Glass Transition Temperature

When an amorphous polymer is heated, the temperature at which the polymer structure turns “viscous liquid or rubbery" is called the Glass Transition Temperature, Tg. It is also defined as a temperature at which amorphous polymer takes on characteristic glassy-state properties like brittleness, stiffness and rigidity (upon cooling).

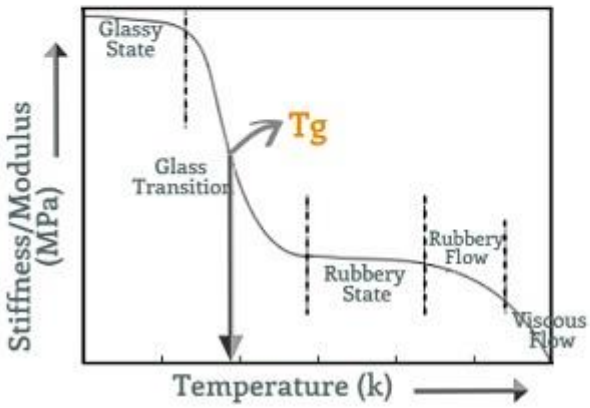
This temperature (measured in °C or °F) depends on the chemical structure of the polymer and can therefore be used to identify polymers.

- Amorphous polymers only exhibit a Tg.
- Crystalline polymers exhibit a Tm (melt temperature) and typically a Tg since there is usually an amorphous portion as well (“semi”-crystalline).

The value of Tg depends on the mobility of the polymer chain, and for most synthetic polymers lies between 170 K to 500 K.

The transition from the glass to the rubber-like state is an important feature of polymer behavior, marking a region of dramatic changes in the physical properties, such as hardness and elasticity.

At Tg, changes in hardness, volume, percent elongation to break and Young’s modulus of solids are mainly seen. Some polymers are used below their Tg (in glassy state) like polystyrene, poly(methyl methacrylate) etc., which are hard and brittle. Their Tgs are higher than room temperature. Some polymers are used above their Tg (in rubbery state), for example, rubber elastomers like polyisoprene, polyisobutylene. They are soft and flexible in nature; their Tgs are less than room temperature.



Applications include Identifying the Tg of polymers is often used for quality control and research and development. Also, it is an important tool used to modify physical properties of polymer molecules.

Amorphous Polymers and Crystalline Polymers

Polymers (plastics, elastomers or rubber) are made up of long chains of molecules and may be amorphous or crystalline. The structure of a polymer is defined in terms of crystallinity. Amorphous polymers have a random molecular structure that does not have a sharp melting point. Instead, amorphous material softens gradually as temperature rises. Amorphous materials are more sensitive to stress failure due to the presence of hydrocarbons. E.g. PC, GPPS, PMMA, PVC, ABS.

Crystalline or Semi-crystalline polymers have a highly ordered molecular structure. These do not soften as the temperature rises, but rather have a defined and narrow melting point. This melting point is generally above that of the upper range of amorphous thermoplastics. E.g. Polyolefins, PEEK, PET, POM etc.

The glass transition temperatures of materials can be measured by using differential scanning calorimetry(DSC) or differential thermal analysis (DTA).

This test method is applicable to amorphous materials or to partially crystalline materials containing amorphous regions, that are stable and do not undergo decomposition or sublimation in the glass transition region. Both methods, DTA and DSC, yield peaks relating to endothermic and exothermic transitions with thermal input and show phase changes or occurrence of reactions.

- In DTA, the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed.

- In DSC, the difference in heat flow to a sample and to a reference is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed.

  Glass Transition Temperature Vs Melting Temperature
  At the molecular level, at Tg, the chains in amorphous (i.e., disordered) regions of the polymer gain enough thermal energy to begin sliding past one another at a noticeable rate. The temperature where entire chain movement occurs is called the melting point (Tm) and is greater than the Tg

1. Glass Transition is a property of the amorphous region while melting is the property of crystalline region
2. Below Tg, there exists disordered amorphous solid where chain motion is frozen and molecules start wiggling around above Tg. The more immobile the chain, the higher the value of Tg.
3. While, below Tm it is an ordered crystalline solid which becomes disordered melt above Tm

The operating temperature of polymers is defined by transition temperatures

Factors Affecting Tg

Chemical Structure

- **Molecular Weight** – In straight chain polymers, increase in MW leads to decrease in chain end concentration resulting in decreases free volume at end group region – and increase in Tg
- **Molecular Structure** - Insertion of bulky, inflexible side group increases Tg of material due to decrease in mobility,
- **Chemical cross-linking** - Increase in cross-linking decreases mobility leads to decrease in free volume and increase in Tg
- **Polar groups** - Presence of polar groups increases intermolecular forces; inter chain attraction and cohesion leading to decrease in free volume resulting in increase in Tg.

Addition of Plasticizers

Addition of plasticizer increases the free volume in polymer structure (Plasticizer gets in between the polymer chains and spaces them apart from each other) This results in polymer chains sliding past each other more easily. As a result, the polymer chains can move around at lower temperatures resulting in decrease in Tg of a polymer

Water or moisture content

Increase in moisture content leads formation of hydrogen bonds with polymeric chains increasing the distance between polymeric chains. And, hence increases the free volume and decreases Tg.

Effect of entropy and enthalpy

The value of entropy for amorphous material is higher and low for crystalline material. If value of entropy is high, then value of Tg is also high.

Pressure and free volume

Increase in pressure of surrounding leads to decrease in free volume and ultimately high Tg. Other factors like branching, alkyl chain length, bond interaction, flexibility of polymer chain, film thickness etc. also have significant impact on glass transition temperature of polymers.

Reference https://omnexus.specialchem.com/polymer-properties/properties/glass-transition-temperature