Prediction of Epoxy Cure Properties Using Pyris DSC Scanning Kinetics Software

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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 upon the completion of cure of a thermosetting resin. The modeling of cure kinetics provides the scientist, engineer or process control manager with valuable information that can be used to optimize processing conditions or to predict the shelf lifetime or 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.

Experimental

DSC measures the heat flow into or from a sample as it is heated, cooled and/or held isothermally. For thermosetting resins, the technique provides valuable information on glass transition temperatures (Tg), onset of cure, heat of cure, maximum rate of cure, completion of cure and degree of cure.

PerkinElmer offers several high performance DSC instruments, with different technologies, to meet various needs and application requirements. The DSC instruments utilize the Pyris for Windows software, which offers a high degree of flexibility, comprehensiveness, extensive validation and ease of use. All of the PerkinElmer DSC's generate high quality kinetics data, which can be easily analyzed using the Pyris Kinetics software.

Experimental Conditions

A sample of a powdered epoxy resin (206N) was analyzed to model the kinetics of its curing behavior. The following conditions were utilized to test the sample:

Instrument:	Pyris 1 DSC
Sample container:	Crimped aluminum pan
Sample mass:	Approximately 10 mg
Temperature program:	Heat from room temperature to 250 C at 10 C/min
Purge gas:	Nitrogen at 20 mL/min

The DSC was calibrated for temperature and enthalpic responses using high purity indium metal.

DSC Curing Results on Epoxy

Displayed in Figure 1 are the DSC results generated on the uncured epoxy powder sample.

These results provide substantial information on the thermal – physical properties of the epoxy resin material. The Tg is observed at 74.7 C with an accompanying large enthalpic relaxation peak. This occurrence of this irreversible relaxation peak is due to the time dependent nature of the glass transition event. As the resin sits at room temperature, it undergoes physical aging; and, the consequences of the 2nd and 3rd Laws of Thermodynamics (entropy effects) cause the molecules to relax over time. When the sample is heated during a DSC experiment, the time scale of the molecular motions are very long in comparison to the time scale of the DSC experiment, and a large overshoot is observed during Tg.

At a sufficiently high enough temperature, the cure reaction begins to proceed and the onset of curing is observed as an exothermic event. The DSC onset temperature provides the temperature at which the reaction begins to progress. The peak maximum represents the maximum rate of cure at the given heating rate condition. The completion of the cure is reflected when the DSC response returns to linear behavior at the upper temperature end. If the area under the exothermic peak is integrated, this yields the heat of reaction (J/g) for the sample. For a given epoxy resin system, the smaller the heat of cure, the more cured the resin is. If the resin is nearly completely cured (100% cured), no residual exothermic

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Figure 1. DSC results on uncured powdered epoxy resin.

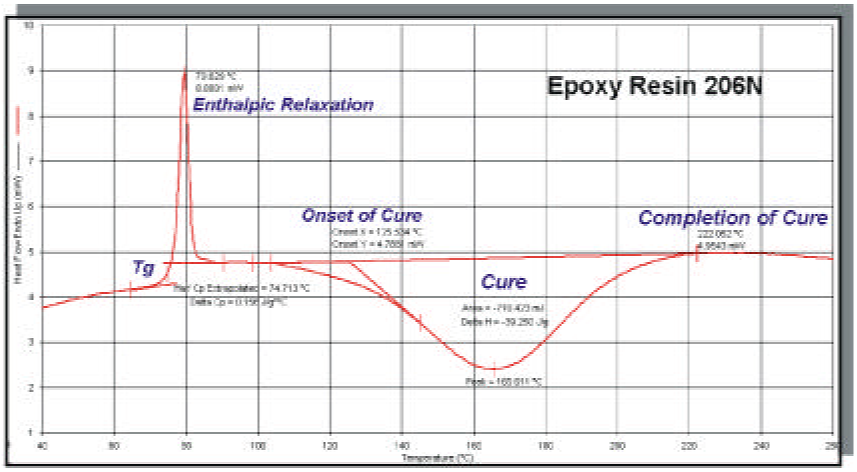
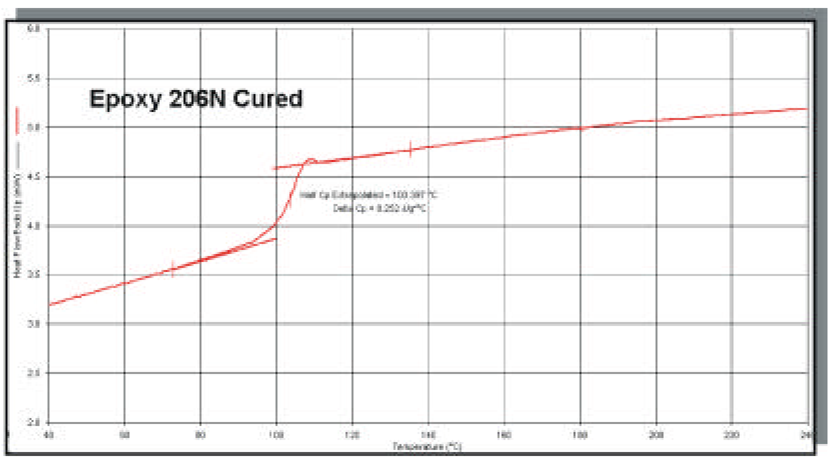


Figure 2. DSC results for completely cured epoxy resin sample.



peak will be observed, as is shown in Figure 2, for the completely cured epoxy resin sample.

The cured epoxy sample yields a Tg at 103 C with no exothermic residual curing peak. The DSC analysis of a post-cured thermosetting product provides useful information on the completeness of cure. In some cases, a small, residual cure peak may be observed, revealing that the resin has not been completely cured during processing. Significant undercure of a thermosetting resin could lead to premature product failure.

Cure Kinetics of Epoxy

The DSC results shown in Figure 1 can be used to determine the cure kinetics associated with the epoxy resin sample. This is easily performed using the PerkinElmer Pyris kinetics software (N537-0610) which is a comprehensive package that handles single run kinetics, isothermal cure studies as well as isothermal crystallization kinetics of thermoplastics.

For the kinetics analysis of the epoxy resin in this study, the scanning run approach was utilized. This is the simplest and fastest means of extracting kinetics information and uses the approach first described by Borchardt and Daniels. The scanning run analysis works for resins which following nth order (not autocatalytic) behavior [1,2]. For resins that are autocatalytic, it is best to use isothermal kinetics in order to successfully model the cure behavior. The PerkinElmer kinetics software does provide this option.

For the modeling of the epoxy cure kinetics, the rate of reaction is assumed to be the product of two functions, k(T) and f(x).[3,4] The temperature dependent function or rate constant, k(T), is:

$$k(T) = Ze^{-Ea/RT}$$

(the Arrhenius equation)

where Ea 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 understood 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:

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

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Figure 3. Log reaction rate versus inverse temperature kinetics plot for epoxy resin.

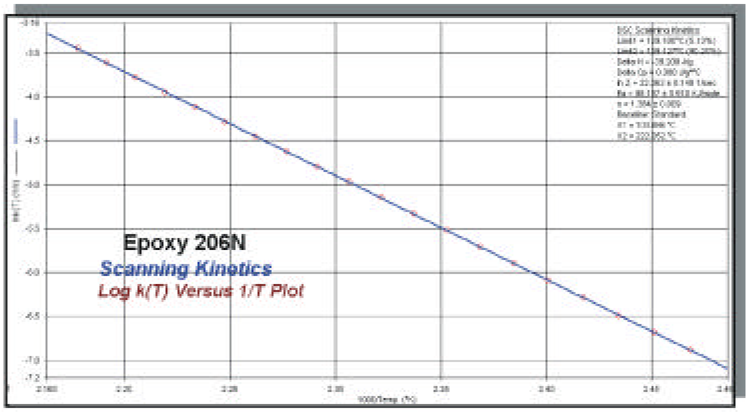


Figure 4. Predicted degree of conversion versus temperature for epoxy resin.

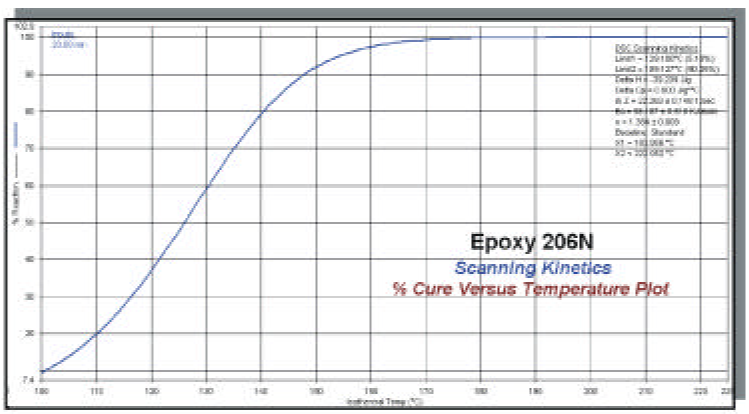
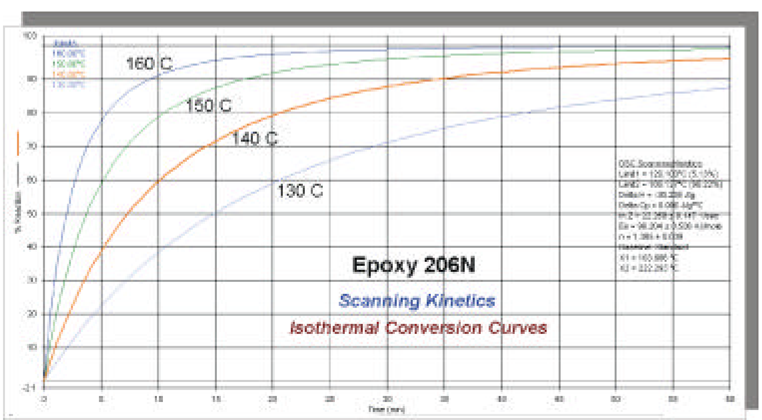


Figure 5. Isothermal conversion curves for epoxy resin sample.



where n is the reaction order and x is the fraction reacted. Adherence to this equation is referred to as n-th order behavior.

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, Ea, the pre-exponential factor, Z, and the order of reaction, n, are determined.

The kinetics analysis was performed on the powdered epoxy resin sample and the log rate constant plot, with the results of the kinetics analysis, is displayed in Figure 3.

The activation energy was determined to be 98 kJ/mole and the order of reaction, n, was found have a best-fit value of 1.4. This information then provides the mathematical parameters necessary for the description of the cure kinetics of the epoxy sample. From this, product lifetimes and degrees of conversion can be predicted.

One important plot that the Pyris kinetics software provides is the degree of conversion (or percent reacted) as a function of temperature. This plot is displayed in Figure 4 for the epoxy resin sample.

This plot shows how the resin cure increases from low to high levels as the temperature is increased. The increase in cure does not follow a linear response, but is S-shaped.

Another highly useful plot, for process control purposes, is the degree of cure versus time under isothermal conditions. These predictive plots are displayed in Figure 5 at various

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isothermal cure temperatures for the epoxy resin sample.

The isothermal conversion curves show that it takes increasingly longer times for the epoxy resin to fully cure as the temperature is decreased. At temperatures below 150 C, the resin does achieve complete cure even after 60 minutes. 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.

Summary

The PerkinElmer Pyris Kinetics software, used in conjunction with the high performance PerkinElmer DSC instruments, 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. Changes in the quantity or chemical makeup of the two-part epoxy system will significantly affect its reaction rate and degree of crosslinking. Accelerants, retardants, and other additives will also significantly affect the reaction process. This kinetics program provides a tool for quantifying these formulation parameters, predicting process rates and estimating product lifetimes. The same approach should be equally useful in characterizing B-stage prepregs and other curing, vulcanizing, and polymerizing reaction systems.

References

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