

Glass Transition Temperature, T_g

So what is the Glass Transition Temperature, T_g ?

We'll often hear someone talking about the Glass Transition Temperature (T_g) of a polymer, but so what? What does it mean, and why should I care about it?

The glass transition temperature is a function of chain flexibility. The glass transition occurs when there is enough vibrational (thermal) energy in the system to create sufficient free-volume to permit sequences of 6-10 main-chain carbons to move together as a unit. At this point, the mechanical behavior of the polymer changes from rigid and brittle to tough and leathery --- the behavior we define as "plastic behavior".

Actually, the glass transition temperature is more important in plastics applications than is the melting point, because it tells us a lot about how the polymer behaves under ambient conditions. The melting temperature is often referred to as the "first-order transition" --- that's where the polymer changes state from solid to liquid. Technically, only crystalline polymers have a true melting point; that's the temperature at which the crystallites melt and the total mass of plastic becomes amorphous. Amorphous polymers do not have a true melting point, however, they do have a first-order transition where their mechanical behavior transitions from a rubbery nature to viscous rubbery flow.

All polymers have some temperature at which their physical properties are rigid and glassy, similar to crystal polystyrene ($T_g = 100^\circ\text{C}$). Take polypropylene ($T_g = 0^\circ\text{C}$) down to -40°C and try to break it, you'll see what I mean. In its glassy state, the mechanical behavior of the polymer is relatively stable. The material is very hard and brittle, and the properties don't change significantly with temperature --- modulus remains high and impact strength is almost nil. However, as the temperature rises, there will be a point where the behavior of the polymer will change fairly rapidly from glassy to a very tough and leathery behavior. This change in behavior is evidenced by a sharp decline in modulus (stiffness), or increase in impact strength as the ambient temperature is increased. This region is termed the glass transition region. The temperature at the midpoint of the transition from glassy to rubbery, the glass transition region, is defined as the glass transition temperature, T_g .

If the ambient temperature is elevated further, the material behavior becomes similar to a rubber. In this region, called the rubbery plateau, the low modulus and high impact strength again become less significantly affected by temperature. However, at some point the material becomes so soft that it will flow under very low pressure, this is the

final transition to viscous rubbery flow. This is considered the “melting” temperature of the polymer, or the first-order transition temperature.

So what does all of this mean? Basically if a polymer’s glass transition temperature is well above (say, 50°C above) ambient room temperature, the material will behave like a brittle glassy polymer --- it’ll be stiff with relatively low impact resistance. Conversely, if the T_g is well below room temperature, the material is what is commonly termed a rubber or elastomer --- soft and easily stretched; and those materials whose T_g is reasonably close to the ambient temperature will exhibit plastic material behavior --- strong and tough with good impact resistance.

In applications that can experience temperature extremes, it is important to know what the potential exposure temperatures are and how they will affect the mechanical behavior of the material. In the earlier example of polypropylene, a tough plastic in room-temperature applications, we saw that it turns glassy and brittle at low temperatures, while at elevated temperatures, the material becomes soft and easily deformed under low loads --- rubber-like. This change in properties is simply the effect of temperature on the mechanical behavior of the material as it proceeds from well below its T_g , through its glass transition and into the rubbery plateau. At even higher temperatures, the crystallites will melt and the material will flow under moderate pressure --- the transition which occurs in the plasticating unit --- and allows us to fabricate parts from a material which we call PLASTIC.

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