Focus on: PTFE

Introduction

Several newsletters ago we covered the fluoropolymer family as a whole and described the general properties of this unique group of polymers. This month, we examine PTFE (polytetrafluoroethylene) in more detail. PTFE was the first of the family to be discovered and in some property areas still remains the most outstanding of the family. The development of the melt processable fluoropolymers required a move away from the pure structure of PTFE and in some cases led to reductions in the properties of the resulting polymer.

\[
\text{Tetrafluoroethylene} \quad \xrightarrow{\text{Polymerization}} \quad \text{PTFE}
\]

This representation does not do justice to the structure of PTFE which has a fully fluorinated carbon-carbon backbone chain. In reality, the large size of the fluorine atoms forces them into a spiral arrangement causing them to pack tightly around the central chain of carbon atoms. This is shown diagrammatically below.

The arrangement of fluorine atoms around the central carbon (C-C) backbone

The spiral packing is very dense (it takes 26 carbon atoms for a full turn of the spiral below 19°C and 30 for a full turn above 19°C), and the interlocking of the fluorine atoms creates an exceptionally stiff long-chain molecule. This is one of the main reasons for the high thermal stability of the resulting PTFE polymer. Equally, inside the molecule the only bonds present are the C-F and C-C bonds and these are very stable with high bond strengths.

Despite the high stiffness and stability of the actual long chain molecule, the degree of attraction between individual PTFE molecules is relatively low, and as a result, PTFE does not posses the
high bulk stiffness and strength that is normally present in polymers with high thermal stability. As always, the structure of polymers largely determines their properties.

PTFE can be classified as a semi-crystalline high performance thermoplastic but the degree of crystallinity can actually be as high as 94% in manufactured parts. The degree of crystallinity affects the mechanical properties and is itself affected by the processing method and the rate of cooling after processing. Higher rates of cooling suppress crystallite formation, resulting in lower degrees of crystallinity.

**PTFE Grades**

PTFE is polymerized by one of two methods. The resulting polymers are either granular or dispersion in type, and their final properties depend on the particle size and molecular weight (a measure of the length of the C-C backbone) of the initial resin. In general, the dispersion type has a lower molecular weight. This raw polymer can then be mixed with a wide variety of fillers and other additives to tailor the final plastic to the needs of the application.

For example, the low coefficient of friction means that PTFE is ideal for bearing materials, and the poor wear resistance of the base polymer can be greatly improved by the addition of glass fibers, bronze or carbon without significantly increasing the coefficient of friction. Special radiopaque fillers, such as barium, bismuth or titanium, can be added to medical products for safety and ease of use.

The grade and formulation of the PTFE to be used should be discussed with the supplier to ensure that the most suitable formulation is prepared.

**Properties**

The general properties of PTFE are typical of other semi-crystalline high performance thermoplastics:

- Low coefficient of friction
- Outstanding temperature stability
- Outstanding electrical properties
- Outstanding chemical resistance
- Outstanding weathering and UV resistance (although PTFE can be degraded by gamma radiation dosages above 70 Mrad)
- Good toughness but generally low mechanical strength
- High specific gravity
- Translucent to opaque
- Higher cost

**Physical and Mechanical**

PTFE has reasonable mechanical properties in comparison to other engineering plastics, but more importantly, they are retained over an exceptionally wide temperature range. Typical mechanical and thermal properties are given in the table below.
<table>
<thead>
<tr>
<th>Property</th>
<th>Approximate Value of Natural Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (@23°C)</td>
<td>2,500-4,000 PSI</td>
</tr>
<tr>
<td>Tensile Modulus (@1% strain @23°C)</td>
<td>80,000 PSI</td>
</tr>
<tr>
<td>Elongation at Break (@23°C)</td>
<td>200 - 400%</td>
</tr>
<tr>
<td>Flexural Strength (@23°C)</td>
<td>No Break</td>
</tr>
<tr>
<td>Izod Notched Impact Strength (@23°C)</td>
<td>160 J/m²</td>
</tr>
<tr>
<td>Coefficient of friction (dynamic)</td>
<td>0.02 – 0.1</td>
</tr>
<tr>
<td>Heat Deflection Temperature</td>
<td>55 – 122°C</td>
</tr>
<tr>
<td>Low Temperature Toughness</td>
<td>~260 – ~160°C</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion (20 – 100°C)</td>
<td>1.6 x 10^{-4}/°C</td>
</tr>
<tr>
<td>Long Term Service Temperature</td>
<td>260°C</td>
</tr>
<tr>
<td>Melting point</td>
<td>335°C</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.1 – 2.2</td>
</tr>
<tr>
<td>Water Absorption</td>
<td>0.005% (50% rh)</td>
</tr>
<tr>
<td>Transparency</td>
<td>Translucent</td>
</tr>
</tbody>
</table>

One of the most outstanding properties of PTFE is the extremely low coefficient of friction (allegedly lower than that of any other solid material), and many important applications take advantage of this. The static coefficient of friction decreases with increasing loads, therefore PTFE bearings are not subject to seizing under high loads.

**Thermal and flammability**

PTFE is one of the few plastics that is both suitable for high and low temperature applications and can be used over a wide range of temperatures (−260°C to 260°C). This is probably the widest application range of any plastic currently available.

The flammability behavior of PTFE is also excellent and has no difficulty in achieving the UL 94 V-0 rating for flame resistance. The Limiting Oxygen Index (LOI) for PTFE is greater than 94, which means that there must be over 94% oxygen present to support combustion (air only contains ~21% oxygen). Therefore a material with an LOI greater than 21 will not support burning in an open air situation.

PTFE does undergo a phase change at 19°C and will increase in volume by 1.2%. This may not appear to be great but is a vital consideration for close tolerance machined parts that are to be used at this temperature.
Electrical

PTFE has outstanding electrical properties that remain stable over an extremely wide range of temperatures and varying environmental conditions. In particular the dielectric strength and surface arc resistance do not vary with temperature and are not affected by long periods of high temperatures.

Chemical resistance

The chemical resistance of PTFE is outstanding even in comparison to other fluoropolymers. The inert and fully packed spiral structure and relatively high degree of crystallinity means that PTFE does not interact with most solvents. At room temperature PTFE is only attacked by molten alkali metals and fluorine.

PTFE is also suitable for medical applications because it is biocompatible (certifiable to USP Class VI) and can be sterilized by either EtO or autoclaving.

PTFE is resistant to UV radiation, but will degrade in gamma radiation dosages greater than 70 Mrad.

Advantages and Limitations

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent high temperature performance for all mechanical properties</td>
<td>Higher cost but the properties can justify this (cost can be minimized by coating large objects with PTFE films)</td>
</tr>
<tr>
<td>Excellent low temperature performance for all mechanical properties</td>
<td>Low wear resistance in the natural state</td>
</tr>
<tr>
<td>Excellent electrical performance at high temperatures</td>
<td>Must be chemically etched to enable adhesive bonding</td>
</tr>
<tr>
<td>Excellent chemical resistance over a wide range of temperatures</td>
<td>Processing is a very specialized</td>
</tr>
<tr>
<td>Excellent weathering and UV resistance</td>
<td>Limited resistance to gamma radiation</td>
</tr>
<tr>
<td>Extremely low coefficient of friction</td>
<td></td>
</tr>
</tbody>
</table>

Processing

The low coefficient of friction and the very high melt viscosity make processing of PTFE by conventional plastics processing impossible and dedicated techniques have been developed to process the resin.

For granular PTFE powders the processing methods for small objects are similar to those used in powder metallurgy (pre-forming followed by sintering).

It is also possible to extrude PTFE using ram/paste extruders (rather than the conventional screw extruders) to produce tubing and custom profiles.
## Processing Method

<table>
<thead>
<tr>
<th>Processing Method</th>
<th>Applicable for PTFE?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molding (pre-form and sintering)</td>
<td>Yes</td>
</tr>
<tr>
<td>Extrusion (profiles, sheet and monofilament)</td>
<td>Yes</td>
</tr>
<tr>
<td>Powder Coating</td>
<td>Yes</td>
</tr>
</tbody>
</table>

## Finishing

PTFE products can be machined using conventional tools, including those with carbide or diamond tips, to give a fine finish for prototype evaluation or small run production. Speeds and feeds should be slow (as with any plastic material) to prevent excessive heat build up in the part. The phase change at 19°C must be considered in any machining at or near this temperature.

PTFE can be bonded using epoxy resins but the surface must first be etched (using a solution of sodium in ammonia) before attempting any bonding process.

PTFE is naturally translucent and milky white. It can be widely colored though there are a limited number of pigments that will withstand the high processing temperatures used for PTFE; therefore many products are made in the natural state.

## Typical Applications

The unique properties of PTFE make it suitable for applications where high temperature stability, chemical resistance and low coefficient of friction make it the ideal material. Typical applications include:

- **Fluid conveying systems**: gaskets, packings, bearings and bushings
- **Chemical processing equipment**: piping and tubing, film linings and jackets, seals, heat exchangers and porous filter media
- **Aerospace**: fuel and lubricant-resistant tubes and seals
- **Medical and analytical equipment**: tubing (single and multi-lumen and heat-shrink), seals and gaskets
- **Electrical equipment**: heat-shrink tubing for sealing and protecting connections, transformers and coils, electrical terminal insulation, wire and cable insulation, and high temperature moldings
- **Non-stick coatings**: cookware and other domestic products; industrial equipment such as rolls, conveyor belts, and welding equipment; and compression and slide bearings

## Special Profiles

PTFE is also supplied as extruded tubing with profiles for a wide variety of industries where the high temperature stability is required. Tubing is produced in stock sizes but custom extrusions
can be developed to meet the specific application requirements. A typical selection of profiles as produced by Zeus is shown below.

![Custom designed extrusions by Zeus](image)

**Summary**
PTFE is a truly unique material that occupies a niche all of its own. The two distinctive factors of mechanical property retention over a wide range of temperatures and an ultra-low coefficient of friction have enabled PTFE to establish itself in key market areas where it is effectively indispensable. PTFE may have been a chance discovery for Roy Plunkett and his coworkers in 1938 but it was a vital one for many areas of industry. For a full listing of PTFE properties, capabilities and products please visit [www.zeusinc.com](http://www.zeusinc.com)

**How Zeus Can Help**
With a technical inside and outside sales force backed up with engineering and polymer experts, Zeus is prepared to assist in material selection and can provide product samples for evaluation. A dedicated R&D department staffed with PHD Polymer chemists and backed with the support of a world-class analytical lab allows Zeus an unparalleled position in polymer development and customization.

Since 1966 Zeus has been built upon the core technology of precision extrusion of high temperature plastics. Today, with a broad portfolio of engineered resins and secondary operations, Zeus can provide turnkey solutions for development and high-volume supply requirements.

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