

Cure Kinetics of T700/BMI Prepreg Used for Advanced Thermoset Composite

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ABSTRACT: A new isothermally based, cure kinetic model for the prepreg was presented using an industrially supplied prepreg rather than pure resin. The matrix resin was bismaleimide (BMI) resins, and the reinforcement was carbon fiber T700-12S. The BMI prepreg was measured from 170 to 220°C by isothermal DSC. The isothermal cure reaction heat increases with the increment of cure temperature. The DSC data were analyzed by the proposed *n*th-order reaction model. An increase in reaction rate was observed at higher temperature in both neat and prepreg. After

reaching the peak value, the reaction rate dropped off faster in prepreg, resulting in a lower average value of the ultimate heat of reaction. It was suggested the presence of carbon fiber had an effect on the cure kinetics as a heat sink. The carbon fibers imposed restrictions on the molecular mobility of the reactive species and did not change the cure mechanism. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2238–2241, 2005

Key words: cure kinetics; DSC; neat BMI; prepreg

INTRODUCTION

The cure kinetic model is an integral part of process simulation because it is crucial for accurately predicting the degree of cure and the amount of heat generation. The mechanical properties of cured composites are determined by the degree of cure, which depends on the kinetic model. Therefore, the knowledge of the kinetic model of prepreg is a fundamental of the processing-structure-property-cost integral design for composite manufacture.

Many researchers have proposed various methods to study cure kinetics of resin systems. Unfortunately, most present cure kinetics models were obtained from neat resin. As we all know, prepreg was the most popular choice in manufacturing composites.

There is no consensus, however, with respect to the influence of fillers or reinforced materials on the cure kinetics.^{1–17} For example, Kim and coworkers⁴ studied the cure kinetics of AS4/3501-6 (graphite/epoxy) prepreg. They found the ultimate reaction heat of prepreg was 8–17% less than the neat resin. Wang and Storm⁵ studied the epoxy prepreg SPX 8800 system. They found no significant difference in cure kinetics for both epoxy prepreg and neat resin. Dutta and Ryan⁶ studied the kinetic effects of carbon black and silica fillers on the cure of an epoxy-amine system, concluding that the heat of reaction is independent of the filler content but dependent on the type of filler.

Han and colleagues⁷ found that the curing rate of a resin is greatly influenced by the presence of fibers and the type of fibers employed. The rate of reaction for a resin-fiber system can be 60% different from that of neat resin, after a 10 min cure. Mijovic and Wang⁸ found that the presence of graphite fiber in a TGDDM/DDS composite caused a slight increase in the reaction rate but had no effect on the degree of cure. Kaelble and coworkers⁹ employed a similar DSC technique to show that differing surface treatments of a graphite fiber did not substantially alter the cure kinetics or degree of cure of an epoxy resin. Grenier-Loustalot and Grenier¹⁰ investigated the curing mechanism of similar TGDDM/DDS systems in the presence of glass and carbon fibers by DSC, NMR, FTIR, HPLC, and microcalorimetry. They concluded that the presence of fibers did not change the reaction mechanism or network structure, but did lead to notable differences in the reaction rate, especially at low temperature.

There are several experimental techniques to characterize thermoset and prepreg, such as DSC,^{1–18} Near-infrared spectroscopy,^{15,16} FTIR,^{10,18–20} and UV-reflection spectroscopy.^{18,21} DSC is the most widely utilized experimental technique to obtain the degree and reaction rate of cure of thermosetting resins.

As a continuation of our comprehensive research program in the area of processing-structure-property-cost relationships in neat thermosets and composites, we have undertaken a study of the cure kinetics of pure BMI resins.¹ In this study, the kinetic model is established for a “benchmark” prepreg system: T700/5429, a carbon fiber reinforced bismaleimide (BMI)

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resin. The DSC data of BMI prepreg are very useful in elucidating the curing process and in determining the kinetic parameters for the model. Its results can be used to optimize the curing process of BMI prepreg in its applications as aircraft and aerospace structures.

EXPERIMENTAL

Materials

The material used in this study was carbon fiber/bismaleimide (T700/BMI) prepreg, which is commonly used as the polymeric matrix in advanced composites employed in aircraft, spacecraft, and other industries. The BMI matrix resins consisted of 4,4'-bismaleimidodiphenylmethane (BMIM, BMPM) and 0,0'-diallyl bisphenol A (DABPA, DABA). BMIM was well mixed with both 87 phr of bisphenol A and other materials, where the unit phr is an abbreviation of "part per one hundred mass base resins," and here BMIM is a base resin. The reinforcement material is carbon fiber (T700-12S). The prepreg is prepared at room temperature by the wet impregnated method. Reactions during mixing were negligible, as confirmed by an uneventful 4-h isothermal (60°C) DSC thermogram. The prepreg was then either tested immediately or stored in the refrigerator. If prepreg wasn't used in one month, it was discarded and a fresh one prepared.

Procedure

Samples were removed from the refrigerator and allowed to warm to 25°C. Small sample quantities (15–30 mg) were then placed in sealed aluminum pans. Calorimetric measurements were made with a Perkin–Elmer Pyris 1 DSC. An intercooler is used to stabilize the system. Nitrogen with a flow rate of 20–30 mL/min was used as a purge gas to minimize oxidation of the sample during the measurements. Before the measurements on the BMI, two standard materials, indium (99.999% pure) and zinc (99.999% pure), are used to calibrate the temperature and energy axis of the Pyris 1 DSC following the manufacturer's manual. Thermal equilibrium is regained within 1 min after sample insertion, and the exothermic reaction is considered complete when the recorder signal levels off to the baseline. The heat of reaction was determined by carrying the reaction isothermally to completion at the following temperatures: 170, 180, 190, 200, 210, and 220°C. The total area under the exothermic curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure, H_T , at a given temperature.

After the isothermal cure was completed, the sample was cooled rapidly in the DSC to 50°C. It was then heated at 10°C/min from 50 to 350°C to determine the residual heat of reaction, H_{res} . The sum of the isother-

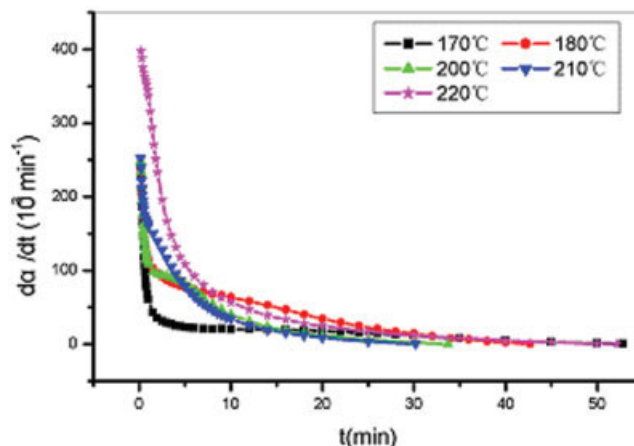


Figure 1 Cure rate as a function of time at different temperatures.

mal heat (H_T) and the residual heat (H_{res}) was taken to represent the ultimate heat of cure (H_u). Finally, the samples were weighed again and compared to the initial weight. Weight losses were negligible in all cases.

RESULTS AND DISCUSSION

A series of isothermal DSC thermograms of prepreg systems were obtained and are shown in Figure 1. The reaction rate, which is proportional to the rate of heat generation, passes through a maximum and then decreases as a function of curing time. Also, with a decrease in cure temperature, the cure reaction shifts to a longer curing time. The maximum in the cure curves appears at about $t = 0$, meaning that the cure reaction follows an n th-order reaction. Such behavior is typical of n th-order reactions and is analogous to that observed and reported in the neat resin.¹ We can also observe that the isothermal DSC curve of 220°C is different from other temperatures, because the sample was stored a few days in the air before the experiment. We will study the aging effect on kinetics in the future. The reaction rate equation used to describe the cure kinetics is:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E}{RT}\right)(1-\alpha)^n \quad (1)$$

where $d\alpha/dt$ is the cure rate, α is the degree of cure, $k(T)$ is the rate constant, defined by an Arrhenius type of relationship, n is the reaction order, R is the universal gas constant, A is the frequency factor or pre-exponential constant, E is the activation energy, and T is the processing temperature expressed in Kelvin. The reaction rate was determined from the DSC trace, as the expression:

TABLE I
The Ultimate Heat of Cure as a Function of Cure Temperature

Temperature (°C)	Neat BMI resin (J/g)	Prepreg (J/g)
170	68.4	71.22
180	128.5	135.71
190	180.2	149.83
200	212.4	184.45
210	264.6	206.43
220	288.44	221.93

$$\frac{d\alpha}{dt} = \frac{1}{H_u} \frac{dH}{dt} \quad (2)$$

where H_u , the ultimate heat of cure, is the sum of the isothermal heat of cure (H_T) and the residual heat ($H_{res.}$) obtained in the subsequent dynamic DSC run. To calculate the extent of reaction (α), the DSC curves were integrated and normalized with respect to H_u and sample weight. We also note that the calculations of heats of reaction (H_T and $H_{res.}$) in reinforced systems were normalized with respect to the mass of BMI.

Values of the ultimate heat of cure, for both neat and prepreg cured at different temperatures, are summarized in Table I. The average value of H_u was higher for neat than that for reinforced resin. It appears then that the presence of carbon fiber contributes to a decrease in the overall number of chemical reactions and, hence, a lower value of H_u . After reaching the peak value, the reaction rate falls off to the baseline faster in reinforced resins.

The plot of the degree of cure as a function of time for prepreg is shown in Figure 2. The degree of cure increased with increasing temperature. A direct comparison with the behavior of neat resin revealed a slight difference, in that the curves for prepreg were

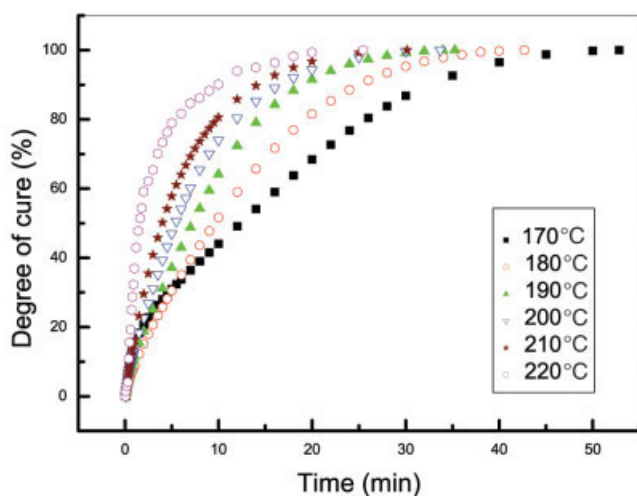


Figure 2 Degree of cure as a function of time at different temperatures.

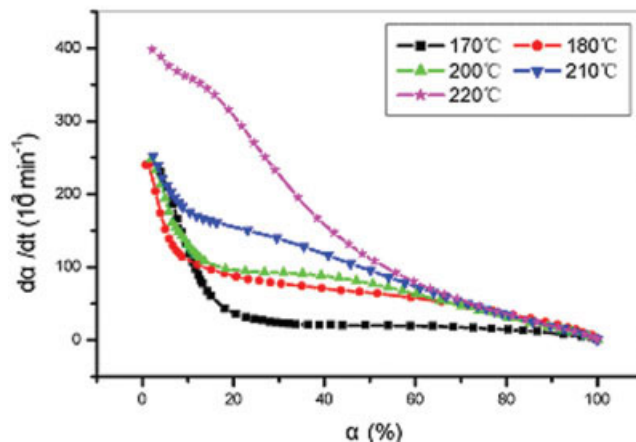


Figure 3 Cure rate as a function of degree of cure at various temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

somewhat below the corresponding isotherms for neat resin.

Reaction rate as a function of degree of cure, with temperature as a parameter, is shown in Figure 3. Once again, the observed dependence was very similar to that reported for neat resin.¹ It is seen in Figure 3 that the maximum reaction rate occurs between 0 and 0.04% conversions. The n th-order reaction is generally characterized by the maximum rate at zero conversion.² By analysis of all isothermal cure temperature DSC curves, it is found that the time required to reach the maximum reaction rate is approximately identically zero. It is the same as neat resin.

Now we will determine the reaction model by the reduced time method, which is also called the Sharp method.²² For this prepreg system, Figure 4 is the result when experimental data were compared with theoretical data where $G(\alpha) = \ln(1 - \alpha)$. It is clear that

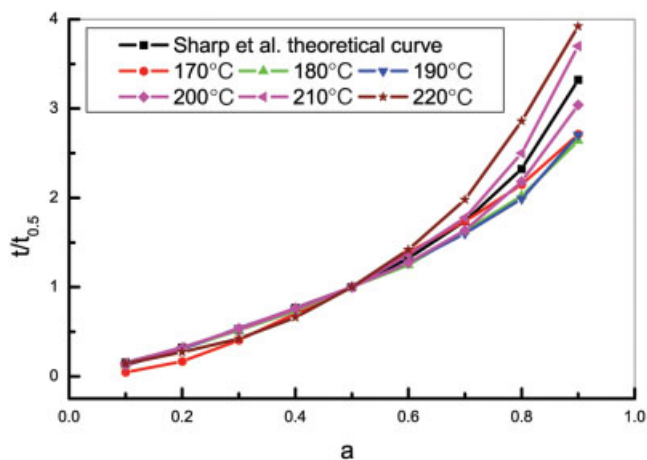


Figure 4 The comparison of experimental data and theoretical data for BMI resin.

they agree very well. This means that the conversion function $f(\alpha)$ is equal to $(1 - \alpha)$.

As expected, the time required to reach the peak (t_p) was found to decrease with increasing temperature, in a linear fashion, as shown in Figure 5. It is interesting to note, however, that the curves for the prepreg lie above those of neat resin. Hence, at a given temperature, it took a little longer to reach the maximum rate peak (t_p) in the presence of reinforcement.

The kinetic rate constant k was read off the original DSC trace and was normalized with respect to the sample weight. The temperature dependence of the reaction rate constant k for both neat resin and prepreg can be presented by the Arrhenius equation. A summary of the corresponding kinetic parameters is given in Table II. It was observed that the k values for neat resin were bigger than those of the corresponding prepreg.

Although the effect of the reinforcement on cure kinetics was not only very pronounced, there are several points that should be emphasized. As one would expect, a higher cure temperature resulted in an increase in the reaction rate in both neat and prepreg. The lower value of H_u in prepreg suggested the role of carbon fiber in restricting the molecular mobility of reactive species. The value of the cure rate constant k was slightly lower for the prepreg than for neat resin. The restrictions to molecular mobility imposed on the resin become more pronounced as the reactions proceed because of the concomitant increase in viscosity. As the diffusion control becomes progressively more important, the molecules in the vicinity of reinforcement are "shielded" (by carbon fiber) and, hence, are increasingly less likely to encounter a reactive species than the molecules in the bulk. That could be the reason why the reaction rate, after going through the maximum, falls off to the baseline noticeably faster in the prepreg.

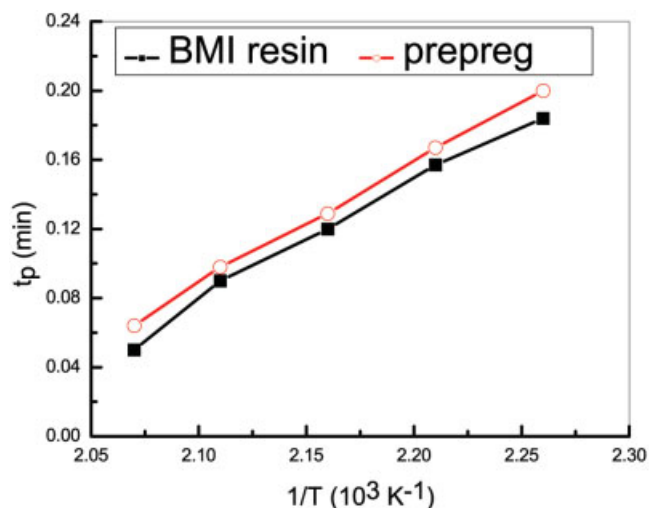


Figure 5 [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Summary of Kinetic Parameters ($n = 1$)

	Neat resin	Prepreg
$A/(\text{min}^{-1})$	4.95×10^8	4.11×10^5
$E/(\text{kJ mol}^{-1})$	83.3	59.35

CONCLUSIONS

BMI prepreg, the maximum reaction heat of isothermal cure, can also be achieved at 220°C. The degree of cure at isothermal cure temperatures below 220°C is less than 1. In the earlier stage of isothermal cure reaction, the cure rate at the higher temperatures is faster than the cure rate at the lower temperatures; whereas in the late cure stage, the cure rate is lower at the higher temperatures.

Experimental results were described well by an n th-order reaction model. In all cases, higher cure temperature led to an increase in reaction rate. The degree of cure at the maximum rate of reaction was independent of temperature but took a longer time to attain in prepreg. Values of the reaction rate constant, k , were slightly lower for the prepreg. Also, the values of H_u were lower for prepreg. An explanation was offered in terms of the restrictions to molecular mobility imposed by the carbon fiber. The fibers act as heat sinks, reducing the peak exotherm, delaying the cure. The presence of fibers did not change the reaction mechanism or network structure.

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