SII NanoTechnology Inc.

DSC AS PROBLEM-SOLVING TOOL: LIFETIME PREDICTIONS USING DSC KINETICS

Problem

A scientist working for a company which produces epoxy coatings wishes to have an easy to use means of assessing the cure kinetics associated with the thermosetting resin. This information is useful in optimization processing conditions and in determining the relative lifetime of the resins. To take the best advantage of thermosetting materials requires detailed knowledge of the handling, processing and curing of the base resins.

Solution

Differential scanning calorimetry (DSC) provides a straightforward means of examining the cure kinetics associated with thermosetting materials. This is done through the application of the Ozawa approach, which entails heating the resin at different heating rates in the DSC instrument. It is observed that for a reactive material, as the heating rate is increased, the exothermic peak temperature also increases systematically. This systematic increase can be used to determine the reaction kinetics associated with a thermosetting material.

The basis behind the DSC kinetics approach involves determining the rate of conversion of the reactive components at a given temperature:

$$d\square/dt = k(T)\,[1 - \square],$$

$k(T) = A \exp -(E/RT)$
$\square$ = fractional conversion of monomer
$d\square/dt$ = rate of conversion (1/sec)
A = pre-exponential factor (1/sec)
E = Arrhenius activation energy (J/mole)
R = gas constant (8.314 J/mole K)
k(T) = rate constant (1/sec)

The basic kinetics expression can be reformulated to be expressed in terms of the DSC heating rate, B, where B = dT/dt:

$$d\square\tilde{}dT = \{1/B\}\, k(T)\, [1 - \square]$$

This expression can be integrated and solved to yield the activation energy, E, as a function of the DSC heating rate, B:

$$\log B = -0.4567\, \{E/R\}\, \{1/T_p\} + \text{constant}$$

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This equation shows there is a linear relationship between log B and the measured DSC exothermic peak temperature, Tp. As the DSC heating rate is increased, the exothermic peak temperature increases and this data can be used to determine the value of the activation energy, E. A plot of log B versus 1/Tp, for a reactive material, yields a straight line whose slope is -0.4567 E/R, where R is the gas constant.

The assessment of the activation energy and the other kinetic parameters is greatly simplified with the use of the Seiko DSC-Kinetics software. The software package automatically computes the kinetic parameters for a reactive material.

The Seiko DSC offers the thermal analyst the following advantages in the characterization of reactive materials:

- DSC kinetics software
- exceptionally stable baseline performance
- high sensitivity
- precise temperature control

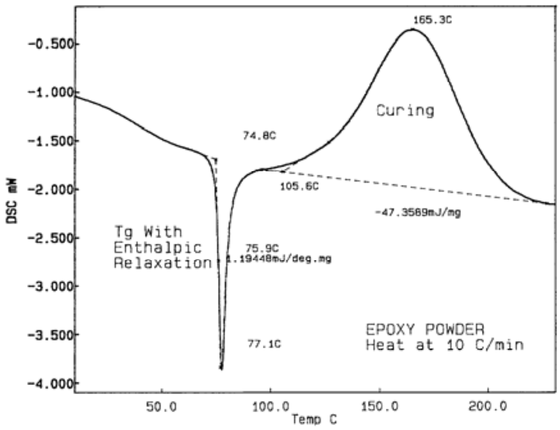

Figure 1

Displayed in Figure 1 are the DSC results obtained on a partially reacted or B-staged epoxy resin material using a heating rate of 10°C/min. The sample exhibits its glass transition event (with a large enthalpic relaxation peak) at 75.9°C. The resin begins to undergo curing at a temperature of 105.6°C and the peak temperature occurs at 165.3°C. This represents the maximum rate of cure at the given heating rate conditions.

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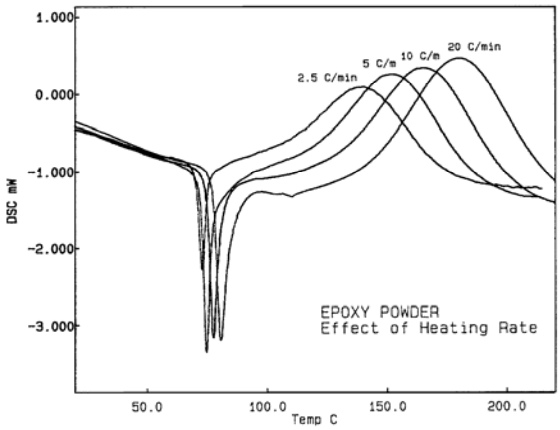

Figure 2

If the sample is analyzed at various heating rates, the cure kinetics associated with the epoxy resin can be established using the Seiko DSC-Kinetics software. In addition to a heating rate of 10°C/min, the resin was heated at rates of 2.5, 5, and 20°C/min. It is recommended to use at least three different heating rates which increase by a factor of two between each successive heating rate. These DSC results are shown in Figure 2. As may be seen, as the heating rate is increased, the exothermic peak temperature also increases, as is to be expected. This systematic increase in the peak temperature can be used to assess the material's activation energy.

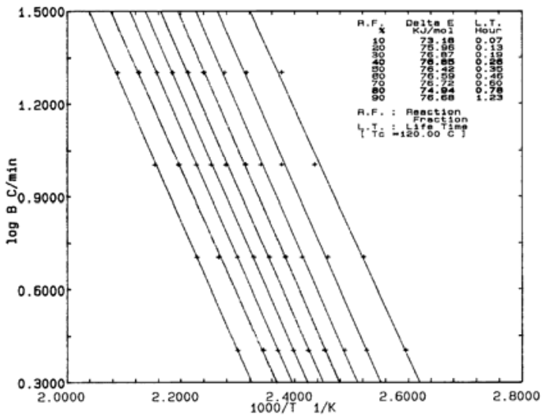

Figure 3

Displayed in Figure 3 are the results obtained on the epoxy resin using the Seiko DSC-Kinetics software. This plot shows the log of the DSC heating rate versus the inverse of

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the DSC exothermic peak temperature at levels of conversion ranging from 10 to 90% in increments of 10%. The activation energies obtained at each of the conversions are displayed in the table in the upper right corner of Figure 3 and these values are essentially identical over the entire conversion range. The average value of the activation energy is 76.6 KJ/mole.

From the determination of the activation energy, the lifetime of the resin can be predicted. Shown in Figure 3, in the upper right corner in the rightmost column, is a table of the lifetimes or conversion times at a reaction temperature of 120.0°C. To achieve 50% conversion for the epoxy resin at 120°C would take 0.35 hour. The half life time, or the time that it takes a reactive material to reach 50% conversion, is a useful parameter to assess relative reactivities for thermosetting materials.

Summary

The modeling of cure kinetics by DSC provides the scientist or engineer with valuable information regarding the optimization of processing conditions or the prediction of lifetimes of thermosetting resins. The analysis of the cure kinetics associated with a resin can be accurately and easily determined using the Seiko DSC-Kinetics software.

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