



Characterization of Epoxy Resins Using DSC

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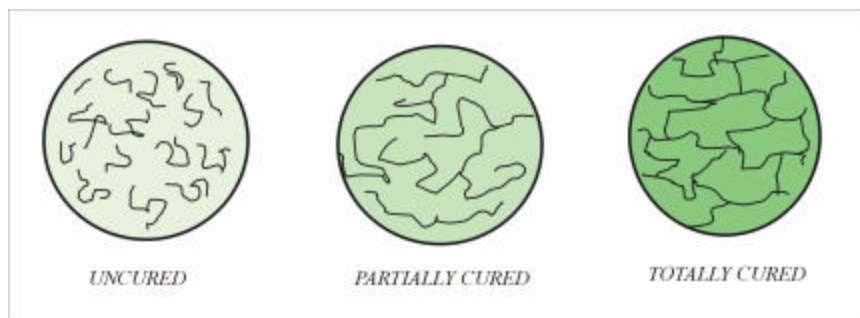
Introduction

Thermosetting materials are those which exist in an unreacted or partially reacted state and which will undergo crosslinking after mixing the base components or heating to elevated temperatures. The properties of thermosetting materials are very much dependent upon their chemical formulation or composition along with the conditions (e.g., time and temperature) to which the resins are exposed during processing. Small changes in the formulation or processing conditions, which can affect the curing of the resins, can significantly affect the properties of the end product. The use of thermal characterization studies on thermosetting resin materials will help to avoid production problems and will be useful for troubleshooting purposes. One of the best means of analyzing the properties of unreacted thermosets and the end product is with differential scanning calorimetry (DSC). DSC has proven itself to be a very useful, if not indispensable, analytical technique for the characterization of thermosetting materials.

Differential Scanning Calorimetry

The DSC instrument measures heat flow into or from a sample under heating, cooling or isothermal

Figure 1. Representation of increase in crosslink density of a thermosetting material.



conditions. DSC measures the quantitative heat flow as a direct function of time or of the sample temperature. This heat flow – temperature data provides extremely valuable information on key physical and chemical properties associated with thermosetting materials, including:

- Glass transition or softening temperature (T_g)
- Onset and completion of cure
- Heat of cure
- Maximum rate of cure
- Percent cure
- Heat capacities (C_p)

These properties can then be used to address some of the everyday problems, which confront the manufacturer, or user of thermosetting resins. Example include:

- Quality assurance
- Establishment of optimal processing conditions
- Estimation of percent cure of end product
- Product integrity
- Analyses of competitive materials

PerkinElmer offers a variety of state-of-the-art DSC instruments for the characterization of a wide range of materials and applications, including the characterization of thermosetting materials.

Curing of Thermosets

A thermosetting resin undergoes an irreversible chemical reaction during curing. As the components in the resin system cure, heat is evolved by the resin, which is monitored by the DSC instrument. Figure 1 represent the changes taking place

Figure 2. DSC results on an uncured epoxy resin.

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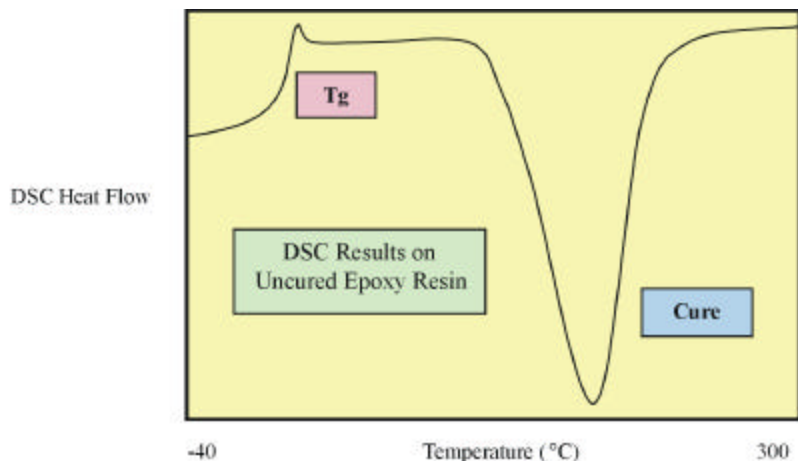
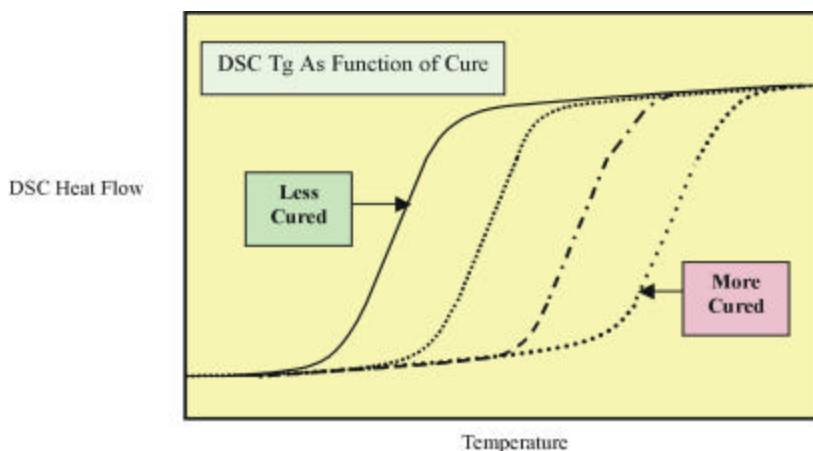


Figure 3. Increase in DSC Tg as a function of cure for a thermosetting resin.



crosslinking and these changes can be readily observed by DSC.

DSC Results on Epoxy Resin

Displayed in the Figure 2 are the DSC results obtained by heating an uncured epoxy resin system at a rate of 20 C/min. The plot shows the heat flow as a function of the sample temperature.

The glass transition event, Tg, is observed at 0 C as an endothermic stepwise increase in the heat flow or heat capacity. Tg represents the region in which the resin transforms from a hard, glassy solid to a viscous liquid. With a further increase in the sample temperature, the resin eventually undergoes curing and this is observed as a large exothermic peak. The onset

of cure is the temperature at which the heat flow deviates from a linear response and the exothermic peak temperature reflects the maximum rate of curing of the resin. At the completion of curing or crosslinking, the DSC heat flow returns to a quasi-linear response. The area under the exothermic can be integrated to give the heat of cure, ΔH_{cure} (J/g).

As a thermosetting resin cures or crosslinks, two main things happen:

- Tg increases
- Heat of cure decreases

The changes in Tg and the heat of cure can be used to characterize and quantify the degree of cure of the resin system. As the resin system approaches complete cure, the Tg will achieve a maximum value, $Tg(\infty)$. This is shown in the Figure 3

The increase in the Tg observed as a function of curing represents the increase in the molecular weight of the resin system. The actual value of $Tg(\infty)$ is dependent upon the chemical make-up of the particular resin system.

The increase in Tg with regards to cure time is shown in the Figure 4 for a given epoxy resin powder system.

As the resin becomes more crosslinked, the heat of curing becomes increasingly smaller and, as the material becomes completely cured, the heat of cure becomes undetectable. This is shown in the Figure 5.

The heat of cure may be used to determine the percent cure of a resin material. The following simple calculation provides this information:



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Thermal Analysis

Figure 4. Increase in Tg of epoxy resin with increasing cure levels.

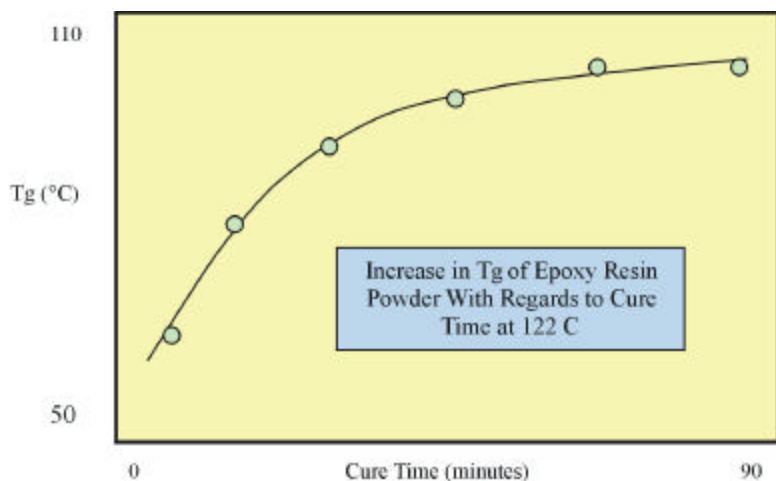
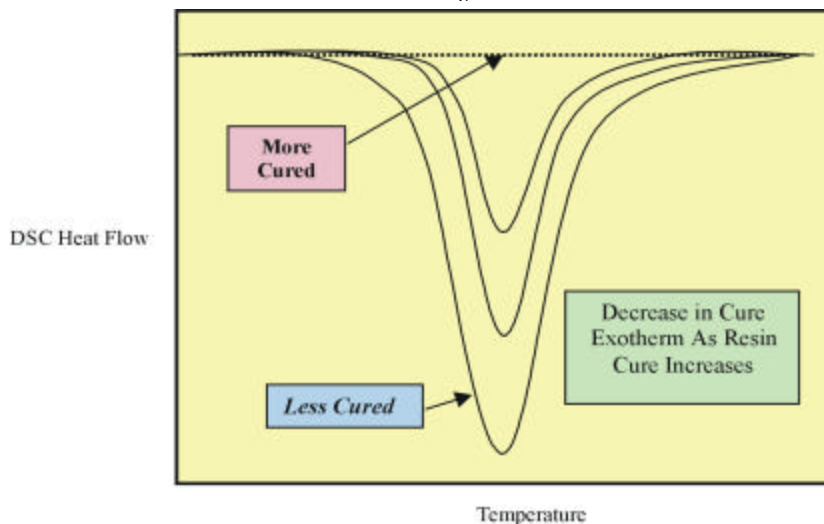


Figure 5. Decrease in residual cure exotherm for epoxy resin with increasing cure levels.



$$\% \text{ Cure} = \frac{[\Delta H_{\text{uncured}} - \Delta H_{\text{cured}}]}{[\Delta H_{\text{uncured}}]} \cdot 100\%$$

In this relationship, $\Delta H_{\text{uncured}}$ represents the heat of cure of the uncured resin material and ΔH_{cured} is that of the partially cured resin. If no heat of cure is observed, then the value of % Cure is 100% and it is

assumed that the resin is completely cured. In reality, the resin may still have some lingering residual cure, but the DSC is no longer sensitive enough to detect this. Dynamic mechanical analysis (DMA), with its very high inherent sensitivity, may still detect subtle changes in the crosslink density of the

thermosetting resin system. However, for most resin materials, DSC does an excellent job of providing percent cure information and in making distinctions in resins, which are not fully cured.

The percent cure value is important for end products generated from thermosetting resins as it is related to the following properties:

- Brittleness
- Impact resistance
- Long term stability
- Creep or 'cold flow'
- Solvent resistance
- Product integrity

Figure 6 shows an example of the percent cure determined for an epoxy resin powder material.

The unreacted resin had a heat of cure of 45.7 J/g while the resin powder being evaluated had a heat of cure of 14.2 J/g. The percent cure obtained on this epoxy resin powder was calculated to be 69% based on the DSC results. This value is very useful for quality assurance and for process optimization purposes. If the percent cure for a particular resin is too low, the resin (and product) may fail in usage as the resin will exhibit a low Tg and will be unstable. Similarly, for some applications, there is a

danger if the resin achieves too high of a cure, as some resins can become too brittle at high levels of cure.

Summary

DSC is a valuable analytical tool for the analysis and characterization of thermosetting materials, such as epoxies. DSC can provide informative data on such key properties as:



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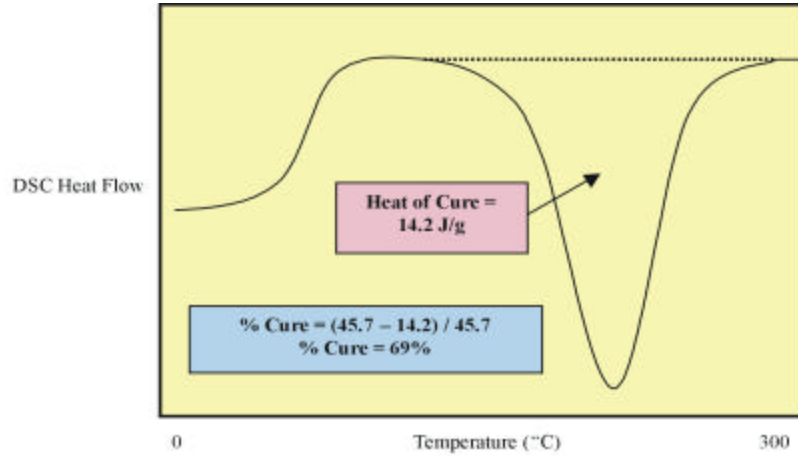
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Figure 6. Determination of % cure of partially cured epoxy resin by DSC.



- Softening or glass transition temperatures
- Residual heats of cure
- Percent cure
- Onset temperature of cure
- Maximum rate of cure
- Completion of cure

PerkinElmer offers a number of high performance DSC systems for the complete characterization of thermosetting materials.

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