has a low wear factor that is only 1/10th that of reinforced nylon.
ECTFE (ethylene-chlorotrifluoroethylene) is a partially fluorinated, semi-crystalline, melt-processible polymer best known by the brand name Halar®.

**ECTFE / Halar® Properties**
- High tensile strength
- Ductile, welded corner seams will flatten before breaking
- Extraordinarily high impact strength at temperatures from -100 °F to +300 °F
- Resists permeation by chemicals in the pH 0-14 range, suitable for wetted parts
- Permeation resistance to chlorine gas, oxygen and carbon dioxide 10-100 times better than PTFE
- Excellent chemical resistance over a wide temperature range
- Resists semiconductor process chemicals
- Resists strong polar solvents such as DMF and NMP
- Ultrapure, very low extractable and leaching levels for demanding semiconductor applications
- Low outgassing
- Exceptionally smooth surface
- Easier to fabricate than most fluoropolymers, can be welded, machined, thermoformed and bonded
- Easy to fabricate with conventional welding equipment, with extremely strong welds
- Very good sliding properties
- High density
- Good insulation properties
- Very good weather resistance
- Food safe
- Self-extinguishing
- Approved and listed to the FM Global 4910 Clean Room Fire Safety Protocol as a fire-safe material for clean-room equipment
- The cost of fire-safe tools can be easily offset by eliminating the purchase and installation costs of fixed fire-suppression equipment
- Limited protection against stress cracking above 284 °F

**ECTFE / Halar® Applications**
- Chemical processing industry (CPI) applications
- High-purity semiconductor process tanks, liners and components
- Linings for ultrapure water systems in the semiconductor industry
- Exhaust systems
- Machine building industry applications
- Pharmaceutical applications
- Fluid-handling systems
- High-performance liquid chromatography (HPLC)
- Fire-safe components
- Chemical storage

PVDF (polyvinylidene fluoride) is a fluorinated semi-crystalline thermoplastic that is obtained by polymerizing vinylidene fluoride.

When exposed to harsh chemicals, high temperatures and UV radiation, PVDF exhibits the characteristic stability of fluoropolymers. PVDF exhibits higher dimensional stability, pressure resistance and tensile strength than PTFE, but lesser friction and insulation properties.
**PVDF / Kynar® Properties**
- Excellent chemical resistance at ambient and elevated temperatures, inert in some of the most stringent environments such as concentrate acids and halogens
- Excellent weatherability
- Insensitive to UV rays
- Excellent radiation resistance
- Good thermomechanical properties
- High tensile strength
- High mechanical strength
- Low water absorption
- Excellent barrier properties
- Outstanding toughness in the most extreme exposure conditions
- Abrasion-resistant
- Flame-resistant
- Self-extinguishing
- High purity
- FDA compliant
- Easy to machine

**PVDF / Kynar® Applications**
- Chemical processing industry (CPI)
  - Chemical production
  - Transport and storage systems
  - Filtration and separation equipment
  - Heat exchangers
- High-purity semiconductor market
- Oil & gas industry,
- Automotive
- Electronics
- Chimney linings
- Fuel cells
- Food processing
- Pharmaceutical industry
- High-purity fluid handling
- Aerospace

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