THERMAL ANALYSIS

application note

Measurement of Tg by DSC

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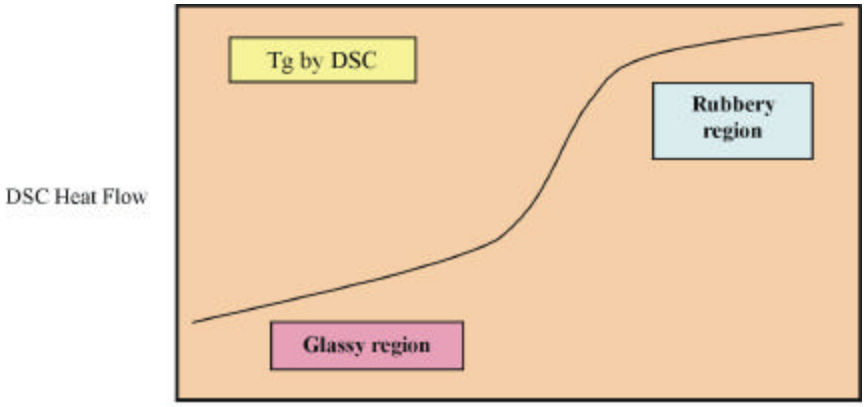
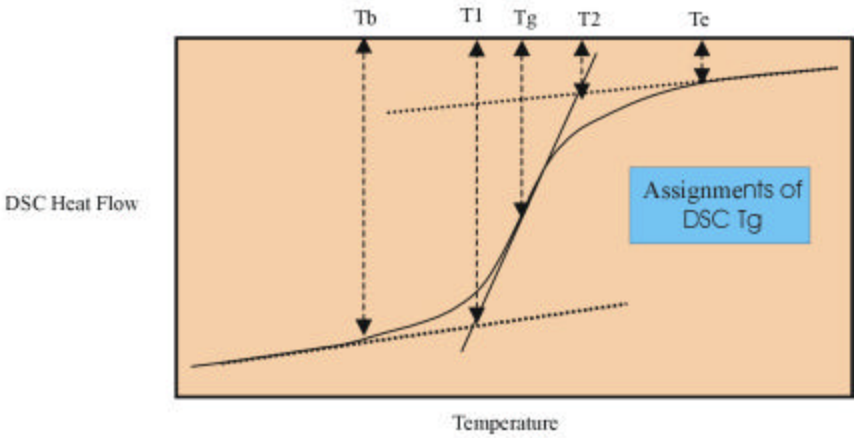
- **What is Tg?** Tg is the accepted abbreviation for the *glass transition temperature*. All amorphous (non-crystalline or semi-crystalline) materials will yield a Tg during heating and Tg is the main characteristic transformation temperature of the amorphous phase. The glass transition event occurs when a hard, solid, amorphous material or component undergoes its transformation to a soft, rubbery, liquid phase. Tg is a valuable characterization parameter associated with a material and can provide very useful information regarding the end-use performance of a product. The 'classic' Tg is observed as an endothermic stepwise change in the DSC heat flow or heat capacity.

- **What is the Practical Importance of Tg?** The glass transition event is one of the most important characteristic properties of a material. It represents the lower end use temperature since a material cannot be processed or worked with once its temperature drops below Tg. The Tg of a material is related to many important end use properties of a wide range of materials. For example, a two-part epoxy thermosetting resin is initially a liquid at room temperature because its Tg is well below 25 C. As the resin crosslinks, its Tg increases and will be well above room temperature after the resin cures. In applications involving epoxy curing, such as coatings for motor windings, it is essential that Tg of the resin be well above the operating temperature to avoid failure of the motor. For foods containing sugar and starches, the crispness exhibited by a cracker or cookie is often related to the sugar/starchy phase having its Tg above room temperature. If the food becomes stale, by absorbing water from the air, the Tg will drop below room temperature due to plasticizing effects, and the food will lose its desired crispness. For clothing containing polyester, when the





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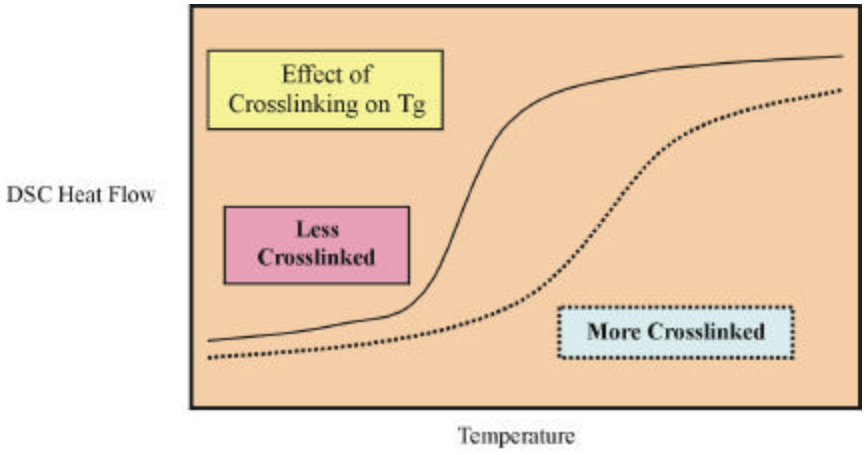
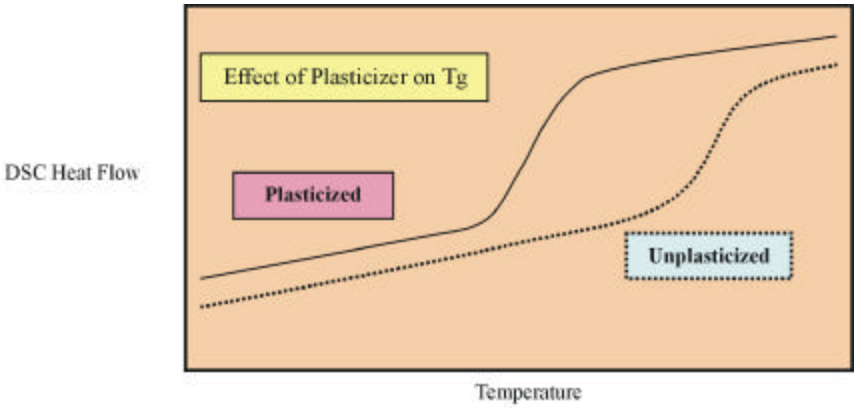
clothes are ironed, the amorphous component in the polyester will exceed Tg and a crease can be placed into the garment. When the iron is removed, the temperature drops below Tg of the polyester, and the crease is set in.

- **Time Dependency of Tg.** When a viscous liquid is cooled without undergoing crystallization, the liquid will (and must) convert to a solid at some temperature, which is Tg. The molecular rotational motions associated with the viscous liquid material will 'freeze' at Tg. At Tg there is a stepwise decrease in the heat capacity of the sample since the solid phase must have a lower value of Cp as compared to the liquid. Unlike the melting transition, there is no latent heat involved in stopping the molecular motions at Tg. The freezing of molecular motions is time dependent and, therefore, Tg is, as a direct consequence, time dependent. Factors such as heating and cooling rates will have a significant effect on Tg. Because of the complex nature of the glass transition event, it becomes more difficult to assign a true transition temperature to Tg. In fact, there are actually 5 accepted ways in which the Tg of a material can be assigned by DSC, as is represented in the following figure. Tb represents the very start of the detection of the change in heat flow or heat capacity at Tg, T1 is the onset temperature, Tg is the mid-point temperature and the most commonly accepted way of defining or reporting the glass transition, T2 is the endset temperature, and Te reflects the very end of the detection of the glass transition event.





- **Polymers and Tg.** Polymeric materials frequently exhibit a Tg even if the polymer is semi-crystalline and not totally amorphous. As a rule of thumb, most polymers will have a ratio of Tg/Tm of between 0.50 and 0.75, where Tm 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 Tg. As the polymeric molecular rotations become more difficult or hindered, the Tg will increase.
- **Molecular weight and Tg.** It is well known that Tg increases with increasing molecular weight, M. This is expressed by the Fox and Flory equation:

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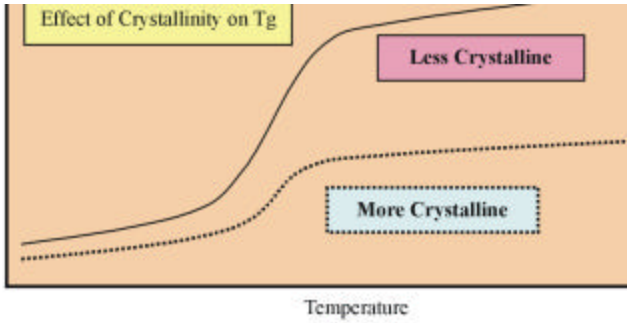
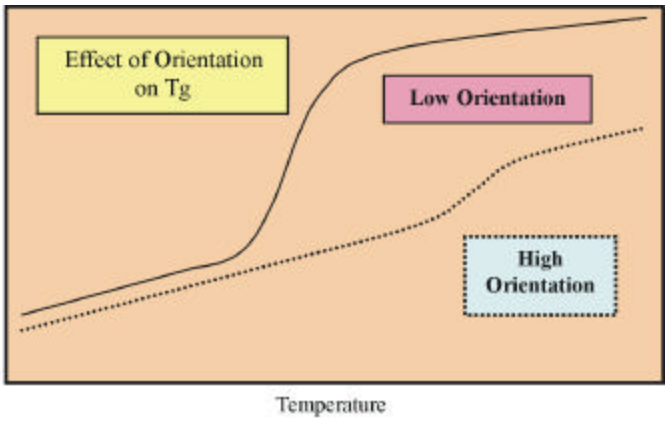
$$Tg = Tg(\infty) - Kg/M$$

where Tg(∞) is the limiting Tg at a very high molecular weight and Kg is a constant.

- **Tg and Degree of Cure.** Thermosetting materials are those which undergo an irreversible, chemical reaction, known as curing, which produces a crosslinked structure. Thermosets remain amorphous, although, above Tg, 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 Tg of a thermoset material is related to the degree of cure. Tg increases significantly as the curing reaction proceeds to completion due to the establishment of a crosslinked molecular structure. Eventually, as the degree of cure of the thermoset approaches 100% or complete cure, the Tg of the material will reach a limiting value, Tg(∞).

- **Tg and Plasticizers.** Plasticizing agents are sometimes added to polymers to improve its flow, processibility and to reduce brittleness. Adding a plasticizer will cause the Tg of the polymer to decrease. If the Tg of the polymer is reduced sufficiently, its properties are 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 Tg. In its unplasticized state, PVC has a Tg 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 Tg is reduced to well below room temperature. An example is disposable gloves where the Tg of the plasticized PVC is approximately -50 C. Absorbed water often functions as a plasticizer on many hydrophilic materials (nylon polymers, starches and sugars, for example).





- **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 Cp at Tg (ΔCp)

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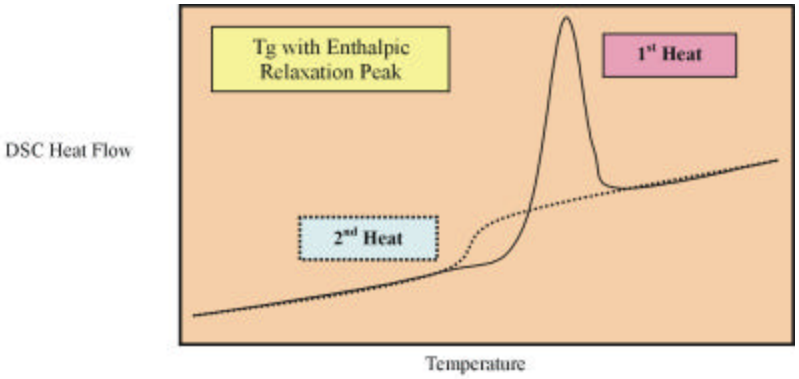
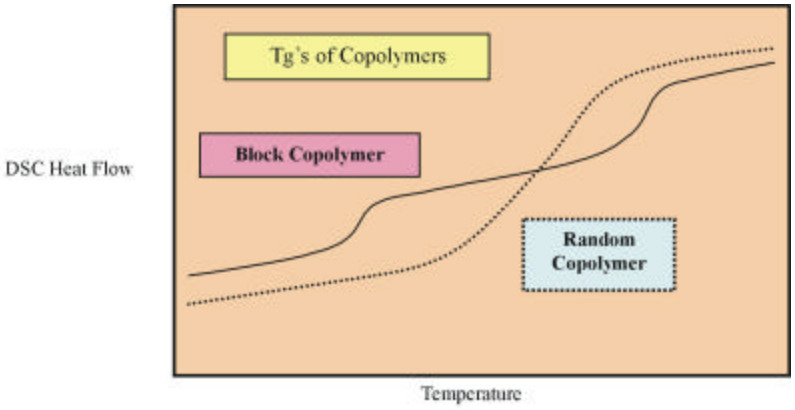
becomes smaller. Eventually, if the polymer becomes highly crystalline, the DSC instrument may no longer have the necessary sensitivity to detect Tg. In general, the Tg temperature will increase somewhat as the crystalline content of the polymer increases.

- **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 yield a Tg that is 20 to 30 C higher than the unoriented, amorphous polymer.

- **Tg and Aging.** If an amorphous polymer yields 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 data. 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 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 will be obtained at Tg, without the occurrence of the enthalpic relaxation peak. The Tg observed during the 2nd heating segment reflects the chemistry of the molecules or material, while the 1st heating step represents the physics as well as the chemistry of the as-received material. When reporting the Tg of a material, it is important to specify the particular experimental conditions that were used to analyze the sample.

- **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





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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, as this provides a better baseline response
  - 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 yields a 'cleaner', easier to interpret Tg during the reheat or 2nd heating segment
  - StepScan DSC provides a clearer evaluation of Tg from the storage Cp signal

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