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DIFFERENTIAL SCANNING CALORIMETRY AS A QUALITY CONTROL METHOD FOR EPOXY RESIN PREPREG

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>Differential scanning calorimetry is a reliable and effective method for the quality control of an epoxy resin prepreg material. There are two basic methods for determining the extent of cure for this material, the glass transition temperature and the heat of reaction. The first method requires the measurement of the glass transition temperature for the uncured material and the glass transition temperature for a fully cured material. This data can then be used to determine the degree of cure for an unknown sample. The

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20. ABSTRACT (CONT'D)

second method requires the measurement of the enthalpy of the cure reaction for an uncured material and relates this value to the enthalpy of a sample. The use of one or both of these methods can be used to evaluate an epoxy resin to determine the extent of cure of the material. (AW)

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INTRODUCTION

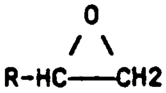
Epoxy resin prepreg can be purchased in various forms with the thermosetting resin completely mixed and partially cured. The cross-linking cure process continues at a slow rate, thus refrigeration is required to produce a useful shelf life of about six months. Poor lamination can result from using material that is overcured, past its shelf life, or processed with an improper curing cycle. Therefore, an evaluation of the curing process and the extent of cure of the material is essential. Differential scanning calorimetry (DSC) is a very useful technique for this purpose. There are two basic approaches that can be taken to measure the percent or degree of cure for an epoxy resin.

1. Glass Transition Temperature (Tg) - As the degree of cure of an epoxy resin increases through the polymerization and cross-linking process, the glass transition temperature also increases to a maximum value. By determining the glass transition temperature of the material, the degree of cure can be determined.

2. Heat of Reaction (ΔH) - The curing process of an epoxy resin is an exothermic process whose enthalpy of reaction can be measured through the use of differential scanning calorimetry. The amount of energy given off indicates the extent the reaction or curing process has progressed. By relating this energy to the total energy of the reaction, the degree of cure can be determined.

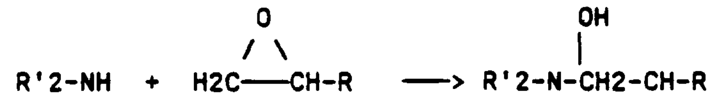
EPOXY RESINS

Epoxy resins are a general class of materials characterized by a chemical structure containing the epoxide or oxirane ring

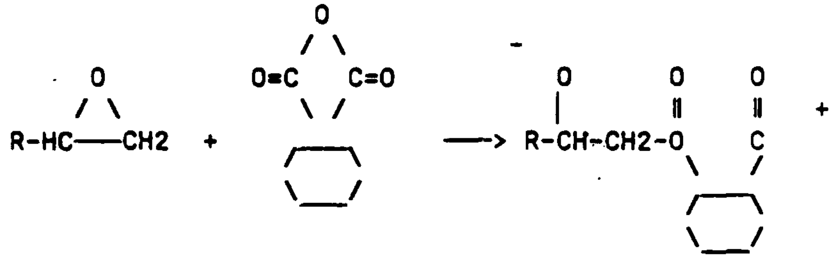


The curing process can be accomplished by a variety of cross-linking agents known as hardeners or by catalysts that promote polymerization. There are three major types of epoxy resins of commercial significance, epichlorohydrin-bisphenol A, epoxy novalak, and epoxidized polyolefin resins. The most commonly used curing agents are amines and anhydrides.

Amines:



Anhydrides:



Epoxy resin prepreg is a thermoset polymeric material that reacts through the curing process to form a cross-linked molecular structure. With the application of temperature, the cross-linking process forms a rigid structure. Generally, the lower the curing temperature, the slower the reaction; the higher the curing temperature, the faster the cure and the greater the risk of polymer degradation (ref 1).

Cured epoxy resins are amorphous organic polymers, glasses that do not have a crystalline structure. Their structure primarily depends on their thermal history, the catalyst used to cross-link the material, and the extent of the cure. The cure of a reactive prepolymer involves the transformation of low

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[1] Cummings, L. C., "Application of Differential Scanning Calorimetry to Cure Optimization and Quality Control of a Vinyl Ester Resin," Polymer Composites, Vol. 4, No. 4, 1987, pp. 201-205.

molecular weight monomers and oligomers from the liquid to the rubber and solid states. Growth and branching of the polymeric chains occur in the liquid state, where the system is still soluble and fusible. The process continues to develop into an infinite network after the gel point, through intramolecular reactions of the branched molecules, and finally leads to an insoluble cross-linked solid.

The temperature variations during cure, which determine the degree of cure in the epoxy resin system, have a high degree of dependence on the heat of reaction, the specific heat, and the thermal conductivity that the material exhibits at various stages of the cure cycle. Through the use of differential scanning calorimetry, these parameters can be evaluated and used to control the curing process and the quality of the material.

DIFFERENTIAL SCANNING CALORIMETRY

The term differential scanning calorimetry was first used to describe the instrumental technique developed in 1963 by the Perkin-Elmer Corporation. It differs from differential thermal analysis in that its prime purpose is to measure the heat flow between a sample and reference rather than the temperature difference. There are two predominate methods for measuring the differential heat flow.

1. Power-compensated DSC - This technique utilizes individual heaters for both the sample and reference cells, holding both isothermally. The difference in the power input to each cell used to maintain isothermal conditions is recorded and plotted on an X-Y recorder. The curve obtained is a recording of the heat flow, dQ/dt, as a function of temperature.

2. Heat flux DSC - This technique measures the temperature difference between the sample and reference cells using thermocouples attached to each

cell. Since there is no direct method for measuring the heat flow, the temperature difference at a thermal resistor of known size is used and the heat flow is given by $dQ/dt = (Ts-Tr)/Rt$, where Rt is the thermal resistance.

The cure analysis of an epoxy resin material can be performed in one of two modes, either isothermal (heated at a constant temperature) or dynamic (heated at a constant rate). When the sample undergoes an enthalpic transition or reaction, there is a temperature difference established between the sample and the reference. The heat flow resulting from the temperature difference is recorded on a thermogram. Depending on whether it is an exothermic or an endothermic event determines the direction of the displacement from the baseline. The area under the curve then becomes a measure of the heat of reaction.

Typically, samples can range in size from 1 to 100 mg and can be heated at scanning rates up to 200°K/min. Though not as accurate as conventional calorimetry methods, DSC can achieve a typical accuracy of one to two percent. However, due to the speed with which an analysis can be performed, it has a distinct advantage over other methods.

GLASS TRANSITION TEMPERATURE

One method of determining the extent of cure of an epoxy resin prepreg is to evaluate the glass transition temperature. As the resin cures, the glass transition temperature increases through the cure to some maximum value. Thus, determining this temperature for a particular material can indicate the extent to which the material has been cured.

The main characteristic temperature of an amorphous material between the solid and liquid states is the glass transition. A polymer cooled through the liquid to the solid states goes through the glass transition temperature at which point large scale molecular motion is restricted without change in structure. Since the heat capacity of the glass is lower than that of the liquid at the same temperature and there is no latent heat stopping molecular motion, the glass transition takes on the appearance of a second order thermodynamic transition, which shows a discontinuance in the heat capacity and expansion coefficient. On heating at the glass transition temperature, the heat flow to the sample increases as the polymer absorbs the thermal energy necessary for molecular rotation. The transition is therefore endothermic. The heat capacity increases discontinuously as the resin changes from a glass to a more fluid rubbery material.

As the molecular weight of a polymer increases via curing, there is an increase in the glass transition temperature as noted in Figure 1 (uncured prepreg Tg = 60°C; cured prepreg Tg = 137°C). A low molecular weight uncrosslinked polymer has a large number of movable segments and chain ends in a given volume. Being less restrained, the chain's end segments are more active and can be taken to a lower temperature before the thermal energy is too low for molecular motion, thus exhibiting a lower glass transition temperature. As the polymer cures and the degree of cross-linking increases, the motion becomes more restricted; thus the glass transition temperature increases. The greater the degree of cross-linking or cure of a polymer, the higher the glass transition temperature until a maximum value is reached at full cure. The relationship between the glass transition temperature and the extent of cure can be noted in Figure 2.

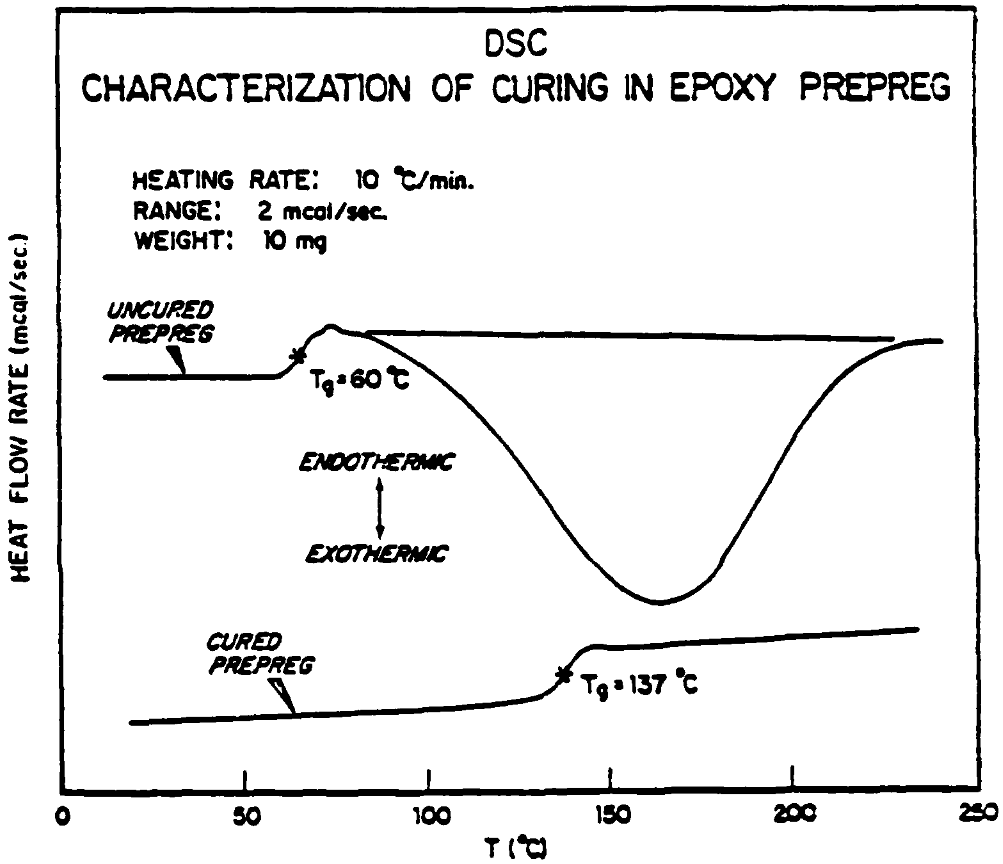

Figure 1. DSC characterization of curing in epoxy prepreg (ref 2).

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[2] Brennan, W. P. and Cassel, R. B., "Applications of Thermal Analysis in the Electrical and Electronics Industries," Thermal Analysis Application Study 25, Perkin-Elmer Corporation, Norwalk, CT, April 1978, p. 3.

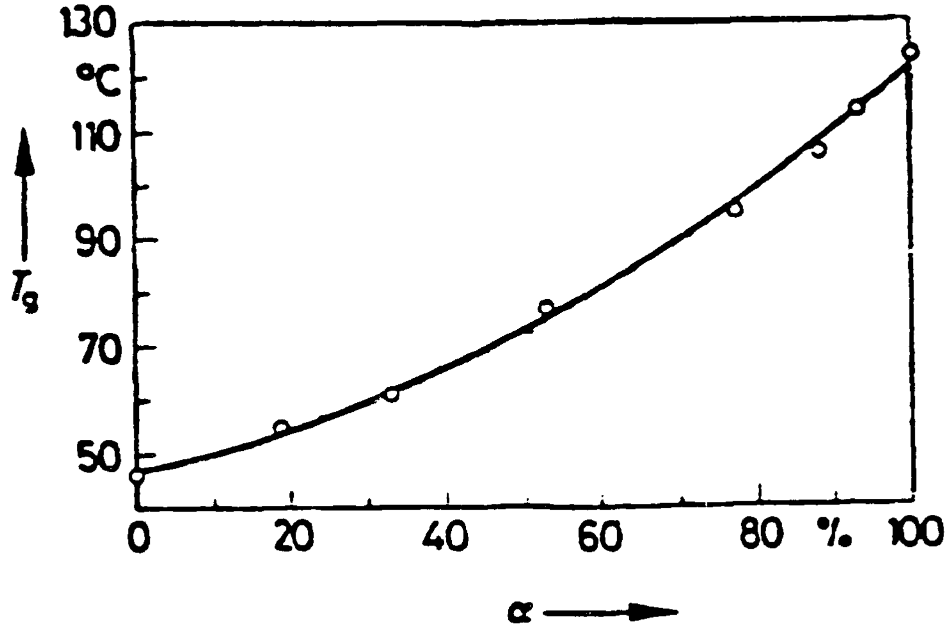

Figure 2. Dependence of glass-transition temperature T_g on degree of conversion α of epoxy resin prepreg (ref 3).

HEAT OF REACTION

The extent of cure of an epoxy resin prepreg also can be evaluated using the cure exotherm obtained by differential scanning calorimetry. Typical thermograms are shown in Figure 3 for three samples analyzed at three various stages of cure. At approximately 100°C, sample 1 (in the uncured or as-received state) begins the curing reaction and reaches a peak maximum at around 180°C. The reaction exotherm is the result of the heat produced by the chemical reactions involved in the curing process. Of particular interest is the area under the curve which correlates to the enthalpy of reaction. It represents the heat of the reaction at constant pressure for the curing process taking place in the calorimeter.

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[3] Kretzschmar, K. et al., "Differential Scanning Calorimetry of Prepregs for Multilayer Printed Circuit Boards," <u>Siemens Forsch-u. Entwickl.-Ber. Bd.</u>, Vol. 16, No. 3, 1987, p. 103.

When a material undergoes a phase change such as melting or a chemical reaction such as curing, changes in enthalpy (H) and heat capacity (Cp) occur and can be related by the equation $Cp = (dH/dT)p$ (ref 4). The heat flow in a differential scanning calorimeter can be related to both the heat capacity and enthalpy by $dQ/dt = mCp\Delta T$ where m is the mass and dQ/dt is the heat flow (ref 4).

The enthalpy of the curing reaction for the uncured resin can be used to correlate the degree to which an epoxy sample is cured. As noted in Figure 3, sample 2 (five-minute cure at 170°C), the enthalpy decreases as the degree of cure increases. This is further shown in Figure 3, sample 3 (ten-minute cure at 170°C). Thus, as the extent of cure increases, the area under the exotherm decreases until the resin is fully cured. The amount of uncured resin in any batch of prepreg is proportional to the enthalpy of the curing reaction upon heating. The enthalpy is thus inversely proportional to the degree of cure (ref 5).

Basically, if the energy evolved in curing an initially uncured sample is Ho and the energy evolved for a partially cured sample is ΔH, then the degree of cure for the partially cured sample is $\Delta Ho - \Delta H/\Delta Ho$ (ref 6). However, this is not such a straightforward measurement. In Figure 3 it is noted that it becomes a problem to accurately determine the baseline for the cure exotherm due to the decomposition at the end of the cure and glass transition prior to the onset.

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[4] Smith, C. A., "The Thermal Characterization of Epoxide Resins," GEC Journal of Research, Vol. 3, No. 3, 1985, pp. 162-166.

[5] Smith, C. A., "Characterization of Polymers Used in Printed Circuit Board Manufacture," Polymer Testing, Vol. 7, 1987, pp. 79-84.

[6] Gray, A. P., "Establishing a Correlation Between the Degree of Cure and the Glass Transition Temperature of Epoxy Resins," Thermal Analysis Application Study 2, Perkin-Elmer Corporation, Norwalk, CT, 1972.

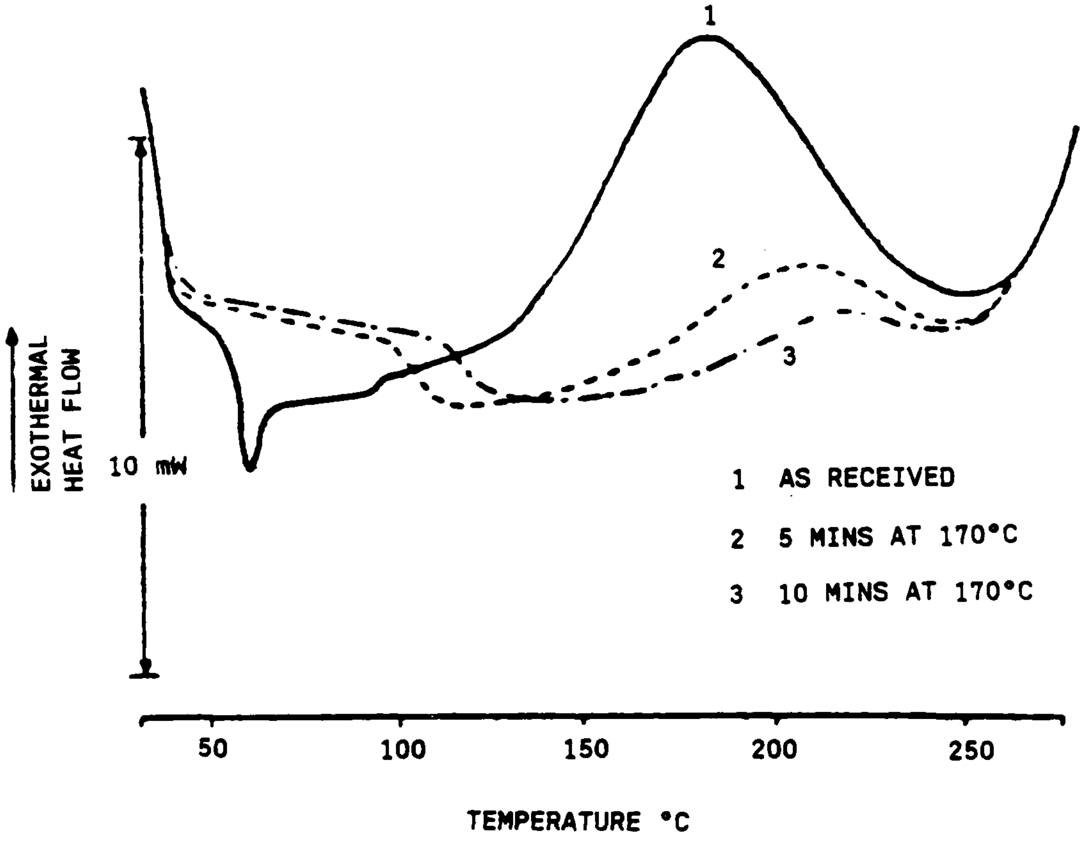

Figure 3. The decrease in enthalpy with degree of cure (ref 4).

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[4] Smith, C. A., "The Thermal Characterization of Epoxide Resins," GEC Journal of Research, Vol. 3, No. 3, 1985, p. 163.

The cure analysis requires consistency in evaluating one cure with the next. Also, the heating rate is critical as it determines the peak temperature of the cure exotherm, the glass transition temperature, and the enthalpy of the reaction.

CONCLUSION

Differential scanning calorimetry is clearly a reliable and reproducible thermoanalytical method of obtaining detailed knowledge of the curing behavior of an epoxy resin prepreg. It was shown that determining the glass transition temperature of a cured epoxy resin could be effectively used to determine the degree of cure. Also, the degree of cure could be determined by comparing the enthalpy of the exothermic reaction of a sample to the exotherm of the uncured material. Since it can be difficult to detect the enthalpy of a reaction for a completely cured epoxy resin, it becomes very important to note the change in the glass transition temperature. Therefore, both sets of data should be used to accurately determine the degree of cure.

It should also be pointed out that variation in the analytical results can be obtained by varying the parameters of the analysis. Variables such as the mass and shape of the sample, the heating rate, and the thermal history of the sample can affect the analytical results obtained. Therefore, it is essential to be consistent from analysis to analysis and to specify the experimental parameters along with the test results for each analysis reported.

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1. Cummings, L. C., "Application of Differential Scanning Calorimetry to Cure Optimization and Quality Control of a Vinyl Ester Resin," Polymer Composites, Vol. 4, No. 4, 1987, pp. 201-205.
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