



Better DSC Isothermal Cure Kinetics Studies Using Power Compensation DSC

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Introduction

One important aspect of a thermosetting resin, such as an epoxy, is the cure kinetics associated with the material. Kinetics refers to the modeling of the effects of temperature and time on the degree of cure of a thermosetting resin. The establishment of cure kinetics provides the scientist or process control engineer with valuable information that can be used to optimize processing conditions or to predict the shelf lifetime of thermosetting resins or composites.

One of the easiest means of determining resin cure kinetics is through the application of differential scanning calorimetry (DSC). The DSC results on a thermosetting resin system can be easily analyzed to obtain the kinetic information.

With DSC, the cure kinetics of a thermosetting resin can be determined by three different approaches:

- Single dynamic heating experiment
- Multiple dynamic heating experiments (3 or more different heating rates)
- Isothermal cure studies at 3 or more different temperatures

The isothermal approach provides the highest degree of accuracy of the cure kinetics of a thermosetting material, such as an epoxy. This is because the maintenance of isothermal conditions eliminates potential problems such as the occurrence of thermal gradients. The isothermal approach is equally valid for standard (nth order) and autocatalyzed resins. The use of the dynamic DSC approach for autocatalyzed systems can result in highly erroneous kinetics results. In addition, for processing optimization, isothermal studies tend to best simulate and mimic the actual processing conditions used to generate the final thermoset product.

Performing proper isothermal cure studies requires a DSC instrument with a very fast response time. This ensures that the sample and instrument can equilibrate quickly once the isothermal target temperature is achieved. A highly responsive DSC ensures that the entire curing exothermic peak will be obtained without losing valuable data.

Power Compensation DSC

The ideal DSC for performing isothermal cure studies of thermosetting materials is the Power Compensation DSC from PerkinElmer Instruments. The very low mass furnaces provide low

thermal inertia and the fastest response time of any DSC instrument on the market. This allows for the ballistic heating of an uncured resin from room temperature to the target temperature (around 150 C) at a rate of 400 or 500 C/min. The rapid response time allows the Power Compensation DSC to quickly 'lock in' on the isothermal target temperature and equilibrate. This provides the best possible isothermal cure peak and minimizes the risk that cure data will be lost, especially at the very crucial beginning portions of the isothermal experiment.

Many epoxy resins follow n-th order kinetics which means that the material exhibits its maximum rate of cure right at the start of the experiment (time = 0). In order to get the complete cure exothermic peak, a highly responsive DSC, such as the Power Compensation DSC, is required.

In contrast, heat flux DSC devices, with their more massive furnace, have a more sluggish responsiveness. This does not allow the heat flux DSC to heat and equilibrate as quickly as the Power Compensation DSC, and valuable data will be lost when attempting to perform isothermal cure studies.

PerkinElmer provides advanced DSC kinetics software (N537-0610) for the most comprehensive analyses of the kinetics associated with thermoset

cure and thermoplastic crystallization.

Experimental

The following conditions were used to assess the cure kinetics associated with a powdered epoxy resin.

Experimental Conditions	
Instrument	Power Compensation DSC
Cooling device	Intracooler II
Sample mass	12 mg
Sample pan	Open aluminum pan
Purge gas	Nitrogen
Isothermal cure temperatures	160, 155, 150, 145 and 140 C
Temperature program	Heat from 25 to isothermal temperature at a rate of 40C/C/min and hold for 60 minutes

Cure Kinetics Using DSC

The assessment of the cure kinetics of a thermosetting resin is easily performed using the PerkinElmer Pyris kinetics software (N537-0610) which is a comprehensive package. For the kinetics analysis of the epoxy resin in this study, the isothermal approach was utilized. This is the best, most accurate and most reliable means of extracting

kinetics information for both n-th order and autocatalyzed resins.

For the modeling of the epoxy cure kinetics, the rate of reaction, dx/dt , is assumed to be the product of two functions, $k(T)$ and $f(x)$.^{1,2,3} The temperature dependent function or rate constant, $k(T)$, is:

$$k(T) = Z e^{-E_a/RT}$$

where E_a is the activation energy, Z is the pre-exponential factor, R is the gas constant (8.314 J/mol deg), and T is the absolute temperature (°K). It is given by this equation that at higher temperatures the reaction rate is greater.

The second function, $f(x)$, gives the dependence of the reaction rate on the extent of reaction. Naturally, as the reactants are used up, the rate decreases. This function is expressed as:

$$f(x) = x^m(1-x)^n,$$

where m and n are the reaction orders and x is the fraction reacted.

This is the autocatalyzed reaction and, when $m = 0$, the resin follows the more common n th order kinetics:

$$f(x) = (1-x)^n$$

The Pyris kinetics software automatically assesses the extent of reaction (or the partial areas of cure) and then performs a best-fit to the above equations in order to extract the kinetic parameters. From this, the values of the activation energy of cure, E_a , the pre-exponential factor, Z , and the order of reaction, n , are determined.

DSC Results for Epoxy Resin

Displayed in Figure 1 are the DSC results generated on the epoxy resin by heating at a rate of 10 C/min. The major transitions are observed including the T_g at 74 C, enthalpic relaxation peak at T_g , and the cure exothermic peak between 125 and 220 C with the peak maxima at 165 C.

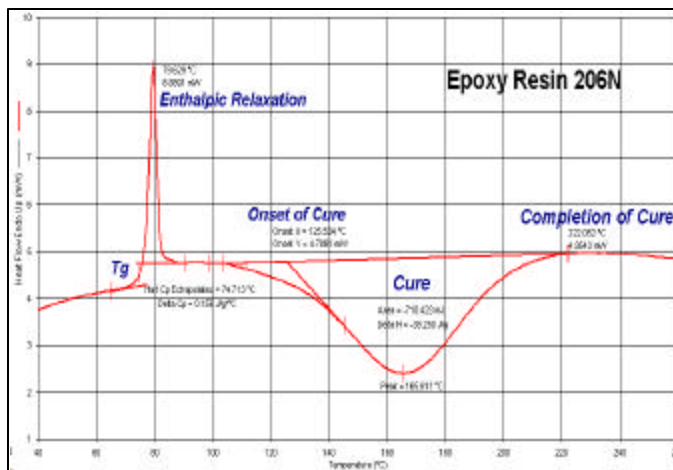


Figure 1. DSC results for uncured epoxy resin

Displayed in Figure 2 are the DSC isothermal cure curves for the epoxy resin at different isothermal temperatures. The need for a DSC with a fast response time is demonstrated in these results as the peak maxima (maximum rate of cure) occurs right at the start of the isothermal holding period. This is the expected behavior of a resin following nth order kinetics. With a heat flux DSC, the initial portion of the cure exotherm would be lost as the instrument attempts to re-establish equilibrium conditions. The lost heat of reaction will yield inaccurate isothermal measurements and problems with the subsequent kinetics analyses.

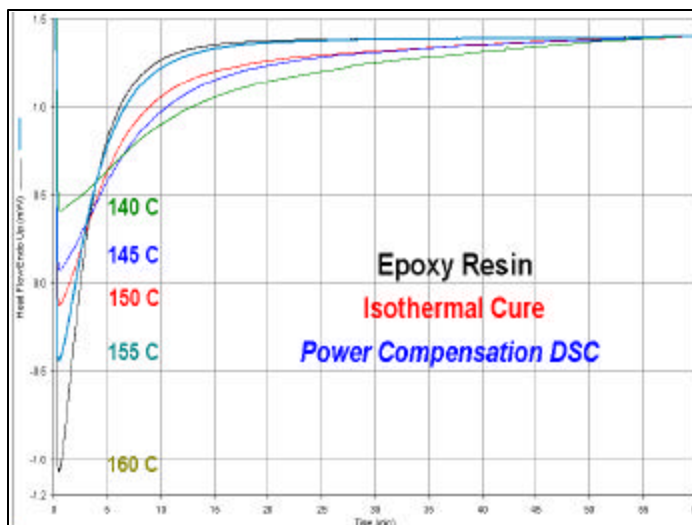


Figure 2. DSC isothermal cure curves for epoxy resin

The isothermal DSC results obtained at 160, 155 and 150 C were assessed using the PerkinElmer kinetics software. Displayed in Figure 3 is the so-called log-log plot which shows the degree of fit of the isothermal DSC results. The kinetics parameters can be determined from these log-log plots. The value of the Arrhenius activation energy, E_a , is found to be 81.4 kJ/mole and the average value of the reaction order is $n = 1.2$, which is consistent with first order kinetics. The pre-exponential function, $\ln Z$, was determined to be 17.2. The determination of these kinetic parameters by the PerkinElmer kinetics software package allows for the modeling of the cure kinetics of the epoxy resin. Cure predictive curves can then be generated and these are highly useful for process optimization and for the estimation of the resin shelf life.

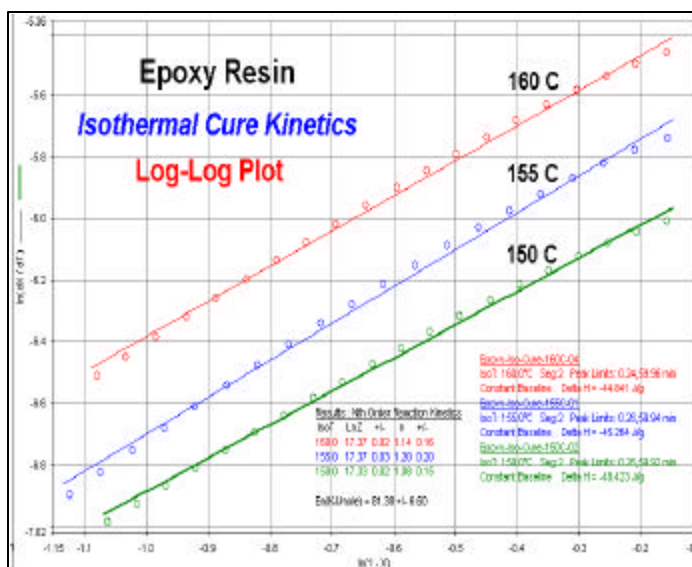


Figure 3. Log-log kinetics plots generated from kinetics software at temperatures of 160, 155 and 150 C

Displayed in Figure 4 are the isothermal conversion predictive curves generated from the kinetics software. These curves show the estimated level of cure (% reacted) as a function of time at different isothermal cure temperatures. This predictive information can be used in the determination of cure schedules for thermosetting resins.

Figure 5 shows the isochronal conversion curves, which present the predicted level of cure as a function of temperature at different time intervals. The cure kinetics establishes the critical link between conversion (% cure), temperature and time.

The iso-conversion curve predictive curves for the epoxy resin are displayed in Figure 6. These curves show the time required to achieve the desired target level of cure as a function of temperature. These curves can be used to estimate the shelf lifetime of a thermosetting resin.

These predictive curves help the process engineer decide upon the most efficient temperature – time conditions for the generation of a component made from a thermosetting resin. The kinetics information is useful for balancing energy consumption versus the completeness of cure for a thermosetting product.

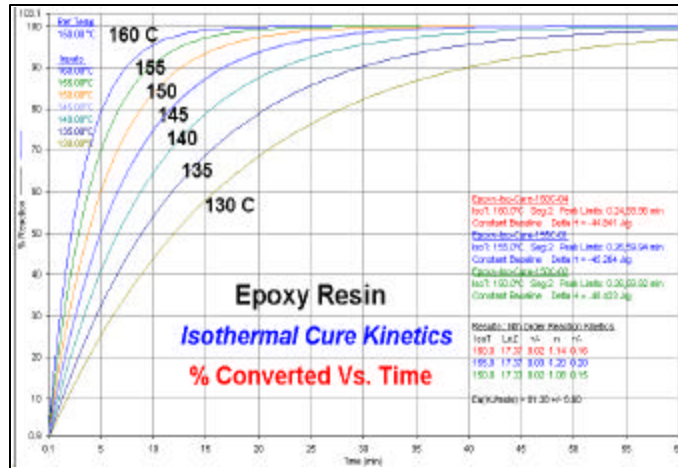


Figure 4. Isothermal conversion predictive curves for epoxy

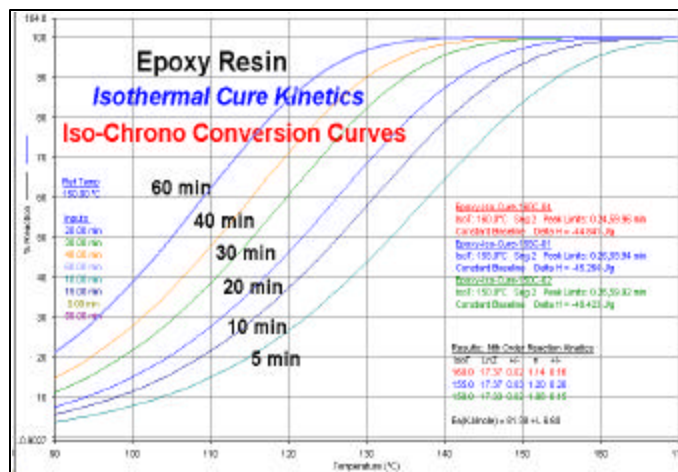


Figure 5. Isochronal conversion predictive curves for epoxy

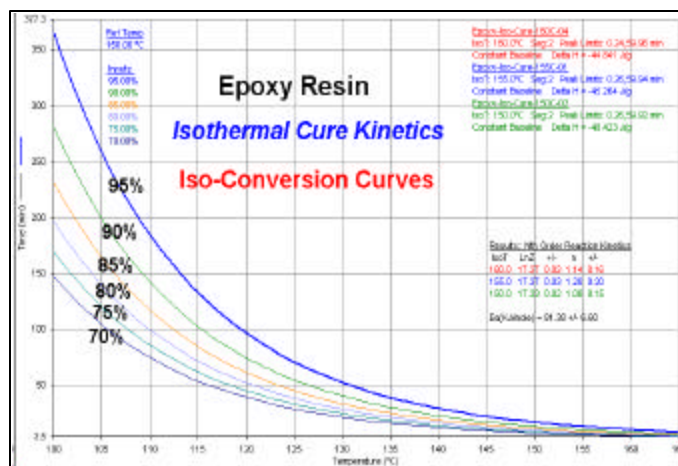


Figure 6. Isothermal conversion predictive curves for epoxy

Summary

The PerkinElmer Pyris Kinetics software, used in conjunction with the high performance PerkinElmer Power Compensation DSC, provides a powerful tool for analyzing cure and crosslinking reactions associated with thermosetting materials. This software provides the means of assessing the quality of the kinetics data, and it provides the flexibility of input to optimize the analysis.

The kinetics analysis provides valuable information on the cure characteristics of a thermosetting resin. The kinetics software can be used to address the quality and consistency of thermosetting resins.

The best, most accurate and most reliable means of assessing cure kinetics by DSC is with the isothermal approach. This provides useful real-life information, as the isothermal approach mimics the actual processing conditions utilized with most thermosetting resins. The establishment of isothermal cure kinetics requires a DSC instrument with a very fast response time. The best DSC for this important application is the Power Compensation DSC from PerkinElmer Instruments given its very fast responsiveness.

References

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