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## MEASUREMENT OF T<sub>g</sub> BY DSC

### What is T<sub>g</sub>?

T<sub>g</sub> is the accepted abbreviation for the *glass transition temperature* or event. All amorphous materials will yield a T<sub>g</sub> during heating and T<sub>g</sub> is the main characteristic transformation temperature of a amorphous material. The glass transition event occurs when a hard, solid, amorphous material undergoes its transformation to a soft, rubbery, liquid phase. T<sub>g</sub> is a valuable characterization parameter associated with a material and can provide very useful information regarding the end-use performance of a product.

### Time Dependency of T<sub>g</sub>

When a viscous liquid is cooled without undergoing crystallization, the liquid will (and must) convert to a solid at some temperature, which is T<sub>g</sub>. The molecular rotational motions associated with the viscous liquid material will 'freeze' at T<sub>g</sub>. At T<sub>g</sub> there is a stepwise decrease in the heat capacity of the sample since the solid phase must have a lower value of C<sub>p</sub> as compared to the liquid. Unlike the melting transition, there is no latent heat involved in stopping the molecular motions at T<sub>g</sub>. The freezing of molecular motions is time dependent and, therefore, T<sub>g</sub> is, as a direct consequence, time dependent. Factors such as heating and cooling rates will have a significant effect on T<sub>g</sub>.

### Polymers and T<sub>g</sub>

Polymeric materials frequently exhibit a T<sub>g</sub> even if the polymer is semi-crystalline and not totally amorphous. As a rule of thumb, most polymers will have a ratio of T<sub>g</sub>/T<sub>m</sub> of between 0.50 and 0.75, where T<sub>m</sub> is the polymer's melting point (°K). The glass transition temperature exhibited by a polymer is dependent upon the chemical make-up of the material. In general, factors increasing the stiffness of the polymeric molecular segments will tend to increase T<sub>g</sub>. As the polymeric molecular rotations become more difficult or hindered, the T<sub>g</sub> will increase.

### Molecular Weight and T<sub>g</sub>

It is well known that T<sub>g</sub> increases with increasing molecular weight, M. This is expressed by the Fox and Flory equation:

$$T_g = T_{g(\infty)} - K_g/M$$

where T<sub>g(∞)</sub> is the limiting T<sub>g</sub> at a very high molecular weight and K<sub>g</sub> is a constant.

## **Tg and Degree of Cure**

Thermosetting materials are those which undergo an irreversible, chemical reaction, known as curing, which produces a cross-linked structure. Thermosets remain amorphous, although, above  $T_g$ , the liquid

state goes from a freely flowing state for the uncured material to a rubbery state for the cured thermoset. The degree of cure is a very important parameter in determining the end-use properties, such as stiffness or creep, for the material. The  $T_g$  of a thermoset material is related to the degree of cure.  $T_g$  increases significantly as the curing reaction proceeds to completion due to the establishment of a cross-linked molecular structure. Eventually, as the degree of cure of the thermoset approaches 100% or complete cure, the  $T_g$  of the material will reach a limiting value,  $T_g(\infty)$ .

## **Tg and Plasticizers**

Plasticizing agents are sometimes added to polymers to improve its flow, and consequently processibility, and to reduce brittleness. Adding a plasticizer will cause the  $T_g$  of the polymer to decrease. If the  $T_g$  of the polymer is reduced sufficiently, its properties change from those of a hard, brittle solid to those associated with a soft, flexible rubber. As an example, dioctyl phthalate (DOP) is added to PVC (polyvinyl chloride) to reduce its  $T_g$ . In its unplasticized state, PVC has a  $T_g$  near 80°C and the unplasticized PVC is used in applications where strength and rigidity are important, such as pipes. If PVC is heavily plasticized with DOP, the PVC becomes soft and flexible since  $T_g$  is reduced to well below room temperature. An example is disposable gloves where the  $T_g$  of the plasticized PVC is approximately -50°C.

## **Tg and Crystallinity**

A semi-crystalline polymer is composed of two main phases: amorphous and crystalline. As a polymer becomes more crystalline, the fraction of the amorphous component becomes increasingly smaller; and, therefore, the change in the sample's  $C_p$  at  $T_g$  ( $\Delta C_p$ ) becomes smaller. Eventually, if the polymer becomes highly crystalline, the DSC instrument may no longer have the necessary sensitivity to detect  $T_g$ . (The Seiko DSC6100 may prove useful for this application since its sensitivity level is a factor of 10 to 30 times greater than other commercial DSC instruments.) In general, the  $T_g$  temperature will increase somewhat as the crystalline content of the polymer increases.

### **Tg and Orientation**

When a molten polymer is subjected to stretching during processing, orientation of the polymer chains occurs. Orientation can cause the Tg of a polymer to increase substantially due to the hindered rotations of the molecules. Highly oriented polymers, such as films or fibers can have a Tg which is 20 to 30°C higher than the unoriented, amorphous polymer.

### **Tg and Aging**

If an amorphous polymer has its Tg above room temperature, physical aging can occur if the material is stored at room temperature for a prolonged period. The effects of aging will be observed as an endothermic peak at Tg in the DSC results. The magnitude of this relaxation peak at Tg will increase as the aging time at room temperature becomes longer. The peak can become large enough that it takes on the appearance of a melting peak; but the transformation does not involve melting processes whatsoever. The peak is simply a consequence of the molecules acquiring a longer overall relaxation time as the amorphous material is permitted to physically age at room temperature. If the aged material, exhibiting the relaxation peak at Tg, is heated to a temperature above its Tg, cooled back to a temperature well below Tg and then immediately heated at the same rate as used for cooling, a simple 'classic' stepwise change in the DSC heat flow or heat capacity will be obtained at Tg, without the occurrence of the enthalpic relaxation peak.

### **Tg and Copolymers**

Block copolymers are those where the polymer main chain consists of alternating long sequences of two chemically different polymers. Block copolymers behave as two phase systems with two distinct sets of physical properties analogous to physical mixtures of the two different polymers. Each phase will exhibit its own distinct Tg. Thus, if the Tg's of the two polymers are different enough, the block copolymer material will exhibit two Tg's during heating by DSC. Random copolymers are those which consist of random alternating blocks along the main polymer chain. For random copolymers, there are no longer two distinct phases and the random copolymers will exhibit a single, broad Tg which lies somewhere between the two Tg's of the individual polymer comprising the copolymer. The relationship between Tg and composition is not always linear for a random copolymer system.

### **Experimental Tips for Measuring Tg by DSC**

Best results, when testing a sample for its Tg, are obtained by using the following suggested guidelines:

- use a sample mass between 10 and 20 mg
- keep the sample as thin and as flat as possible to minimize the occurrence of thermal gradients
- heat the sample at a rate of 10 to 20°C/min
- start the experiment so that three minutes of 'run time' are obtained before the onset of the Tg is encountered
- when analyzing powder, compress the powder into the pan with a glass or metal rod to provide better thermal contact and to give a larger sample mass
- if the Tg is very weak, increase the sample mass
- better identification of weak Tg's can be obtained by subtracting out the baseline results (empty DSC cell) from the sample data file
- a heat-cool-reheat DSC experiment oftentimes provides a 'cleaner' Tg during the reheat segment.