Polymers go through several distinct phase transition points at particular temperatures. These transitions induce changes to their specific volume, mechanical properties, and physical behaviour.

The most significant thermal transition points include melting (thermoplastics only), and glass transition temperature.

This page provides a brief overview to the temperature dependent phase transitions experienced by polymers upon heating and cooling. The key temperature points: melting temperature (Tm) and glass transition temperature (Tg) are discussed for their physical significance.

Upon heating and cooling, polymers experience distinct phase transitions when passing through specific temperatures. When temperature is raised, they physically transition from solid-like glassy to rubbery, and in the case of thermoplastics from rubbery to liquid like flow with additional heating.
These transitions take place in reverse when cooling.

The temperature points where these phase transitions occur are unique to each specific polymer. Awareness of these key temperature points is important as it has direct implications to both the processing and in-service use of the polymer.

**Prerequisites**

Recommended documents to review before, or in parallel with this document:

- Material properties
- Thermoset polymers
- Thermoplastic polymers

**Overview**

Polymers go through several distinct phase transition points at particular temperatures. These transitions induce changes to their specific volume, mechanical properties, and physical state.

The most significant thermal transition points include melting (thermoplastics only), and glass transition temperature. The following figure illustrates these key transition points for thermoset and thermoplastic polymers:

![Thermoset and Thermoplastic Polymers Transition Points](image)

The critical temperature dependent phase transitions for thermoset and thermoplastic polymers.

**Key Temperature Points**

**Glass transition temperature (Tg)** - The temperature region where the polymer behaviour transitions from a hard-glassy material, to that of a soft rubbery material. A sudden loss in mechanical stiffness occurs.

**Melting temperature (Tm)** - The temperature point at which the polymer physically transitions from a solid to viscous flow upon heating, or vice versa - from melt to a solid upon cooling.

Whether or not a polymer exhibits all of the illustrated transitions and whether they occur at a discrete temperature point or a temperature range is dependent on the polymer’s molecular structure.
Behavior Regions[edit | edit source]

**Glassy** - The polymer behaves as a stiff, elastic solid. Polymer chains are locked in their configuration with no mobility to re-orient themselves.

**Rubbery** - Polymer softens and gains flexibility. It behaves as a viscoelastic material. Some mobility of the polymer chains is gained in amorphous regions.

**Liquid Melt** - The polymer behaves with liquid-like fluid motion (viscous material). Polymer chains loosen from their crumpled configurations and are able to move freely, re-orienting in configuration with each other.

Melting Temperature (Tm)[edit | edit source]

*Link to main Melting Temperature page*

![Diagram showing the relationship between temperature and relative molecular mass](image)

Thermoplastic melting temperature dependency on relative molecular mass.

The phase transition of melting is a characteristic exhibited by thermoplastics. For thermosets, melt and subsequent flow is not physically possible due to their fundamental molecular crosslink structure.

Heated beyond the melting temperature (Tm), the polymer transitions from a solid to a viscous liquid like behaviour that can flow. At this phase change, a polymer experiences a large change in specific volume and the polymer chains gain mobility. In reverse, the process of cooling from above Tm, dropping below it to solidify, is referred to as crystallization.

For low relative molecular mass (RMM), 10^3 and below, Tm occurs at a distinct temperature point. At higher RMM, melting occurs over a broadened range of temperature. In reality, even for low RMM and linear polymers, the melting transition is generally observed to take place over a temperature range rather than at a distinct temperature point due to the variation in crystal sizes present in the polymer.

Crystallization[edit | edit source]

*Link to main Melt and Crystallization of Thermoplastic Polymers page*
Upon cooling, polymer chains begin the process of re-organizing themselves from random orientations into packed folded structures of some periodic order (crystals). The crystallization process initiates as nuclei points in the melt. A common crystalline structure formed are spherulites (as pictured).

As cooling continues, the chain folded crystalline structure regions continue to grow in area, while areas of random chain orientation without order are considered amorphous. The term semi-crystalline denotes a polymer consisting of both crystalline and amorphous regions. In the pictured spherulite illustration, the areas between the spherulite crystal structures are amorphous.

For thermoplastics, the transition from glassy to liquid melt is affected by the proportion of crystallinity in the polymer. Specifically, the rubbery transition range is heavily influenced by crystallinity due to the need to unpack and unravel the crystal structures for fluid-like motion to occur.

Specific volume change with temperature - thermoplastic polymers.
The greater the crystallinity, the less rubbery behaviour that is observed in transitioning from glassy to a liquid melt.

Click here to learn more about melt and crystallization of thermoplastic polymers.

**Glass Transition Temperature (Tg)**[edit | edit source]

(Link to main Glass Transition Temperature page)

Example of the effects of softening when polymer is at a temperature above its glass transition temperature (Tg).

Polymers are classified as glassy when their molecular backbones exhibit the inability to move and remain “frozen” in crumpled immobile conformations. Below Tg, upon heating only thermally induced expansion between the molecules occurs. Above Tg, amorphous regions within the polymer observe liquid-like “flow” with the molecular chains gaining rapid ability to move freely, while crystalline regions remain locked in the glassy state configuration.

Specific volume change with temperature - thermoset polymers.
As an outcome of this behavioral transition, a polymer exhibits a sudden change in the response of specific volume to change in temperature (thermal expansion) at the Tg point. Mechanically, a softening drop in mechanical stiffness occurs. This substantial drop in mechanical stiffness is shown in the example picture, showing a polymer below and above its glass transition temperature.

Young's Modulus drop at the glass transition point.

At temperatures above Tg, a substantial reduction in Young’s Modulus (E) is observed between the stiff glassy state and the softened rubbery state. To ensure in service mechanical stiffness of the polymer, the operational temperature should be below Tg. However, there are situations where having the service temperature above the polymer’s Tg to obtain rubbery behaviour is intended. Elastomers are the classic example, where their rubbery behaviour is desired and the material is used above its Tg.

Click here to learn more about glass transition temperature.

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References

The glass transition temperature ($T_g$) is the temperature region where the polymer transitions from a hard, glassy material to a soft, rubbery material. It is one of the most important properties of any amorphous polymer.

Thermosets are a class of polymer that undergo polymerization and crosslinking during curing with the aid of a hardening agent and heating or promoter. Initially they behave like a viscous fluid. During curing, they change from viscous fluid to rubbery gel (viscoelastic material) and finally glassy solid.

If heated after curing, initially they become soft and rubbery at high temperatures. If further heated, they do not melt but decompose (burn)

Comes in two parts: part A (resin) and B (hardener). When mixed, curing reaction starts and is not reversible.

Examples include epoxy or polyester.

A class of polymer, some common examples include polypropylene and polyethylene.

They soften and melt upon heating (i.e. potentially recyclable), high viscosity when melted, therefore difficult to saturate fibres. Usually needs a lot of pressure and heat to process.

Literally “without structure”, randomly coiled molecular polymer chains.

Periodic 3-D, repeating array of molecules.

A portion of the molecular polymer chains tend to ‘fold up’ into densely packed regions called crystals.