RESINATE

SPECIAL EDITION

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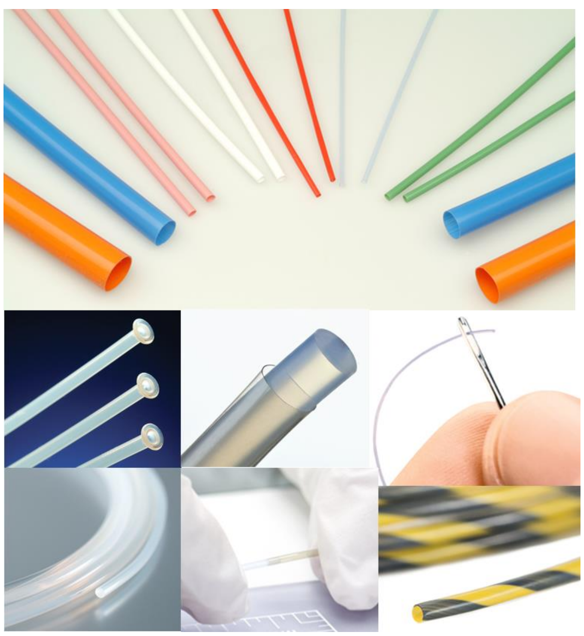
NEW FOCUS ON PTFE



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INTRODUCTION

Fluoropolymers exist in almost every aspect of our lives. From the non-stick coating on our kitchen pots and pans to the packaging of our food, fluoropolymers have proven to be a boon for industry while fulfilling critical needs. Generally chemically resistant and resistant to burning, these materials share their most critical aspect: their carbon-fluorine bonding. These exceptionally stable covalent bonds have been exploited in a multitude of variations to produce the vast fluoropolymer industry as it is today. Homopolymers – those made by combining single identical monomers, and copolymers – those made from combining two different monomers, are but two examples of the templates that have led to extensive fluoropolymer diversity (**Fig. 1**). This vital fluoropolymer industry, however, sprang almost entirely from a single now-classical fluoropolymer: polytetrafluoroethylene, or PTFE.

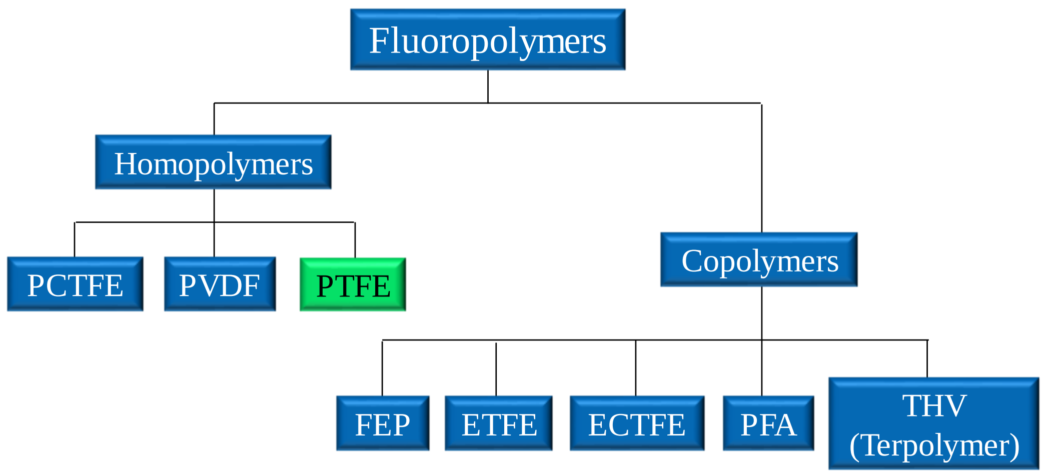

Figure 1: Landscape of popular fluoropolymers. Homopolymers like PTFE are produced through the polymerization of identical monomer units. Copolymers incorporate two or more monomers to produce the final polymer material.

DISCOVERY, SYNTHESIS, AND STRUCTURE

Polytetrafluoroethylene, or PTFE, was the result of a fortuitous albeit nonetheless astute development by researchers at DuPont. Their work built upon earlier efforts carried out by General Motors and DuPont together in the search for refrigerants [1]. Low-temperature liquid tetrafluoroethylene (TFE) had been left unattended in a pressure vessel where later it was found to have spontaneously polymerized. The resulting white waxy solid was discovered as a coating on the inside of the vessel walls; this coating was PTFE. This finding occurred in 1938, but PTFE was not commercialized until 1946 due to its use during WWII on the Manhattan Project – America's secret development of the atomic bomb. Offered as a coating to metal parts, Teflon™ PTFE (or simply Teflon™), has been widely available since then perhaps most universally known as a non-stick coating for cookware.

PTFE is produced from the polymerization of TFE monomers (**Fig. 2**). This process begins with the creation of TFE from hydrofluoric acid (HF), calcium fluoride (mineral, aka fluorspar or fluorite, CaF_2), and chloroform ($CHCl_3$). These reactants are heated to temperatures in excess of 600 °C (1112 °F) to produce TFE gas which is then cooled and purified as a liquid. From this step, TFE monomers are polymerized typically via a radical initiator (such as peroxide, R–O–O–R) to create PTFE. Varying processing protocols can be used to produce PTFE as pellets, powder, or dispersion in aqueous solution [2].

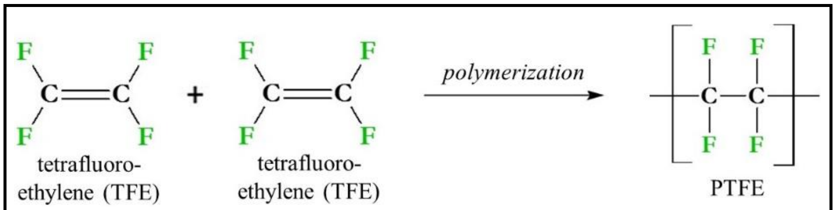

Figure 2: PTFE (polytetrafluoroethylene) and its immediate synthetic precursors. PTFE is made from the polymerization of tetrafluoroethylene (TFE) monomers via a radical reaction.

PTFE is routinely viewed as the premier fluoropolymer plastic because of its many superior beneficial properties over other fluorine-containing polymers. PTFE's properties are the result of it containing exclusively carbon-fluorine (C–F) bonds along its carbon-carbon backbone (C–C) (**Fig. 3**). C–F bonds are very strong, short, and highly unreactive. As such, the C–C backbone of PTFE is surrounded by a sheath of unreactive fluorine atoms. This unique structure is responsible for many of the properties for which PTFE is known. PTFE's very low coefficient of friction ("slippery" feel), low water absorption, and chemical resistance are all the result of PTFE's saturated C–F bonding.

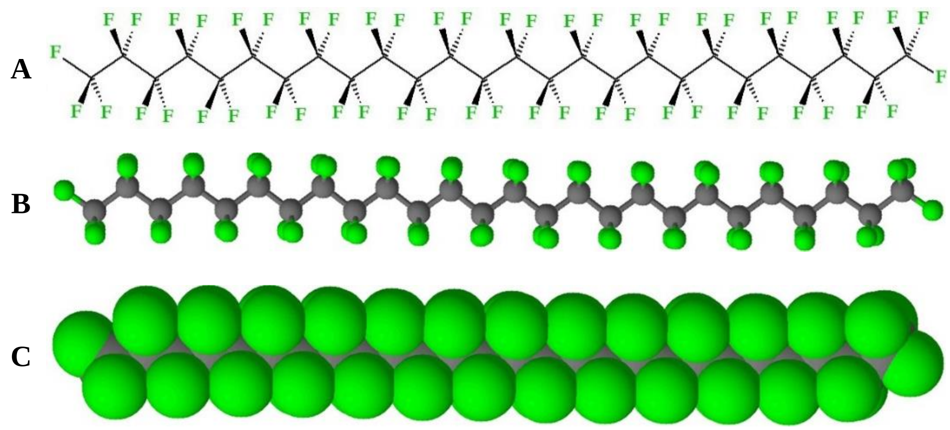

Figure 3: Structure of PTFE. **A)** Stereo bond-line drawing, **B)** ball-and-stick model, and **C)** space-filling model of PTFE (*shown as zig-zag depiction*). (Conformations of PTFE are variable during melt and amorphous phases).

PROCESSING

PTFE is not melt-processable because of its very high melt viscosity. Instead, techniques such as paste extrusion whereby the PTFE resin (as powder) is blended with a lubricant (typically a hydrocarbon) may be used (**Table 1**). This method is used to create a preform which can then be used to produce items such as tubing, sheets, and tapes. PTFE products can also be fabricated by sintering and molding into a billet. This PTFE material can be heated and ram-extruded to create rods, tubing, or pipes. Furthermore, primary PTFE products such as rods can be calendered to produce sheets and membranes. Compression molding can also be used with PTFE for molded parts. Thus, despite its limitation of not being melt-processable, PTFE is nevertheless widely commercialized for a myriad of industries and environments.

Processing Method	Suitability
Injection molding	**No**
Extrusion (profiles, films, sheet, tubing, heat shrink tubing, and cable coating)	**Yes** (as paste)
Blow molding	**No**
Compression molding (preform and sintering)	**Yes**
Impregnation and coating	**Yes** (*coating, as powder*)

Table 1: PTFE processing suitability. Although PTFE is not melt-processable, it is amenable to several other production methods including paste extrusion and compression molding.

PTFE PROPERTIES

PHYSICAL AND MECHANICAL

PTFE is often considered the "gold standard" of fluoropolymers due to many of its exceptional properties. Indeed, because of these attributes, the later development of other polymers such as FEP and PFA were the attempts to refashion the properties of PTFE but in a melt-processable form. PTFE is the most saturated straight-chain perfluorinated polymer, and this quality is responsible for nearly all of its properties (**Tables 2 and 3**). PTFE's C–C bonding and short, strong, and polar C–F bonding create a rigid molecule resulting in a material with high crystallinity and density. Likewise, the sheath of fluorine atoms surrounding the C–C backbone of PTFE is highly hydrophobic and unreactive. These latter qualities in particular render PTFE chemically inert in the body and give it biocompatibility as a Class VI medical grade polymer. PTFE is otherwise highly resistant to a very broad range of chemicals. Despite some limitations in mechanical properties, PTFE surpasses other fluoropolymers in almost all beneficial attributes.

Property	ATSM	Value (natural polymer)
Appearance	–	**Translucent**
Density (g/cm^3)	D792	**2.17**
Specific Gravity	D792	**2.16**
Water Absorption (50% rh; %)	D570/ISO 62-1	**< 0.01**
Refraction Index	D542	**1.35**
Limiting Oxygen Index (LOI)	D2863	**95**
Biocompatible	*USP Class VI	**Yes**
Chemical Resistance	–	**Excellent**
Sterilization	–	**ETO, autoclave**

Table 2: PTFE typical physical properties. PTFE's physical properties place it in a small group of fluoropolymers whose traits are superior to almost all other polymer plastics. (Methods are ASTM test standards except where indicated by *).

PTFE's mechanical properties are closely tied to its crystallinity. PTFE's highly homogenous linear structure results in a very high degree of crystallinity, exceeding 90% for newly produced material. (Compare this to PVDF, another highly homogenous fluoropolymer, whose crystallinity generally falls in the range of 40-70%). Highly crystalline materials typically exhibit brittleness and comparatively reduced tensile strength and elastic properties. To combat these seeming shortfalls, PTFE can be produced with a variety of fillers to address specific mechanical (or other) properties. Additionally, processing details can be varied to influence crystallinity. On the other hand, a high crystalline nature leads to increased hardness and impact strength, critical considerations for applications involving wear. Similarly, PTFE's extraordinarily smooth surface significantly mitigates wear for parts and other surfaces that come into contact with PTFE components. Lastly, also due in large part to its crystalline nature, PTFE shows excellent temperature stability leading to consistent mechanical properties at high and low temperatures.

Property	ASTM	Value (natural polymer)
Tensile Strength (MPa)	D638	**20 – 35**
Elongation at Break (%)	D638	**200 – 550**
Modulus Of Elasticity (GPa)	D638	**0.39 – 0.60**
Flexural Modulus (GPa)	D790	**0.49 – 0.59**
Flexural Strength (GPa)	D790	**No break**
Hardness (Shore D)	D2240	**50 – 65**
Impact Strength (23 °C; J/m)	D256	**186**
Coefficient of Friction	D1894	**0.02 – 0.20**

Table 3: Typical PTFE mechanical properties. While comparatively mechanically weak, PTFE exhibits very low coefficient of friction and very high hardness.

THERMAL

PTFE's strong C–C and C–F bonding are once again demonstrated in its thermal properties (**Table 4**). The C–F bonds of PTFE require more energy (116 kcal/mol) to break than even C–H bonds (99 kcal/mol) [3]. This gives PTFE a very high operating temperature – up to 260 °C (500 °F) – among the highest of any fluoropolymer. PTFE is extremely difficult to burn requiring at least 95% oxygen concentration. (By comparison, normal air contains only about 21% oxygen). These flammability traits of PTFE are especially beneficial for PTFE components used in sensitive or critical applications such as aerospace and automotive environments. Of note, however, is that PTFE undergoes a slight decrease in volume (~ -1.8%) from 30 °C to 19 °C (86 °F to

66 °F) as it shifts to a more tightly wound canonical PTFE helix [4, 5]. This volume reduction can be an important consideration for PTFE parts that require fine tolerances. Below its helical conformation temperature (19 °C; 66 °F), PTFE nonetheless exhibits excellent functional behavior down to -200 °C (-328 °F). PTFE retains many of its most important performance attributes over a temperature range that is among the broadest of any fluoropolymer.

Property	Method	Value (natural polymer)
Thermal Conductivity (W/m-K)	D433 / ISO 22007-4 / C-177	**0.17 – 0.30**
Maximum Service Temperature (°C)	UL 746	**260**
Minimum Service Temperature (°C)	UL 746	**-268**
Melting Point (°C)	D4591 / D3418/ ISO 12086 / DOW Method	**327**
Decomposition Temperature (°C)	E1131	**505**
Coefficient of Thermal Expansion, linear (µm/m-°C)	D696	**100**
Flammability Rating (UL 94)	D2863	**V-0**

Table 4: PTFE thermal properties. PTFE exhibits the broadest temperature usage range of any fluoropolymer. PTFE is also highly resistant to burning and requires very high oxygen content to combust. (Methods are ASTM test standards except where indicated).

ELECTRICAL

PTFE stands out among polymer materials for its electrical properties (**Table 5**). PTFE's highly polar C–F bonds support superior dielectric aspects and across a very broad frequency span. Indeed, PTFE's dissipation factor and dielectric constant are very stable from room temperatures down to temperatures as low as -250 °C (-418 °F) and at frequencies up to 10 GHz [6, 7]. PTFE dielectric breakdown (aka breakdown voltage) can be improved further still by minimizing voids within the PTFE material during the manufacturing process [6]. PTFE's dielectric strength likewise is highly insensitive to heat and thermal aging [7]. On whole, PTFE's insulating properties outperform almost every other solid material.

Property	ASTM	Value (natural polymer)
Dielectric Constant (1 MHz)	D150	**2.1**
Dielectric Strength (V/mil)	D149 / IEC 60243-1	**457 – 483**
Volume Resistivity (Ω–cm)	D257 / IEC 60096	**$\leq 10^{18}$**

Table 5: PTFE electrical properties. PTFE's perfluorinated nature containing strongly polar C–F bonds results in highly beneficial insulating characteristics. PTFE's dielectric benefits remain almost unchanged across a very broad frequency range. (Methods are ASTM except where indicated).

FINISHING

PTFE is amenable to most common machining and fabrication techniques. A variety of products, shapes, and types can be produced from solid processed PTFE. Basic machining techniques such as turning, threading, tapping, grinding, skiving, drilling, and others are applicable to PTFE with no machine modifications. Despite being a plastic, however, PTFE exerts tool wear comparable to stainless steel [7]. Conversely, this aspect allows PTFE parts to be turned to very fine tolerances < ± 0.001″ (0.025 mm) [7]. A brief heat treatment (annealing) is recommended to attain tightly controlled tolerances [7]. PTFE can also be *pre-expanded* to produce PTFE heat shrink tubing for encapsulation uses; this specialty product hardens or sets in a solid-to-nearly-solid form. A variation on sheet and membrane PTFE is that these forms can be stretched or mechanically expanded (differently than for PTFE heat shrink) in a highly controlled manner to create *expanded* PTFE (ePTFE). This material is microporous and has opened up many new avenues for PTFE use, particularly in the medical sector and for specialized filtration applications. Finished PTFE goods can be bonded but most often will require a chemical etching treatment using concentrated alkali metal hydroxide solutions or metal hydrides [6]. PTFE can be colored though pigment options are limited to those that tolerate the high PTFE processing temperatures. PTFE's post-extrusion-friendly traits have played a significant role in expanding its preference and high-performance uses into a broad range of industries.

APPLICATIONS

PTFE continues to occupy the largest market share of commercial polymer plastics today [2]. Its unreactive, temperature insensitive, and highly crystalline nature have resulted in PTFE products in widespread use across almost all commercial industries (**Table 6**). From pharmaceutical to aerospace and automotive to chemical and electrical industries, PTFE is seated in a unique place where it can fill these and many more niches. Extruded PTFE can now be formed into such products as tubing, extruded over wire, monofilament with and without profiles, compression molded, calendered into membranes and sheets, and stretched to create heat shrink and microporous ePTFE. This high-performance fluoropolymer can also be extruded with special profiles which would otherwise be difficult or impossible to produce (**Fig. 4**). Raw PTFE parts can be machined and modified to form highly specific finished goods as well as being suited for the creation of products that have yet to be conceived. These manufacturing and material traits of PTFE have led to its dominance in the fluoropolymer industry.

Application or Industry	Key Benefits
Fluid handling • tubing, piping • joint seals • vessel linings ➢ ePTFE	Chemical resistance Filtration
Automotive Aerospace	Chemical resistance Dielectrics Temperature resistance
Medical • catheter mandrel • catheter base liner ➢ ePTFE (*as implantables*)	Biocompatibility, chemical resistance • lubricity • bondable (etched) ➢ microporous, cellular ingrowth
Electrical	Dielectrics, insulation (*as coating over wire*)
Heat shrink	Encapsulation, protection (AMS-DTL-23053™/12 compliant)
Fiber Optics	Lubricity Abrasion resistance

Table 6: Survey of PTFE applications. PTFE's temperature tolerance, ability to be sterilized, and ability to be produced in forms such as ePTFE and PTFE heat shrink have made it one of the most widely used fluoropolymers.

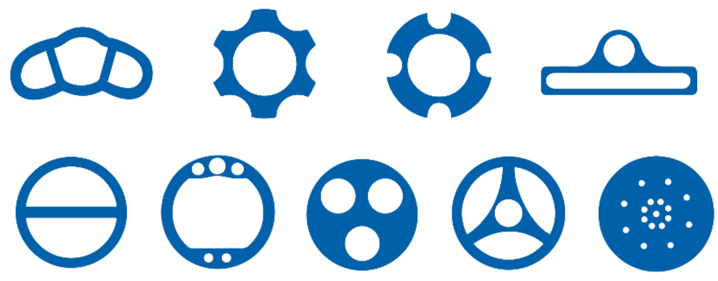

Figure 4: Extruded PTFE profiles. Zeus can extrude PTFE in nearly unlimited customized profiles (and multilumen forms) like those shown here which otherwise would be difficult to produce.

SUMMARY

PTFE was the first in a long line of fluoropolymers that has become among the most important commercial plastics ever created. This durable homopolymer, composed entirely of very stable and unreactive C–F bonds along its carbon backbone, is the most fluorinated of the fluoropolymers. This characteristic allows PTFE to exceed nearly all other fluoropolymers in critical yet beneficial attributes and across the most diverse conditions. PTFE's strong bonding elevates its melt temperature and is partly responsible for its high melt viscosity. As a consequence, PTFE cannot be melt-processed but instead can be paste and ram extruded. PTFE parts can also be formed via compression molding. PTFE can be machined using conventional techniques and equipment and can even be stretched to form heat shrinks and microporous ePTFE. For bonding applications, PTFE can be chemically etched to overcome its extremely non-stick surface. This product versatility has contributed to PTFE becoming the most widely used industrial plastic.

PTFE specifically stands out with respect to its properties. As a fully fluorinated polymer (apart from its C–C backbone), PTFE is the archetype for the fluoropolymers that followed it. PTFE's C–F and C–C bonding convey extremely broad chemical resistance to the material. PTFE's strong bonding gives it superior temperature stability, and PTFE is highly disinclined to burn requiring $\geq$ 95% oxygen to sustain combustion. PTFE's superb insulating characteristics are highly prized in electrical applications. With some mechanical limits, PTFE possesses very high hardness along with concomitant very low coefficient of friction. These two attributes are especially beneficial for part wearing. Viewed collectively, PTFE's beneficial properties eclipse those of almost every other polymer (**Table 7**).

Advantages / Benefits (+)	Limitations (–)
• Broad-spectrum chemical resistance • High temperature tolerance (260 °C / 500 °F) • Low temperature tolerance (<-200 °C / -328 °F) • Low coefficient of friction • Superior weathering	• Poor mechanical strength • Not melt-processable • Chemical etching needed for adhesive and bonding • Limited radiation resistance • High comparative cost

Table 7: PTFE advantages and limitations. PTFE can be used in almost every application where mechanical strength is not required with the exception of radiological uses. Broad chemical, temperature, and weathering resistance place PTFE in a group by itself in the landscape of performance fluoropolymer extrusions.

ABOUT ZEUS

Zeus is the world's leader in polymer extrusion technologies. For over 50 years, Zeus has been serving the medical, aerospace, energy exploration, automotive, and fiber optics industries. Headquartered in Orangeburg, South Carolina, Zeus employs approximately 1,500 people worldwide and operates multiple facilities in North America and internationally. You can find us at www.zeusinc.com.

CONTACT US

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