

# Modeling the Curing Kinetics for a Modified Bismaleimide Resin Using Isothermal DSC

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**ABSTRACT:** The kinetics of curing for a modified bismaleimide (BMI) resin was investigated to ascertain a suitable cure model for the material. The resin system used in this study was composed of 4,4'-bismaleimidodiphenylmethane (BMIM) and 0,0'-diallyl bisphenol A (DABPA, DABA). The BMIM was the base monomer and the DABPA was the modified agent. A series of isothermal DSC runs provided information about the kinetics of cure in the temperature range 170–220°C. Regardless of the different temperatures, the shape of the conversion curves was similar, and this modified BMI resin system underwent an  $n$ th-order cure

reaction. Kinetic parameters of this BMI resin system, including the reaction model, activation energy, and frequency factor, were calculated. From the experimental data, it was found that the cure kinetics of this resin system can be characterized by a first-order kinetic model. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3338–3342, 2004

**Key words:** bismaleimide (BMI); curing of polymers; kinetics (polymer); differential scanning calorimetry (DSC);  $n$ th-order reaction

## INTRODUCTION

The most widely used composite matrixes in the aerospace industry are epoxy resins. In recent years, however, additional performance requirements have led to the development of poly(etherether ketone) (PEEK), polyimides (PI), and bismaleimides (BMI). BMIs are widely used as matrix resins for advanced composites, based on the fact that their cured resins have high heat resistance, mechanical strength, high fatigue resistance, and hot/wet resistance compared with those of epoxy resins. In addition, the cure conditions for BMI resins closely mimic epoxies, so that special processing equipment is not required. The main disadvantage of BMI resins is their brittleness, which is a direct consequence of high crosslink density and inherent aromatic structure. Commercial systems are therefore formulated with various additives to increase their fracture toughness.<sup>1–4</sup> A general scheme for the synthesis of a typical aromatic BMI is given in Figure 1.

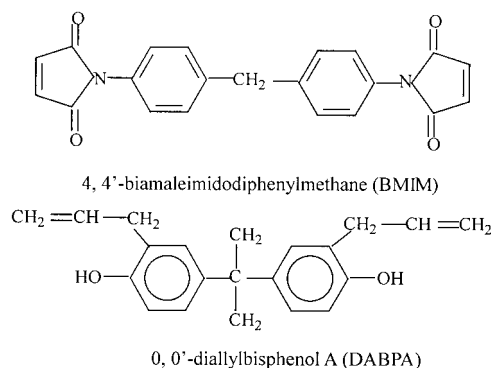
Boey et al.<sup>5</sup> attempted to describe the curing kinetics of BMIM/DABPA, amine, and epoxy and found that the reaction process was dominated by a different mechanism at different stages of the cure process, with an initial autocatalytic reaction shifting into an  $n$ th-order reaction as the reaction proceeded. They investigated the cure kinetics only at 170, 190, 210, and 220°C. However, they did not explain why there were

no experimental data below 180 and 200°C. Acevedo et al.<sup>6</sup> investigated the curing kinetics of the system containing *N*-phenylmaleimide and curing initiator dicumyl peroxide in the temperature range 120–160°C. He used a first-order model to fit the experimental data, and the first model could be fit better up to 70% conversion. Goodwin<sup>7</sup> explored the curing kinetics of BMI and a bisphenol A derivative in the temperature range 180–200°C. He also used an  $n$ th-order model to fit the experimental data. Mijovic and Andjolic<sup>8</sup> studied the isothermal BMI cure by remote fiber-optic near infrared spectroscopy in the 140–250°C range. They reported the relative rates of allyl and maleimide consumption and that the essentially complete conversion of these groups occurs at 200°C. Also, they observed the onset of dehydration at low temperature, 140°C, over periods of hours.

As a continuation of our comprehensive research program in the area of processing–structure–property–cost relationships in neat thermosets and composites,<sup>9,10</sup> we have undertaken a study of cure kinetics of the neat resins in this article. The objective of this study was to use isothermal DSC to evaluate the cure mechanism of BMI resins. When combined with carbon fibers, the resins studied here become promising candidates for high-performance composite structures in aerospace applications.

The search for a mathematical description of the DSC data is usually sought in terms of a “kinetic triplet” [i.e., Arrhenius parameters  $A$ , also called frequency factor; activation energy  $E$ ; and the reaction model  $f(\alpha)$ , also called the conversion function].

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**Figure 1** Chemical structures of an aromatic bismaleimide.

## EXPERIMENTAL

The BMI resin used in this study was composed of the 4,4'-bismaleimidodiphenylmethane (BMIM) and 0,0'-diallyl bisphenol A (DABPA, DABA) (Fig. 1). 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 base resins"), and here BMIM is a base resin. The BMI resin was stored at  $-5^{\circ}\text{C}$  to prevent the cure reaction during the storage.

A variety of experimental techniques have been used to study the kinetics of thermosetting resins. Differential scanning calorimetry (DSC) is the most widely used experimental technique to obtain the degree and reaction rate of cure as well as the specific heat of thermosetting resins. DSC can operate under isothermal or dynamic (nonisothermal) conditions. To measure the total heat, evolved during the complete cure, dynamic DSC analysis was carried out from 50 to  $350^{\circ}\text{C}$ , at a heating rate of  $10^{\circ}\text{C}/\text{min}$ , and to measure cumulative heat  $H_{\text{iso}}$ , at a time, isothermal DSC analyses were performed at 170, 180, 190, 200, 210, and  $220^{\circ}\text{C}$ .

In the present work, the heat of reaction of this BMI resin was measured using the Perkin-Elmer (PE) Pyris 1 DSC (Perkin Elmer Cetus Instruments, Norwalk, CT). 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 resin, two standard materials, indium (99.999% pure) and zinc (99.999% pure), were used to calibrate the temperature and energy axis of the Pyris 1 DSC following the manufacturer's manual. Thermal equilibrium was regained within 1 min after sample insertion and the exothermic reaction was considered complete when the recorder signal leveled off to the baseline. The final baseline was extrapolated to determine the total area under the exotherm curve. The total areas of DSC curves are the isothermal heats of cure  $H_{\text{iso}}$  under isothermal DSC and total heats of cure  $H_{\text{u}}$  under dynamic DSC. The sample was weighed before and after each experiment to deter-

mine any mass loss during the measurements: an electronic balance with 0.005 mg accuracy was used for measurements. In all cases for these experiments, the mass loss was found to be negligible.

## RESULTS AND DISCUSSION

The mechanism for crosslinking of thermosetting resins is very complex because of the relative interaction between the chemical kinetics and the physical properties,<sup>11</sup> and it is still not perfectly understood. Two distinct approaches can be used: phenomenological (macroscopic level) and mechanistic (microscopic level).<sup>12</sup> The former is related to an overall reaction (only one reaction representing the whole process), and the latter to a kinetic mechanism for each elementary reaction occurring during the process.

The phenomenological models are semiempirical and thus do not provide a clear description of the curing process and its chemistry. The mechanistic models are more representative of the resin curing kinetics because they are based on stoichiometric balances of reactants involved in the elementary reactions. As a consequence, they are much more complex than the phenomenological models. This study is focused on phenomenological models. They are based on eq. (1)<sup>13–15</sup>:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

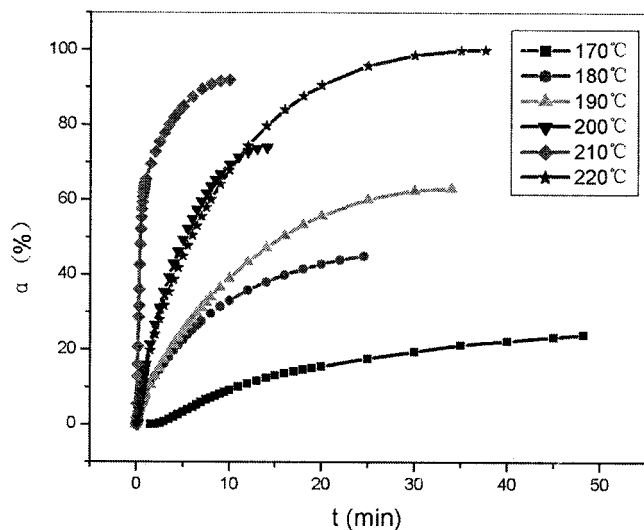
where  $\alpha$  is the conversion or the degree of cure;  $t$  is the reaction time;  $f(\alpha)$  is a function representing the amount of reaction resin, which is determined for each system; and  $k$  is a rate constant, defined by an Arrhenius type of relationship, eq. (2):

$$k(T) = A \exp\left(\frac{-E}{RT}\right) \quad (2)$$

where  $A$  is the frequency factor or preexponential constant;  $E$  is the activation energy;  $R$  is the universal gas constant; and  $T$  is the processing temperature, expressed in Kelvin. A few functions for  $f(\alpha)$  are proposed in the literature, with the most common being eq. (3):

**TABLE I**  
Total Heat of Reaction for BMI Samples Cured at Different Temperatures

Property	Temperature ( $^{\circ}\text{C}$ )					
	170	180	190	200	210	220
$H_{\text{u}}$ (J/g)	68.4	128.5	180.2	212.4	264.6	288.4



**Figure 2** Degree of cure versus curing time at several temperatures for BMI resin.

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

corresponding to a  $n$ th-order reaction and eq. (4):

$$f(\alpha) = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (4)$$

related to an autocatalytic reaction, where  $m + n$  represents the reaction order,  $k_1$  is a constant, and  $k_2$  is described by the Arrhenius equation. Variations of  $f(\alpha)$  can be found depending on the type of thermosetting resin and experimental conditions. Because the cure of thermosetting resins is an exothermic process and the only thermal event that exists, the degree of cure  $\alpha$  can be related to heat (enthalpy) released during the reac-

tion of the components (basically a monomer and a curing agent). Thus, we have eq. (5):

$$\alpha = \frac{H_t}{H_u} \quad (5)$$

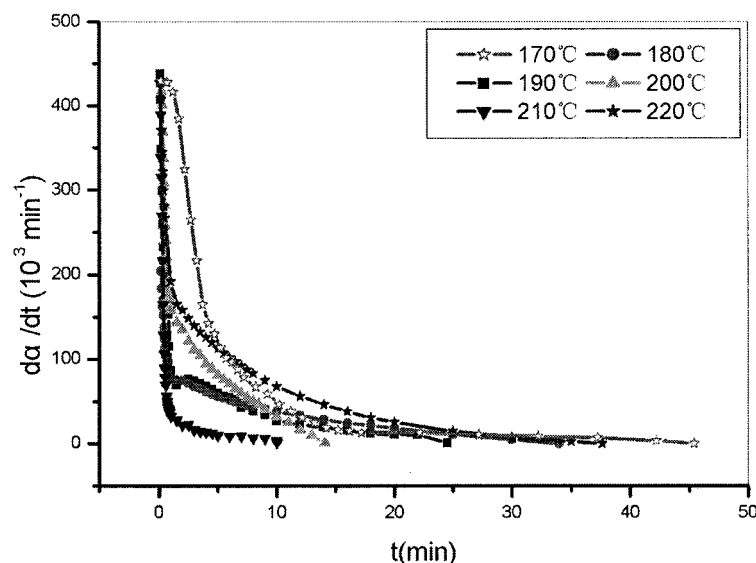
where  $H_t$  is the enthalpy at a specific time and  $H_u$  is the total enthalpy (or the total heat of reaction) at the end of the curing process when  $\alpha = 1$ . The reaction rate, represented by eq. (6), is then

$$\frac{d\alpha}{dt} = \frac{1}{H_u} \frac{dH}{dt} \quad (6)$$

because the total heat of reaction is a constant for a particular resin.<sup>2</sup>

After the isothermal cure was completed, the isothermally cured sample was cooled rapidly to 50°C in the DSC. It was then analyzed using dynamic DSC at a heating rate of 10°C/min from 50 to 350°C to obtain the residual heat of reaction. Table I gives the total heat evolved per unit mass of the sample at all isothermal temperatures. From the dynamic DSC experiment we know the total heat was 288.4 J/g.<sup>9</sup> These measurements indicate that complete cure is never achieved when the cure temperature is below 220°C.

A series of isothermal reaction rate curves for BMI at six different temperatures are shown in Figure 2. In all cases, the degree of cure increases rapidly with curing time at the initial stage. In this stage, the reaction is chemically controlled. After this stage, it gradually decreases and then finally levels off because of diffusion-controlled reactions. Further study will be focused on this respect. The value of Figure 2 also shows that the degree of cure was higher at higher



**Figure 3** Cure rate as a function of time at several isothermal temperatures for BMI resin.

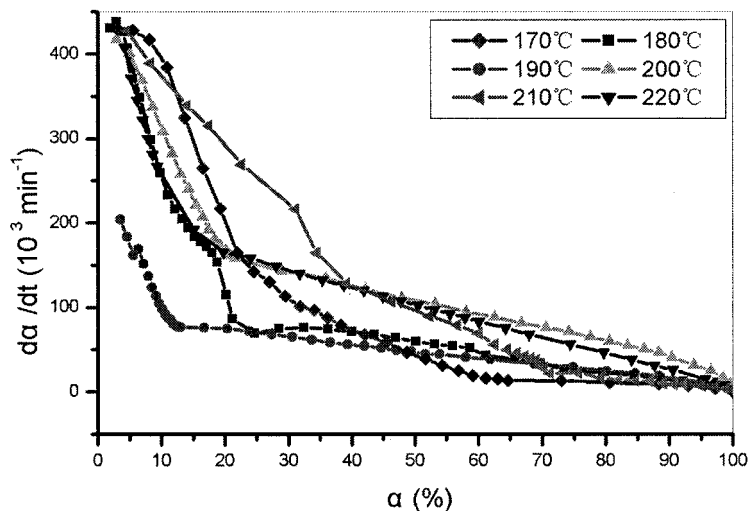


Figure 4 Cure rate versus degree of cure with temperature for BMI resin.

temperature of isothermal curing for the same curing time. The data shown for curing at 220°C differ from those at the other lower temperatures. This phenomenon can probably be attributed to the decomposition of BMI when it was cured at higher isothermal curing temperature, which was also observed in other studies reported in literature.<sup>5,16</sup>

Figure 3 shows the results of plotting the cure rate versus curing time, where the data indicate that the maximum cure rates appear at about  $t = 0$ , which means that the cure reaction follows an  $n$ th-order reaction. Therefore, the cure kinetics of this BMI resin can be investigated by eq. (7):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E}{RT}\right)(1 - \alpha)^n \quad (7)$$

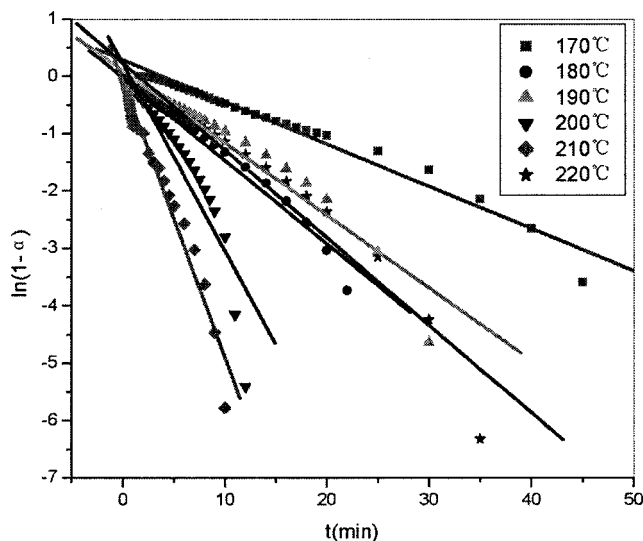


Figure 5 Plot of  $\ln(1 - \alpha)$  versus cure time at several temperatures.

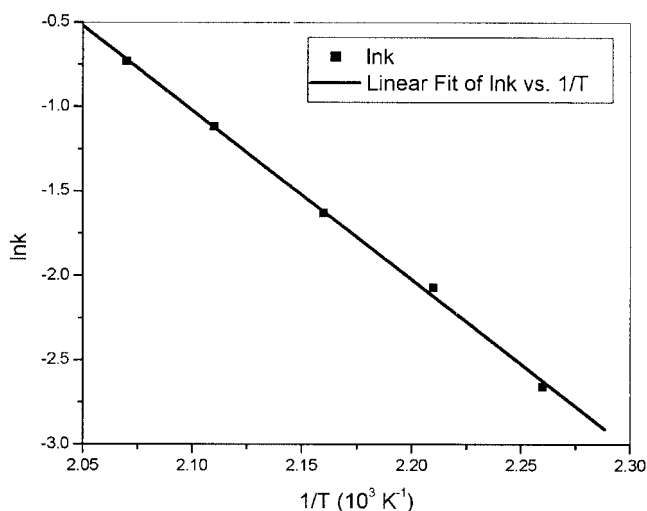
The cure rate as a function of the degree of cure is shown in Figure 4. The cure rate values at the peak ( $\dot{\alpha}_p$ ) are all the same, except the temperature 210°C, which may have been caused by the experimental operators. It may be observed in Figure 4 that the maximum reaction rate occurs between 0 and 0.04% conversions. The  $n$ th-order reaction is generally characterized by the maximum rate at zero conversion.<sup>12</sup> It is further seen in Figure 4, when the conversion is greater than 10%, that the cure rate versus degree of cure is linear. This suggests that the reaction order  $n = 1$ . The slope is equal to the reaction rate constant  $k$ , which can be expressed by an Arrhenius equation [eq. (2)].

Figure 5 depicts the curves of  $\ln(1 - \alpha)$  versus cure time. The slope is almost constant at each isothermal temperature; this also means that the cure reaction can be expressed by the first-order reaction. The rate constant  $k$  is seen in Table II. It should be noted, however, that the degree of cure is not greater than 0.7 in Figure 5. When the degree of cure is greater than that, the curves of  $\ln(1 - \alpha)$  versus cure time evidently appear as nonlinear, which may be caused by diffusion control in the late cure stage.

The rate constant  $k$  exhibits Arrhenius behavior, as shown in Figure 6. In the method attributed to Barrett,<sup>17</sup> a plot of  $\ln k$  versus  $T^{-1}$  will be linear for an  $n$ th-order reaction. Values for frequency factor  $A$  and

TABLE II  
Rate Constant  $k$  of the Kinetic Parameters at Different Temperatures

Variable	Temperature (°C)				
	170	180	190	200	210
$k$ (min <sup>-1</sup> )	0.067	0.121	0.196	0.327	0.480



**Figure 6** Kinetic constant  $k$  as a function of reciprocal cure temperatures for BMI.

activation energy  $E$  are then obtained from the intercept and slope, respectively. The frequency factor is  $4.95 \times 10^8 \text{ min}^{-1}$  and the activation energy is 83.31 kJ/mol, which are consistent with values reported in the literature.<sup>18,19</sup>

### CONCLUSIONS

From the isothermal DSC data, it was found that the first-order kinetic expression was correct to analyze the cure of this modified bismaleimide resin. Kinetic parameters, which all agreed well with values reported in the literature, were calculated. An increase in the degree of cure was observed at higher cure temperature. In the initial stage, the reaction was controlled by chemical reaction. With the cure processed,

the reaction rate gradually decreased and then finally leveled off because of diffusion-controlled reactions.

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