



TECHNICAL WHITEPAPER

Low Temperature Properties of Polymers

Introduction

Most plastics at room temperature show their familiar properties of flexibility (a low Young's modulus) and high resistance to cracking but when the temperature decreases this can change rapidly and many common plastics become brittle with low failure stresses.

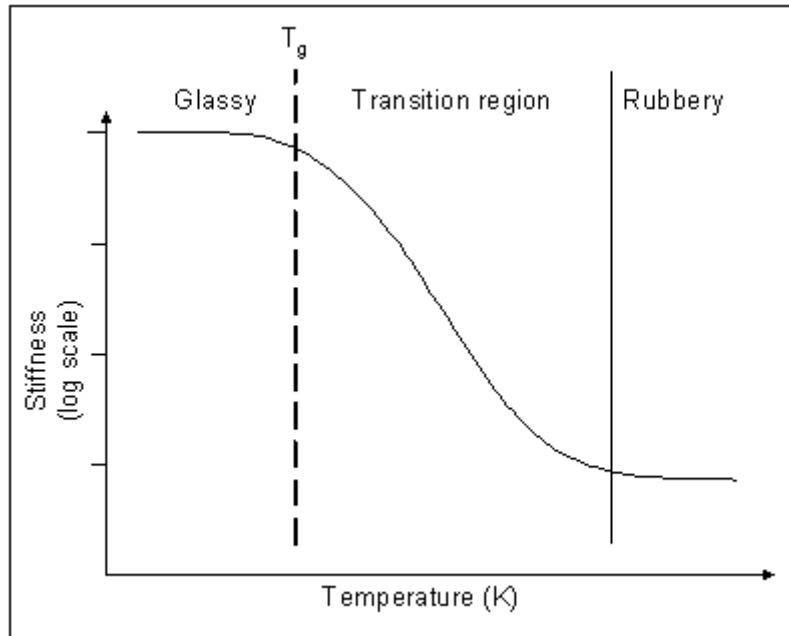
Low temperatures can be more harmful to plastics than high temperatures. Catastrophic failures can occur if materials selection does not take account of the low temperature properties of plastics.

What are low temperatures for plastics?

Plastics consist of long chain molecules that are entangled with one another. The degree of entanglement varies with the length and exact shape of the polymer molecule. A basic model to visualize this is to consider a bowl of cooked spaghetti – it is tangled up and each strand of spaghetti can be thought of as a long chain polymer molecule. When spaghetti has just been cooked and is still warm the long strands can 'slither' over one another and the spaghetti easily takes up the shape of the plate or bowl. However, when the spaghetti is cooled then the strands begin to stick to one another and the individual strands of spaghetti no longer slither about – the spaghetti becomes fixed in the shape of the bowl and is much easier to handle but less tasty.

Similarly, long chains in most polymers at moderate temperatures are able to slither over one another and the material is flexible and does not crack – they are considered to be in a 'rubbery' state. As the temperature is decreased, most polymers begin to stiffen up and they go through what is known as the 'glass transition' to become effectively glassy solids with all the properties of glass i.e. they become very hard and also very brittle.

This is shown in the graph below for a typical polymer and the stiffness can rapidly increase by a factor of 10000 or more in the glass transition region:



The Phases of Polymer Behavior

The temperature of this transition is called the glass transition temperature (T_g) but it is important to note that there is rarely a clear transition between the rubbery and glassy regions – the glass transition takes place over a range of temperature (between 10 to 50°C) and in design terms the glass transition is as much a region as a definite temperature. Once a plastic has been cooled below T_g then, in general, it is stable and no other transitions occur.

In these terms, low temperatures for plastics can be easily defined – it is any temperature below T_g for the particular plastic.

Below T_g , commodity plastics begin to act as stiff and glassy solids, impact resistance is hugely decreased and low energy brittle failure becomes the main cause of failure.

Low temperatures are not necessarily benign in terms of the performance of plastics.

Tg in Real Plastics

The actual value of Tg for real plastics will vary greatly with the, specific molecular structure of the base polymer, the molecular weight and the molecular weight distribution of the polymer, the additives incorporated into the mix and a variety of other factors.

The table at right gives some typical values for Tg for some common polymer families but these should be regarded as indicative rather than definitive.

Polymers that have a Tg greater than room temperature are in the glassy state at room temperature and examples of these are plastics such as PS, PMMA and PET. These plastics tend to be brittle and easy to break at room temperature. PVC is in the glassy state at room temperature but is a special case because it can be easily modified to be rubbery by the addition of plasticizers.

Polymers that have a Tg less than room temperature are in the rubbery state at room temperature and examples of these are plastics such as PP and PE of most varieties (LD, HD, UHMW etc.). These plastics tend to be flexible and difficult to break at room temperature.

One of the most significant special cases is that of PTFE which has a Tg of approximately 130°C. On the basis of conventional plastics PTFE should be brittle at room temperature and below but this is not strictly the case. PTFE has a unique structure and even at the nominal melting point of around 400°C it has considerable strength, equally at temperatures considerably below Tg it can deform plastically to a limited extent.

The Test Methods

While Tg has a distinct physical meaning the most common method of defining the onset of the glassy phase is by establishing the 'brittleness temperature'. The brittleness temperature is useful in assessing the relative merits of competing materials but it is only truly relevant for the materials and conditions specified in the test.

Polymer Family	Glass Transition Temperature (°C) (approx)
PCTFE*	120 - 215
PTFE*	130
PS	100
PMMA	100
PVC	90
PET*	70
PA (Nylon)*	50
Room Temp.	20
POM	-15
PP	-20
PVDF*	-45
PE-LD	-120 to -100
Note: Specific grades and types will vary	
* = Samples Available	



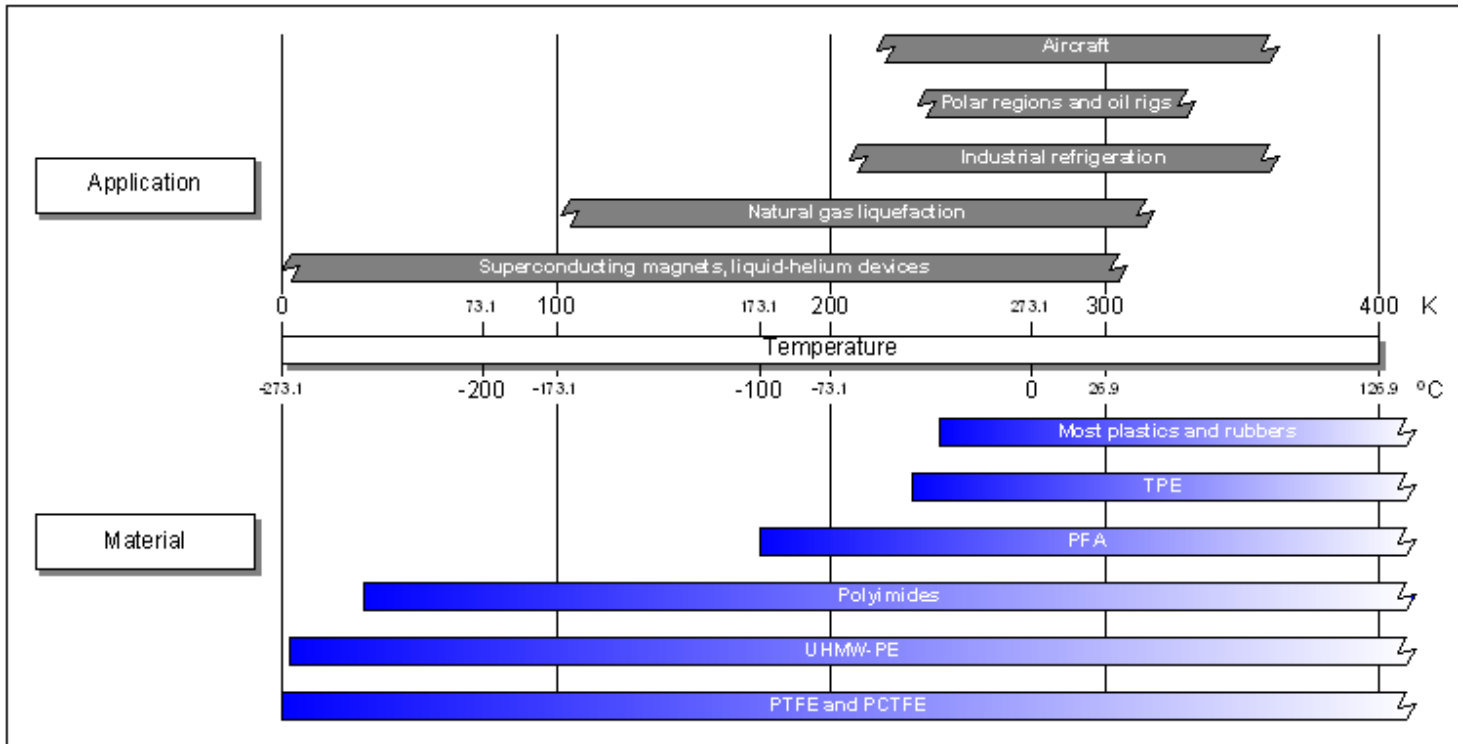
The values obtained should not be directly applied to other shapes and conditions and the value does not put a lower limit on the service temperature for end-use products, it simply indicates the temperature at which brittle fracture becomes the dominant failure mechanism.

The test method is given by ASTM D746-04 – Standard Test Method for Brittleness Temperature of Plastics and Elastomers by Impact. The test establishes the temperature at which plastics exhibit brittle failure under specified impact conditions. The onset of the glassy phase is more of a region than a discrete temperature and therefore the test examines multiple specimens and determines the temperature with a 50% probability of giving brittle fracture of the test piece.

Note 1: This test method is technically equivalent to ISO 974-2000 – Determination of the brittleness temperature by impact when using some fixtures and specimens but differs in the minimum number of specimens that are required to be tested.

Note 2: When testing rubbers for impact brittleness, ASTM D 2137 is used.

Note 3: It is worthwhile noting that the concept of time-temperature superposition means that low temperatures alone are not necessary for brittle failure of plastics. A rapidly applied load at room temperature can have exactly the same effect as a much higher load at low temperatures – brittleness in plastics is as much a function of time as it is of temperature.





The Decreasing Choices

As with high temperature applications, it is immediately evident from the chart that as the specified service temperature decreases then the number of possible and suitable plastics materials also rapidly decreases.

At room temperature the designer can choose from almost any of the available plastics but below -40°C there are a very limited number of plastics that are suitable and more importantly this number decreases rapidly as the application temperature decreases.

The Application Requirements

At extremely low temperatures other factors become important. Many of these applications involve contact with Liquid Oxygen (LOX) and most plastics are incompatible with LOX and burn violently in its presence - understandably it is not recommended to use any plastic where contact with LOX is involved.

The table at right provides guidance on LOX compatibility for a variety of plastics and the small number of compatible plastics families further reduces the available choices for low temperature applications of plastics.

Assessing the performance of plastics in a low temperature application is therefore a complex task. As with any plastics application, essential factors such as the rate of loading, the load itself and the nominal surface stress will inevitably be different from the testing conditions and this is especially true for very low temperatures where test data is often sparse and incomplete and environmental conditions are especially severe.

Polymer Family	Liquid Oxygen Compatibility
PTFE	EXCELLENT
FEP	EXCELLENT
PCTFE	EXCELLENT
PVF	GOOD
PVDF	GOOD
PET	MODERATE
PI	MODERATE
ABS	NO
PA	NO
PC	NO
PE-LD	NO
PMMA	NO
POM	NO
PP	NO
PVC	NO
TPE	NO
Note: Specific grades will vary	

The Available Materials

The application requirements chart (above) also includes details of plastics that are capable of use in low temperature applications and this can be combined with the LOX compatibility chart to give first guidance on possible low temperature plastics.

The fluorocarbon family (PTFE, PCTFE, FEP etc.) is particularly well suited for low temperature applications because they are excellent insulators, have excellent chemical resistance (specifically to LOX) but most importantly they are the only known materials that retain a measurable ductility (approximately 1%) at temperatures very close to absolute zero (-269°C).



This makes them suitable for use as insulators and, when suitable designs are used, as static seals at these temperatures.

The Available Processes

Fortunately for the designer, the fluorocarbons can be processed to create a range of extruded products suitable for use at low temperatures.

Extrusion allows the production of tight tolerance products in a variety of formats such multi-lumen tubing and heat shrinkable tubing. Extrusion also allows the design and production of custom profiles for specific customer applications and the incorporation of special fillers such as radio-opaque products, glass fibers, carbon or other special fillers can also be used to modify tubing products for specific applications.

The Available Processes

For most materials low temperatures present a challenging environment and plastics are no exception.

Regardless of this, the correct selection of the plastic to be used allows engineers to solve low temperature design issues and create solutions in the most demanding environments.

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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