

What is a Relaxation?

A relaxation in a material is an event where the conformation of the molecules, or ability of the molecules to move, changes. This kind of event is normally observed as a function of temperature but can also be observed as a function of frequency (in the case of DMA), humidity or other invasive factors. The main relaxation event of a material is the glass transition (T_g) but other, mainly, lower temperature transitions also exist.

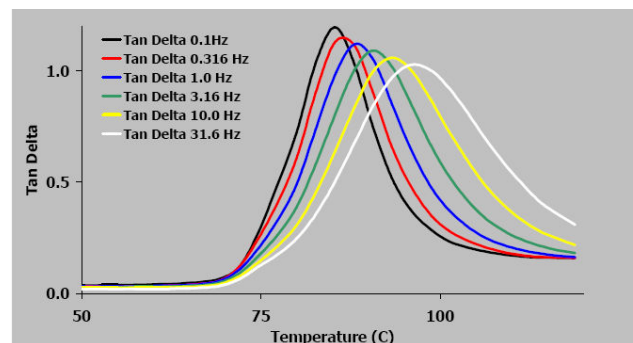
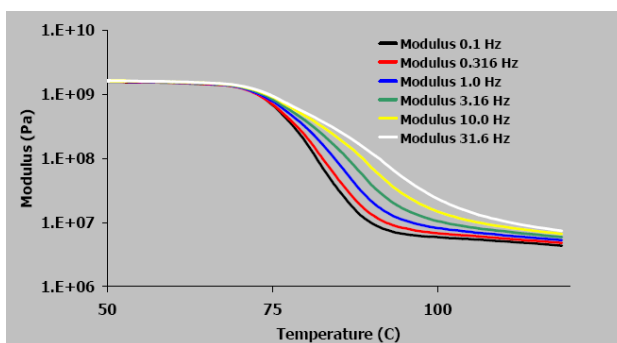
Glass Transition Temperature, T_g

A material's glass transition temperature (T_g) is the temperature below which molecules have very little mobility. On a larger scale, polymers are rigid and brittle below their glass transition temperature but above it can undergo plastic deformation. The T_g is usually applicable to amorphous phases and is commonly applicable to glasses and polymers. Many natural materials, as well as synthetic, have a glass transition. It can be an important property for many materials from foodstuffs to synthetic polymers.

In essence, the glass transition is the temperature range over which the polymer backbone changes from being rigid and goes to a "floppy" relaxed structure. The rigid structure is referred to as "glassy" and the relaxed structure is referred to as "rubbery".

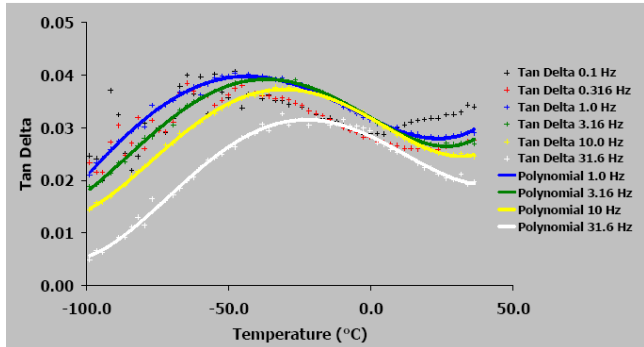
If a polymer melt is cooled extremely rapidly, the polymer will not have time to organise itself into a crystalline structure. The molecular structure will have an amorphous, or partially amorphous, disorganised form. Some polymeric materials, such as PET, will have a tendency to form a crystalline structure if they are allowed to cool slowly. It is therefore essential to rapidly cool this material, if a clear amorphous material with the associated properties of the amorphous form, is required e.g. a plastic drinks bottle. The amorphous form is far less brittle and also transparent compared to a crystalline PET. Many polymeric materials have a mixture of crystalline and amorphous phase present. The properties of these materials often reflect this blend. Only the amorphous component of a polymer will show a glass transition.

The two graphs below show the modulus and the $\tan \delta$ response from PVC. In the modulus graph, the glass transition is reflected in frequency dependence and a corresponding drop in modulus as the material goes from the rigid glassy to the softer rubbery state. The $\tan \delta$ graph shows an increase in the damping properties of the material as it goes through the glass transition. The frequency dependence is also observed.



Beta Relaxations, β

Like the glass transition, β relaxations are conformation changes in a material but occur at a much lower temperature. The size of the event observed, independent of the technique used, is often much smaller as the conformation change is not as large as a glassy to rubbery state. Although it depends on the polymer used, the β relaxation is often attributed to rotation of the polymer backbone. This movement has a restricted effect on the conformation but can be observed using relaxation methods like DMA. The graph on the right shows the β relaxation for PVC run at multiple frequencies. The peak in the $\tan \delta$ shows the β relaxation position. There is an increase in the damping properties of the material during the β relaxation as there was for the T_g . For clarity, only the $\tan \delta$ is plotted although the modulus will show a frequency dependence and, like the T_g , a drop in modulus through the transition.



Gamma Relaxations, β and other low temperature relaxations

Gamma relaxations can sometimes be detected in materials and are often found at very low temperatures. They are often attributed to configurational changes in side groups of polymers where movement is restricted below the relaxation and free above.

Below is a graph indicating the number of polymers with T_g or β relaxation in a specific temperature range. The data was correlated from internal data at Triton Technology and also the Handbook of Chemistry and Physics. It can be seen that the T_g is most often found in the range of 0 to 100°C whereas the β relaxation is nearly always found below 0°C and sometime below -170°C. No relaxation events are seen above 340°C.

