DESIGN CONSIDERATIONS FOR THE USE OF PLASTIC MATERIALS IN CRYOGENIC ENVIRONMENTS

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Plastics offer a number of benefits for cryogenic applications including low thermal conductivity, electrical insulating properties, sealing performance, and the ability to function as friction and wear surfaces without external lubrication.

A great deal of research was conducted by NASA and other government agencies in the 1960s and 1970s to better understand the performance of plastic materials in cryogenic environments (temperatures below -150°C). Much of this research was done for the purpose of improving the seals, pumps, valves, and bearings used for spacecraft applications. Today, a wide variety of emerging technologies require devices capable of performing at cryogenic temperatures. These include liquid hydrogen storage and processing equipment, spacecraft hardware, particle accelerators, cryogenically cooled supercomputers, freezers for pharmaceutical and biosciences applications, and superconducting magnets.

Plastics offer a number of benefits for cryogenic applications including low thermal conductivity, electrical insulating properties, sealing performance, and the ability to function as friction and wear surfaces without external lubrication. That being said, when plastics are cooled to cryogenic temperatures, they exhibit certain unique behaviors that must be allowed for during part design so that the finished device will perform as required. The purpose of this paper is to describe the mechanical, thermal, and friction and wear behavior of plastic materials at cryogenic temperatures so that engineers will be aware of important considerations as they design devices that must operate at low temperatures. A complete review of the technical literature on the cryogenic behavior of plastics is beyond the scope of this article. Instead, the intention is to provide examples that illustrate typical responses of plastic materials to cold temperatures. Whenever possible, the data presented pertain to widely used, commercially available polymers such as PEEK, PTFE, and polycarbonate so that the reader will be able to relate the information to familiar industrial materials. Many of the figures are taken from research that was conducted at universities or national laboratories. The source for each figure is indicated and a list of references is provided for those wishing to develop a deeper understanding of the behavior of plastic materials at cryogenic temperatures.
MECHANICAL PROPERTIES

As plastics are cooled from room temperature toward cryogenic temperatures they tend to exhibit increasingly hard, stiff, and brittle responses to mechanical loads. Figure 1 shows the increasing compressive modulus (stiffness) of PTFE (polytetrafluoroethylene), a material commonly used for gaskets and seals, when the polymer is cooled from room temperature to 20°K (-424°F). Over this temperature range, the modulus of PTFE increases from approximately 100 kpsi to 900 kpsi. Clearly this increase in compressive stiffness will require that higher loads be placed on the material in order for it to conform to a mating metal part to achieve a seal. Interestingly, this graph shows curves for PTFE with three different levels of crystallinity (50%, 56%, and 68%), illustrating that the degree of crystallinity has an influence on the stiffness of the polymer (higher crystallinity being associated with greater stiffness at any given temperature).

Figure 1. Compressive Stiffness of PTFE at Various Temperatures

![Graph showing compressive stiffness of PTFE at various temperatures](source: Schramm, R., Clark, A., & Reed, R., (1973))

Figures 2 and 3 show increases in the tensile strength and hardness of PTFE as it is cooled to cryogenic temperatures. Figure 2 further demonstrates the influence of crystallinity on the mechanical properties of PTFE with the lower crystallinity grades exhibiting higher tensile strength at any given temperature.

Toughness can be loosely described as the amount of energy necessary to cause a material to fail. There is no single agreed upon measure for this characteristic of a plastic material, however a number of metrics can be considered when evaluating the toughness of a polymer. These include Izod impact strength, tensile elongation, the shape of the tensile stress-strain curve, and the area under the tensile stress-strain curve. Additionally, it is important to consider if a plastic material will fail in a brittle or ductile manner under a given set of conditions. Generally speaking, polymers will become less tough (more brittle) at cold temperatures as demonstrated by a number of different metrics. First, plastics exhibit reduced tensile elongation (the amount of linear stretching prior to breaking when the material is placed under a tensile load) in cold temperature conditions.
Figure 2. Tensile Strength at Yield of PTFE at Various Temperatures

Source: Schramm, R., Clark, A., & Reed, R., (1973)

Figure 3. Hardness of PTFE at Various Temperatures

Source: Schramm, R., Clark, A., & Reed, R., (1973)
**Figure 4** shows the decreasing elongation of polycarbonate as it is cooled from room temperature (approximately 18% elongation) to nearly 0°K (approximately 1% elongation). This reduction in elongation has important implications for seals that must operate under compressive loads since polymers that become brittle in cryogenic conditions have the potential to crack rather than deform under compressive stress. One exception is DuPont™ Vespel® polyimide, which has been shown to maintain ductility and create reliable seals at cryogenic temperatures [1].

**Figure 4.** Elongation of Polycarbonate at Various Temperatures

![Elongation of Polycarbonate at Various Temperatures](source)

**Figure 5** shows tensile stress-strain curves for polycarbonate at 4°K and 250°K. Clearly the area under the 4°K curve represents reduced toughness (a smaller area under the curve) compared with the curve for same material at 250°K.

**Figure 5.** Tensile Stress-Strain Curves for Polycarbonate at Various Temperatures

![Tensile Stress-Strain Curves for Polycarbonate at Various Temperatures](source)
Notch sensitivity is an important consideration in plastic part design, which is why sharp corners and sharp screw threads are to be avoided whenever possible for plastic parts that might experience impact loads.

Figure 6 shows reduced notched Izod impact strength and un-notched Izod impact strength for polycarbonate at cold temperatures. This graph illustrates the influence of a notched geometry on impact strength, with the notched specimens exhibiting reduced impact strength due to the stress concentration associated with the notch. Notch sensitivity is an important consideration in plastic part design, which is why sharp corners and sharp screw threads are to be avoided whenever possible for plastic parts that might experience impact loads.

Figure 6. Notched and Unnotched Izod Impact Strength of Polycarbonate at Various Temperatures

Source: Schramm, R., Clark, A., & Reed, R., (1973)
Figure 7 shows the influence of molecular weight (related to the length of the polymer chains for a plastic material) on the cold temperature impact strength of polycarbonate, with the higher molecular weight grades exhibiting superior cold temperature impact resistance compared with the lower molecular weight grades. Molecular weight is an important variable for plastic materials, influencing a wide range of performance characteristics including rheology, chemical resistance, environmental stress crack resistance, fatigue life, and wear performance.

Each of the curves in Figure 7 shows a sharp drop in impact strength from approximately 800 J/m to approximately 100 J/m as the material is cooled. This drop represents a transition from a ductile failure mode (stretching) at warmer temperatures to a brittle failure mode (cracking) at colder temperatures.

To summarize mechanical property effects, plastics will generally become stronger, stiffer, harder, and more brittle in cold temperatures.

Figure 8 shows the ductile failure of a candy bar experiencing an impact load at room temperature and brittle failure when a candy bar is impacted after first being cooled in a freezer. This is analogous to the ductile to brittle transitions exhibited by polymer materials. Failure mode at various temperatures is an important consideration when designing plastic parts since polymers are often selected for applications because of their ability to respond to an impact load in a ductile rather than brittle manner. The ductile to brittle transition for 22 MFR (melt flow rate) polycarbonate is indicated by the red dashed vertical line in Figure 7.

The underlying mechanisms for the transition from ductile to brittle failure are beyond the scope of this article, but it is important to note that they differ for amorphous and semicrystalline polymers. Semicrystalline polymers include both ordered and amorphous regions in their molecular structures and a semicrystalline plastic will fail in a brittle manner when it is cooled to a temperature below the glass transition temperature of its amorphous segments. In contrast, amorphous polymers lack structured regions and they will tend to fail in a brittle manner when cooled below a temperature referred to as the DBTT (ductile-to-brittle transition temperature) [2]. It is noteworthy that cold temperature is only one variable that can result in the brittle failure of a polymer. Other factors such as low molecular weight, a high strain rate, the presence of impurities, voids in the material, sharp notches in the part geometry, or the presence of chemicals can all cause a plastic part to fail in a brittle rather than ductile manner.

To summarize mechanical property effects, plastics will generally become stronger, stiffer, harder, and more brittle in cold temperatures. That being said, it is important to recognize that a number of other factors such as crystallinity (for semicrystalline polymers), molecular weight, strain rate, and part geometry can influence the mechanical performance of a plastic material in cold temperatures.

Figure 8.

The candy bar fails in a ductile manner at room temperature and in a brittle manner after first being placed in a freezer. This behavior is analogous to polymers becoming more brittle in cold temperature environments.
THERMAL PROPERTIES

One of the most significant challenges associated with designing machinery that must operate in cryogenic temperatures is the relatively high CTE (coefficient of thermal expansion) of polymers compared with the CTEs of other industrial material such as metals and ceramics. Clearly, if a plastic component shrinks more during cooling than a mating metal or ceramic part, it can result in poor fit and function for the finished device throughout some portion of the operating temperature range. For this reason CTE mismatch between materials must be carefully considered when specifying dimensions and tolerances. Figure 9 shows thermal contraction for aluminum, and three fluoropolymers: PTFE, FEP, and PCTFE when the materials are cooled from room temperature to nearly absolute zero. PTFE exhibits the greatest dimensional change, contracting approximately 2.2%. In contrast, aluminum contracts less than 0.5% over the same temperature range. Clearly this difference in thermal expansion coefficients has the potential to be problematic when designing parts such as seals where metal and plastic components must remain in intimate contact for the device to function properly.

There is considerable variability in the CTEs of unfilled polymers. Figure 10 shows dimensional change for two plastic materials, PTFE and DuPont™ Vespel® SP1 polyimide, as the materials are heated from -200°C to 250°C. Throughout this temperature range, PTFE grows approximately 5.5% while Vespel® grows only 2%. Generally speaking, polymers such as Vespel® with relatively low CTEs simplify the design of devices that must operate over large temperature ranges since there is less concern over dimensional change of the polymer components relative to mating metal parts.
Because of the relatively high CTEs of polymers compared with those of metals, plastics are often filled with other materials such as glass fibers, graphite, or molybdenum disulfide to reduce dimensional change during heating and cooling. Figure 11 shows thermal expansion for unfilled VICTREX® PEEK™ and 30% glass fiber reinforced PEEK when the materials are heated from nearly absolute zero to 300°K. The unfilled PEEK expands approximately 1% over this temperature range, while the 30% glass fiber reinforced PEEK expands only 0.3%. The additional dimensional stability achieved due to the filler helps to mitigate the issue of CTE mismatch between plastic parts and mating metal components. In summary, when polymers are required for applications that involve large changes in temperature, best practices involve selecting a filled grade of a stable (low CTE) base polymer. When fillers are added to highly stable base polymers such as VICTREX® PEEK or DuPont™ Vespel®, the resulting composites exhibit extremely low CTE values (for a polymer), which makes these materials good candidates for applications requiring plastics with CTEs as close as possible to those of metals.
Thermal conductivity is a property that describes the rate at which heat will transfer through a material. Generally speaking, the thermal conductivity of polymers is considerably lower than that of other materials such as metals or ceramics. For some applications such as wear surfaces, high thermal conductivity is desirable to remove frictional heat from the system. For other applications such as mechanical supports for cryogenic instruments, low thermal conductivity may be desirable to prevent unwanted heat from transferring into a device. **Figure 12** shows the thermal conductivity of PTFE from room temperature to cryogenic temperatures. Two items are noteworthy. First, the figure illustrates that thermal conductivity steadily declines as the material is cooled to cryogenic temperatures. Additionally, the curves illustrate that PTFE with higher crystallinity exhibits higher thermal conductivity than PTFE with lower crystallinity at any given temperature. This correlation between degree of crystallinity and thermal conductivity is typical for semicrystalline polymers.
Table 1 shows thermal conductivity values for a variety of non-metallic materials at the extreme low end of the cryogenic temperature range. The very low thermal conductivity values for the various grades of VICTREX® PEEK™ and DuPont™ Vespel®, along with the superior machinability of these materials help to explain why these products are so often specified for cryogenic applications.

**Table 1. Thermal Conductivities of Non-Metallic Materials at Various Cryogenic Temperatures**

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity @0.3 K (mW/m·K)</th>
<th>Thermal Conductivity @1.4 K (mW/m·K)</th>
<th>Thermal Conductivity @4.2 K (mW/m·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vespel® SP-1 (unfilled)</td>
<td>0.553</td>
<td>3.21</td>
<td>9.74</td>
</tr>
<tr>
<td>Vespel® SP-22 (40% graphite filled)</td>
<td>0.217</td>
<td>2.46</td>
<td>14.3</td>
</tr>
<tr>
<td>PEEK</td>
<td>1.00</td>
<td>5.31</td>
<td>12.0</td>
</tr>
<tr>
<td>PEEK (30% carbon fiber filled)</td>
<td>0.823</td>
<td>4.66</td>
<td>10.6</td>
</tr>
<tr>
<td>PEEK (30% glass filled)</td>
<td>0.812</td>
<td>6.20</td>
<td>19.6</td>
</tr>
<tr>
<td>Pulltruded Glass/Epoxy Rod</td>
<td>1.08</td>
<td>17.8</td>
<td>73.2</td>
</tr>
<tr>
<td>PAI (12% graphite powder, 3% PTFE)</td>
<td>1.06</td>
<td>11.8</td>
<td>28.5</td>
</tr>
<tr>
<td>G-10/FR-4</td>
<td>1.64</td>
<td>20.6</td>
<td>65.6</td>
</tr>
<tr>
<td>Machinable Glass-Ceramic</td>
<td>0.199</td>
<td>8.85</td>
<td>81.4</td>
</tr>
<tr>
<td>Graphite (5 micron particle size, 1.73 g/cc apparent density)</td>
<td>0.366</td>
<td>2.66</td>
<td>22.7</td>
</tr>
</tbody>
</table>

FRICTION AND WEAR

Friction and wear performance describes the ability of a plastic material to function as a bearing surface when sliding in intimate contact with a mating surface which is usually metal. One of the advantages of polymer bearing materials is that they can often function without the addition of liquid lubricants. Lubricants are problematic for many cryogenic applications due to issues such as the lubricant freezing in extreme cold temperatures, the lubricant outgassing in a vacuum environment, or concerns over contamination.

A number of factors should be considered when evaluating the low temperature friction and wear performance of a plastic material including its coefficient of friction and its wear rate. It is important to recognize that wear testing at cryogenic temperatures is complicated by the cooling media, since liquid hydrogen or liquid oxygen may act as lubricants between the polymer and the mating material, separating the two surfaces to some extent and also transferring heat away from the contact area [3,4]. This makes it somewhat difficult to make direct comparisons to the unlubricated wear performance of the polymer in room temperature air.

**Figure 13** shows the coefficient of friction of VICTREX® PEEK™ at room temperature in air, at -196°C in liquid nitrogen, and at -253°C in liquid hydrogen. The graph illustrates the reduced COF of thermoplastics at cryogenic temperatures due in part to the stiffening and hardening of the polymer, which reduces deformation of the plastic as it contacts the mating metal surface.

This concept is illustrated in **Figure 14**, which is a schematic showing the microscopic roughness of “smooth” plastic and metal mating surfaces in a bearing application. The top picture shows how the plastic deforms under load at room temperature, increasing the contact area between the two surfaces, resulting in a relatively high coefficient of friction. The bottom picture shows how the same plastic, which is harder and stiffer at cryogenic temperatures, deforms less, resulting in less contact area and therefore lower friction.
To better relate to this phenomenon, one only has to consider the experience of walking on a hard floor while wearing athletic shoes with soft rubber soles compared with walking on the same floor while wearing dress shoes with hard leather soles. The athletic shoes deform at the surface of the floor, providing high friction. In contrast, the dress shoes deform less at the surface and provide a slippery feel while walking. As a polymer cools and becomes stiffer, it will behave more like a dress shoe, resulting in lower friction as it slides against a mating metal surface.

**Figure 14. Microscopic Roughness**

Schematic of the microscopic roughness of "smooth" plastic and metal surfaces. The top figure shows how the plastic at room temperature deforms under load to a greater extent which increases the contact area between the two surfaces, creating a higher coefficient of friction. The bottom figure shows how the same plastic deforms less at cryogenic temperatures, resulting in less contact area and lower friction.

**Figure 15** shows the wear of bearing grade PEEK (formulated with 13% carbon fiber and 10% PTFE) at room temperature in air and at -253°C in liquid hydrogen, illustrating the improved wear rate of this material in cryogenic conditions compared with its wear rate at room temperature. Reduced friction and improved wear are typical for many thermoplastics in cryogenic conditions.

**Figure 15. Wear Rate of Bearing-Grade PEEK (13% Carbon Fiber and 10% PTFE) Against Steel Discs at Room Temperature in Air and at -253°C in Liquid Hydrogen**

Source: Theiler, G., & Gradt, T., (2007)
There is considerable variability in the wear rate of different polymers at cryogenic temperatures. Figure 16 shows the coefficients of friction and the wear rates for several unfilled plastic materials in liquid hydrogen. Although the COF varies little for most of the polymers tested, the wear performance of PTFE, acetal copolymer, and polyimide are superior to those of the other materials shown for this particular set of conditions.

Various filler such as molybdenum disulfide, PTFE, and graphite have been successfully used to improve the friction and wear performance of polymers at room temperature. These same fillers have not always proved to be as effective at cryogenic temperatures and different investigations have yielded mixed results.

In summary, thermoplastics generally exhibit low friction and good wear performance in cryogenic applications.
Figure 17 shows the coefficient of friction and wear rate for Nylon 6/6 with various fillers. In this example, only the highly loaded 60% graphite-filled Nylon exhibits a reduced wear rate relative to the base polymer.

In summary, thermoplastics generally exhibit low friction and good wear performance in cryogenic conditions. One note of caution is that friction and wear additives that enhance tribological performance at room temperature may not be as effective at improving friction and wear performance under cryogenic conditions.

Figure 17. Coefficient of Friction and Wear Rate for Nylon 6/6 with Various Fillers

Wear and friction of various grades of polyamide (nylon6/6) sliding against 17-4 PH stainless-steel disks in liquid hydrogen. Sliding velocity, 2300 feet per minute (701 m/min); load, 1 kilogram; run duration, 20 to 30 minutes; disk hardness, Rockwell C40.

CONCLUSION

This article has provided an overview of the mechanical, thermal, and friction and wear properties of plastic materials at cryogenic temperatures. This is an exciting field of study and it is expected that cryogenic applications for polymers will continue to proliferate as emerging technologies create demand for plastic seals, bearings, and structural components capable of operating in extreme cold temperature environments.
REFERENCES


Figures 1, 2, 3, 4, 5, 6, and 12:

Figure 7:

Figure 9:

Figure 10:


Figure 11:

Figure 13:
REFERENCE CONTINUED...

Figure 15:

Figure 16 and 17:

Table 1:

ABOUT THE AUTHOR

Dr. Keith Hechtel is Director of Business Development for Curbell Plastics, Inc., based in Orchard Park, NY. Dr. Hechtel has a Bachelor of Science Degree in Geology, a Master of Science degree in Industrial Technology, a Doctor of Business Administration degree, and over 25 years of plastics industry experience. Much of his work involves helping companies to identify plastic materials that can be used to replace metal components in order to achieve quality improvements and cost savings. Dr. Hechtel is a recognized speaker on plastic materials and plastic part design. He has conducted numerous presentations for engineers, designers, and fabricators in both industrial and academic settings.
TECHNICAL EXPERTISE

Curbell white papers are intended to provide engineers and designers with basic information about the engineering polymers available as sheet, rod, tube, and film stock from Curbell Plastics. We invite you to contact Curbell via e-mail at technicalsupport@curbellplastics.com to discuss applications in detail.

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