

# Polymer: the glass transition



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## ***Formulation Chemistry – Polymer: The Glass Transition***

In the solid state, semicrystalline polymers exhibit both amorphous and crystalline morphology. The glass transition is a property of only the amorphous portion of a semi-crystalline solid. <sup>[1]</sup> The glass transition temperature,  $T_g$ , is the temperature at which the amorphous materials change between the glassy and rubbery form.

### **1. 1 Amorphous and Crystalline Polymers**

The *amorphous* polymers consist of molecules that are oriented randomly, unlike the *crystalline* ones which have polymer chains packed in ordered, repeating patterns in the three-dimensional crystal lattice. However the glass transition is different to melting because only amorphous polymers undergo the glass transition. Melting is a transition that occurs in crystalline polymers when these chains are disoriented from the crystal structures and become liquid. A sample of semicrystalline polymer can be composed of both amorphous and crystalline portions, therefore it can have both a glass transition temperature and a melting temperature.

### **1. 2 Glassy and Rubbery States**

Below  $T_g$ , the amorphous regions of a polymer are in a glassy state and most joining or contact bonds are intact. <sup>[2]</sup> The molecules may be able to vibrate slightly, but are virtually motionless in which portions of the molecule wiggle around. Therefore polymer is generally hard, brittle and rigid. As the polymer is heated until it eventually reaches its glass transition temperature, the molecules start to wiggle around. In inorganic glasses, more bonds are broken with increased thermal fluctuations; while in organic polymers, non-

covalent bonds between chains also become weaker. By heating above  $T_g$ , there is long-range segmental motion where the polymer chains can move around easily. It is now described in its rubbery state which offers flexibility and softness for plastic deformation without fracture.

Below  $T_g$ , the chains are firm and unbendable to relieve the force being applied. This is due to either (a) the chains are strong to resist the stress; or (b) the force applied is excessive for the motionless polymer chains to overcome, so the polymer sample will just break or shatter. [1]

Such mobility with temperature is heavily dependent upon the “heat” content because  $T_g$  is a kinetic parameter. The  $T_g$  decreases with slower melt cooling rate. It is also affected by other factors listed in section 1.4. Heat is a form of kinetic energy that causes random motion of molecules and the pliability of polymer, in comparison to “cold” polymers which lack kinetic energy to move around and hence are brittle on cooling.

Example of this behavior is the glass transition of chewing gum. It is soft and pliable at body temperature, characteristic of an amorphous solid in its elastic, rubbery condition. The gum then turns hard and rigid when it comes into contact with cold drink or ice cube in the mouth.

### **1.3 Glass Transition vs. Melting**

The differences are outlined in the table below: