

# Cure Kinetics of a Glass/Epoxy Prepreg by Dynamic Differential Scanning Calorimetry

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**ABSTRACT:** Dicyandiamide (DICY)-cured epoxy resins are important materials for structural adhesives and matrix resins for fiber-reinforced prepregs. Dynamic differential scanning calorimetry (DSC) with heating rates of 2.5, 5, 10, and 15°C/min was used to study the curing behavior of the epoxy prepreg Hexply 1454 system, which consisted of diglycidyl ether of bisphenol A, DICY, and Urone reinforced by glass fibers. The curing kinetic parameters were determined with three different methods and compared. These were the Kissinger, Ozawa, and Borchardt–Daniels kinetic approaches. The lowest activation energy (76.8 kJ/mol) was obtained with the Kissinger method, whereas the highest value (87.9 kJ/mol) was obtained with the Borchardt–Daniels approach. The average pre-exponential factor

varied from  $0.0947 \times 10^9$  to  $2.60 \times 10^9 \text{ s}^{-1}$ . The orders of the cure reaction changed little with the heating rate, so the effect of the heating rate on the reaction order was not significant. It was interesting that the overall reaction order obtained from all three methods was nearly constant ( $\cong 2.4$ ). There was good agreement between all of the methods with the experimental data. However, the best agreement with the experimental data was seen with the Ozawa kinetic parameters, and the most deviation was seen with the Borchardt kinetic parameters. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 62–69, 2011

**Key words:** activation energy; composites; curing of polymers; differential scanning calorimetry (DSC)

## INTRODUCTION

The curing of the matrix resin is a determining step in the manufacturing of fiber-reinforced thermoset composites. The quality of the composites is controlled, to a great extent, by the cure cycle parameters. Because the cure temperature, cure time, and other factors have a large effect on the final properties of the cured composites, it is important to study the cure kinetics and the correlation between the degree of cure ( $\alpha$ ) and the thermal and mechanical properties to design the optimum cure conditions. Differential scanning calorimetry (DSC) has been used extensively to characterize the cure kinetics of thermosetting systems for a wide variety of applications with regard to shelf-life predictions and the optimization of the processing conditions.<sup>1–4</sup>

The cure kinetics can be followed with two DSC methods: dynamic and isothermal. The dynamic cure kinetics are very different from the isothermal cure kinetics. In the dynamic method, the rate constant is a function of temperature, so it will change during the heating process. The kinetic parameters obtained from an isothermal cure study may not be accurate in predicting the dynamic cure behavior,<sup>5,6</sup> and the best

way to understand the dynamic curing process is through the dynamic curing experimental data. Although a correct kinetic model should fit both the isothermal and dynamic experimental data, apparent kinetic models that are useful in the design of cure cycles should not be considered mechanistic models.

In this study, the cure behavior of a commercial and widely used glass/epoxy prepreg, HexPly 1454, was studied by DSC at different heating rates. The results of the isothermal DSC cure characteristics of this prepreg were published elsewhere.<sup>7</sup> This prepreg was based on a dicyandiamide (DICY)-cured diglycidyl ether of bisphenol A epoxy resin system. No cure kinetic parameters have been published for this advanced material, and only a few articles have been published on DICY-cured epoxy resins.<sup>8–14</sup> The experimental data were modeled by autocatalytic cure kinetics. The kinetic parameters were determined with three different methods. These were the Kissinger, Ozawa, and Borchardt–Daniels approaches. These methods were then compared, and their advantages and disadvantages are discussed.

## EXPERIMENTAL

### Materials

The material used in this study was a glass-satin-fabric-reinforced epoxy prepreg (HexPly 1454), supplied by Hexcel Composites (Montluel Cedex, France). On the basis of our analysis, the basic

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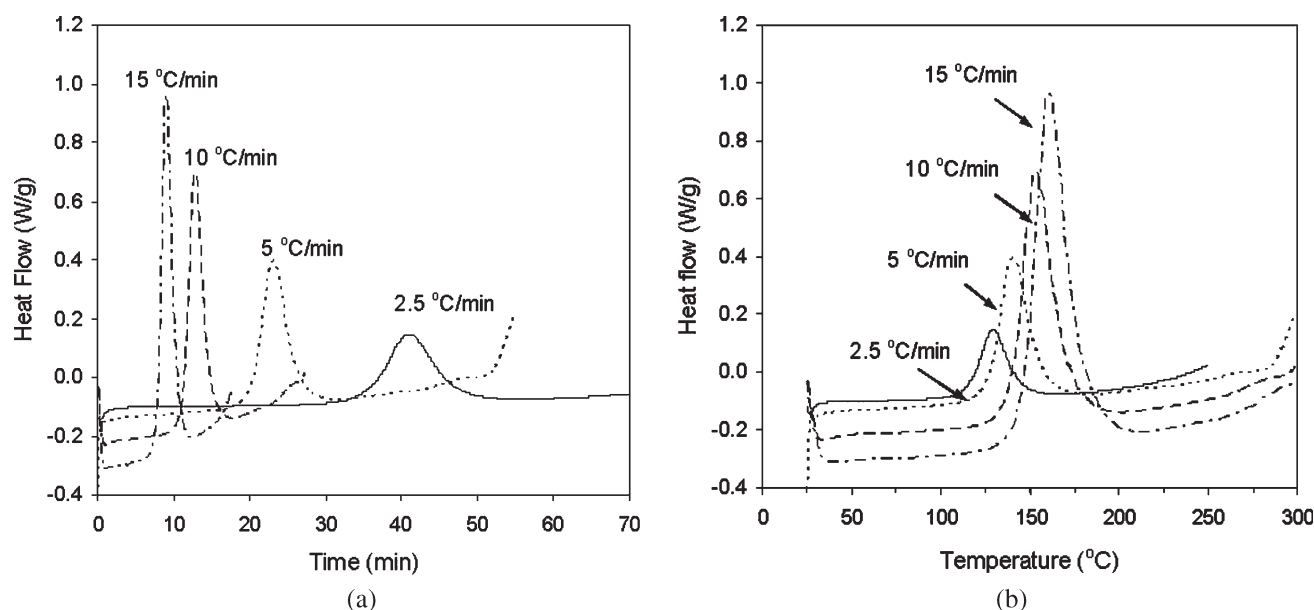


Figure 1 Heat flow versus the (a) time and (b) temperature at different heating rates (2.5, 5, 10, and 15 °C/min).

formulation of the matrix resin contained the popular 125 °C curable diglycidyl ether bisphenol A (DGEBA)/DICY/Urone with a 305 g/m<sup>2</sup> fiber area weight (Satin 8HS) and 49 wt % resin content.

### Experiments

DSC measurements were performed on a Netzsch DSC 200 F3 instrument (Selb, Germany). Dynamic heating experiments were conducted in a flowing nitrogen environment (50 mL/min). The uncured prepreg samples, 12 ± 2 mg in size according to the content of the resin in the prepreg, were placed in an aluminum pan with a pierced lid and placed opposite to the empty reference pan in the DSC chamber. The DSC instrument was then set for temperature range 25–300 °C with four different heating rates: 2.5, 5, 10, and 15 °C/min. The sampling time was set to 6 s per point.

## RESULTS AND DISCUSSION

The heat flow changes measured by DSC during the heating process are shown in Figure 1. Figure 1(a), which shows the heat flow changes versus the time, was used to calculate the cure reaction heat by the method of integration. In this study, a straight baseline was used to integrate the peak of the heat flow with respect to time to give the reaction heat. Table I shows the values of the total reaction heat at each heating rate and the exothermal peak characteristics. As shown in Figure 1(b), which shows the heat flow changes versus the temperature, the start and the end points were shifted to higher temperatures as the

heating rate was increased. The maximum heat flow and the exothermal peak temperature were also increased. The average cure reaction heat was 113.2 ± 4.9 J/g without an apparent relation with the heating rates adopted in this study. Once the reaction heat at each time or temperature and the total reaction heat at each heating rate were determined,  $\alpha$  at each time or temperature could be calculated. By differentiating  $\alpha$  with respect to time, we determined the relationship between the curing reaction rate ( $d\alpha/dt$ ) and the time or temperature. These data were used as the source data to simulate the dynamic curing process.

For the dynamic curing process,  $d\alpha/dt$  is not only a function of  $\alpha$  but also a function of temperature.  $d\alpha/dt$  can be expressed as a function of conversion and temperature<sup>15</sup>:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where  $k(T)$  is the reaction rate constant and  $f(\alpha)$  is a conversion-dependent function.  $k(T)$  has been described by the Arrhenius expression, namely

$$k(T) = A \exp(-E_a/RT) \quad (2)$$

where  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the absolute temperature.

As mentioned before, the cure kinetics can be followed with two DSC methods: dynamic and isothermal. The isothermal method can identify two types of reactions:  $n$ -order and autocatalytic reactions. If the maximum peak of the isotherm is close to  $t = 0$  (where  $t$  is the cure time), the system obeys the

TABLE I  
Total Dynamic Heat of Reaction and Dependence of the Peak Properties  
on the Heating Rate

	Heating rate (°C/min)			
	2.5	5	10	15
Total heat of reaction (J/g)	113.6	119.9	109.4	109.7
Peak temperature (°C)	129.3	141	153	160.1
Conversion at peak ( $\alpha_p$ )	0.47	0.45	0.43	0.42
$(d\alpha/dT)_p$ (1/K)	0.0492	0.0494	0.0473	0.0441
Time to the peak (min)	41	23.1	12.8	9

kinetics of  $n$  order [ $f(\alpha) = (1 - \alpha)^n$ ], and it can be studied either by dynamic or isothermal methods. When the maximum peak is formed between 30 and 40% of the total time of the analysis, the cure is autocatalytic. The autocatalytic model considers the independent reaction orders  $m$  and  $n$ . In the autocatalytic model with an initial  $d\alpha/dt$  of zero, the term  $f(\alpha)$  may have the following form<sup>16</sup>:

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

For a dynamic curing process with a constant heating rate, the temperature increases with the increment of  $t$ . The relationship between  $d\alpha/dt$  and the derivative of the degree of cure with respect to temperature ( $d\alpha/dT$ ) can be expressed as follows:

$$\frac{d\alpha}{dt} = \left(\frac{dT}{dt}\right) \frac{d\alpha}{dT} \quad (4)$$

where  $dT/dt$  is the constant heating rate. The substitution of eqs. (2)–(4) yields

$$\frac{dT}{dt} = A \left(\frac{d\alpha}{dT}\right)^{-1} \alpha^m(1 - \alpha)^n \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

With the logarithm on both sides of eq. (5) taken

$$\ln\left(\frac{dT}{dt}\right) = \ln A - \ln\left(\frac{d\alpha}{dT}\right) + \ln(\alpha^m(1 - \alpha)^n) + \left(-\frac{E_a}{R}\right) \frac{1}{T} \quad (6)$$

$A$  and  $E_a$  can be determined by the Kissinger<sup>17</sup> and Ozawa<sup>18</sup> kinetic approach. The Ozawa and Kissinger methods assume that the DSC exothermal peak is isoconversional and that its value is independent of the heating rate.

Equation (6) can be used to describe the relationship between the heating rate and the exothermic peak temperature.  $A$  changes with the heating rate, so the average value of  $A$  at different heating rates can be used. The derivative of  $d\alpha/dt$  with respect to temperature equals zero at the peak temperature, so  $d\alpha/dT$  at the peak temperature should be constant,

regardless of the heating rates. The term  $\ln[\alpha^m(1 - \alpha)^n]$  at the peak temperature changes with the heating rate, but compared to the term  $\ln A$ , its value is very small on the basis of the previous considerations. The general linear form between the heating rate and the reversal of the peak temperature is

$$\ln\left(\frac{dT}{dt}\right) = c + \left(-\frac{E_a}{R}\right) \left(\frac{1}{T_p}\right) \quad (7)$$

where  $[-(E_a/R)]$  is the slope of the curve and  $c$  is the intercept:

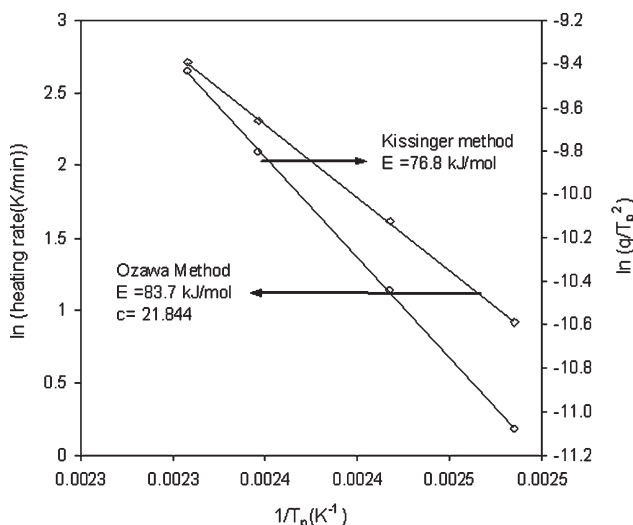
$$c = \ln \bar{A} - \ln\left(\frac{d\alpha}{dT}\right)_p + \ln \alpha_p^m(1 - \alpha_p)^n \quad (8)$$

where  $\bar{A}$  is the average value of the pre-exponential factors at the four heating rates. The term  $T_p$  is the absolute temperature at the exothermic peak,  $(d\alpha/dT)_p$  is the derivative of the degree of cure to temperature at the exothermic peak, and  $\alpha_p$  is the degree of cure at the exothermic peak. Their values are shown in Table I. The differences in the  $(d\alpha/dT)_p$ 's at the different heating rates were small.  $\alpha_p$  decreased with increasing heating rate. The logarithmic plot of the heating rate to the reciprocal of the absolute peak temperature is given in Figure 2. There existed a very good linear relationship between the heating rate and the reciprocal of the exothermic peak temperature. The values for the intercept and  $E_a$  calculated according to the Ozawa method were 21.844 and 83.7 kJ/mol, respectively.

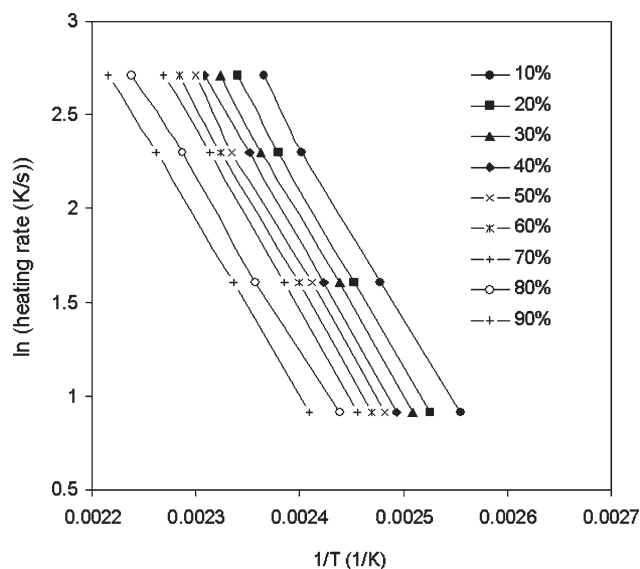
According to the method of Kissinger,  $E_a$  was obtained from the maximum reaction rate, where  $d(d\alpha/dt)/dt$  is zero at a constant heating rate. The resulting relation can be expressed as follows:

$$\frac{d[\ln(q/T_p^2)]}{d(1/T_p)} = -\frac{E}{R} \quad (9)$$

where  $T_p$  is the maximum rate temperature,  $q$  is a constant heating rate, and  $E$  is the activation energy. Therefore, a plot of  $\ln(q/T_p^2)$  versus  $1/T_p$  gives  $E_a$  without a specific assumption of the  $f(\alpha)$ .<sup>16</sup>



**Figure 2**  $E_a$  values obtained with the Ozawa and Kissinger methods. The  $E_a$  values were determined by the peak temperatures at heating rates of 2.5, 5, 10, and 15°C/min.



**Figure 3** Isoconversional plots for the logarithm of the heating rate versus the reciprocal of  $T$ . The apparent  $E_a$  values were determined from the isoconversional plots.

According to the Kissinger method, the value calculated for  $E_a$  was 76.8 kJ/mol (Fig. 2). The Ozawa and Kissinger methods gave similar  $E_a$  values. The difference between the  $E_a$  values obtained by two methods was about 8%. On the basis of the literature, the deviation of the  $E_a$  values between both methods was less than 10%.

On the basis of eq. (6), a series of isoconversional plots were obtained. In this case, each plot had the same  $\alpha$ . At different heating rates, the temperature required to achieve the same  $\alpha$  was different. It increased with increasing heating rate. At each isoconversional curve, the apparent  $E_a$  was constant. The isoconversional plots of the logarithm of the heating rate versus the reciprocal of  $T$  are shown in Figure 3. For all of the isoconversional curves, a good linear relationship was observed between the logarithm of the heating rate and the reciprocal of  $T$ . The apparent  $E_a$  at each  $\alpha$  was calculated from its slope in the isoconversional curve, and their values are listed in Table II. The isoconversional plots helped us to understand the details of the curing process. As shown in Figure 3 and Table II, the apparent  $E_a$  was almost constant in the 10–90% conversion range.

The rearrangement of eq. (8) gives an expression for  $\bar{A}$ :

$$\bar{A} = \frac{e^c \left( \frac{d\alpha}{dT} \right)^p}{\alpha_p^n (1 - \alpha_p)^n} \quad (10)$$

With  $\bar{A}$  and  $E_a$ , the actual  $A$  and orders of the cure reactions at each specific heating rate need to be determined. To reflect the change in  $A$  with the heating rate,  $\bar{A}$  is modified by the introduction of a parameter ( $A_r$ ) for obtaining an expression for  $A$  at each heating rate. If we let  $A_r = A/\bar{A}$ , eq. (10) can be written as follows:<sup>6</sup>

$$A = A_r \frac{e^c \left( \frac{d\alpha}{dT} \right)^p}{\alpha_p^n (1 - \alpha_p)^n} \quad (11)$$

where  $A_r$  is the correction factor of the specific pre-exponential factor to the average pre-exponential factor, which varies with the heating rate. The regression process indicated that the introduction of  $A_r$  greatly improved the fitting results. The substitution of eqs. (2), (3), and (11) into eq. (1) and rearrangement resulted in the final expression for the dynamic  $d\alpha/dt$  as follows:

**TABLE II**  
 $E_a$  Values Calculated from Isoconversional Plots with Different  $\alpha$  Values

	$\alpha$									Average
	10%	20%	30%	40%	50%	60%	70%	80%	90%	
$E_a$ (kJ/mol)	77.9	80.1	80.2	80.2	80.8	79.6	79.7	75.4	77	79

The  $E_a$  values were determined from the plots in Figure 3.

**TABLE III**  
Dynamic Kinetic Parameters Obtained by a Method Based on the Ozawa Approach

Parameter	Heating rate (°C/min) <sup>a</sup>			
	2.5	5	10	15
$A_r$	0.994	0.987	0.959	0.979
$A$	$7.25 \times 10^8$	$6.97 \times 10^8$	$6.68 \times 10^8$	$6.60 \times 10^8$
$m$	0.79	0.78	0.79	0.82
$n$	1.54	1.54	1.59	1.64
$R^2$	0.99974	0.99871	0.99705	0.99735

<sup>a</sup>  $E_a$  and  $c$ , calculated according to these results, were 83.7 kJ/mol and 21.84, respectively.

$$\frac{d\alpha}{dt} = A_r e^c \left( \frac{d\alpha}{dT} \right)_p e^{-\left( E_a/RT \right)} \frac{\alpha^m (1-\alpha)^n}{\alpha_p^m (1-\alpha_p)^n} \quad (12)$$

$A_r$  and the orders of the cure reaction  $m$  and  $n$  were determined by a multiple nonlinear least-squares regression method that was based on the Levenberg–Marquardt algorithm. The dynamic kinetic parameters ( $A_r$ ,  $A$ ,  $m$ , and  $n$ ) obtained by the Ozawa method at different heating rates are listed in Table III. The cure reaction exhibited the behavior of an autocatalytic reaction. The average values for  $m$  and  $n$  at the studied heating rates were 0.80 and 1.58, respectively. The orders of the reactions changed a little with the heating rate, so the effect of the heating rate on the reaction orders was not significant. The average of the total reaction order of the cure reaction was about 2.37 at all of the heating rates. This was close to the reaction order of 2, which was reported elsewhere.<sup>19,20</sup>

As shown in Table III, all of the values for  $A_r$  at the studied heating rates were less than 1. With eq. (11),  $A$  at each heating rate could be calculated, and the results are listed in Table III. Unlike the reaction orders, the changes in  $A$  with the heating rate were apparent, where  $A$  decreased with increasing heating rate. This implied that the kinetic rate constant of the same temperature decreased with increasing heating rate.

Having the kinetic parameters, one can calculate the values for  $\alpha$  and  $d\alpha/dt$  by solving the differential equation. The substitution of eqs. (2)–(4) into eq. (1) and rearrangement gives

$$\frac{d\alpha}{dT} = \left( \frac{dT}{dt} \right)^{-1} A e^{-\left( E_a/RT \right)} \alpha^m (1-\alpha)^n \quad (13)$$

Equation (13) is a nonlinear ordinary differential equation, where the dependent variable is  $\alpha$  and the independent variable is  $T$ . There is no analytical solution to this equation. Matlab software (Mathworks Inc., version 6.5) was used to find the numerical solution. The solver used was ode45, which was based on the Runge–Kutta (4, 5) algorithm. The calculated results for  $\alpha$  at each heating rate are plotted in Figure 4. As shown in Figure 4, the calculated total  $\alpha$

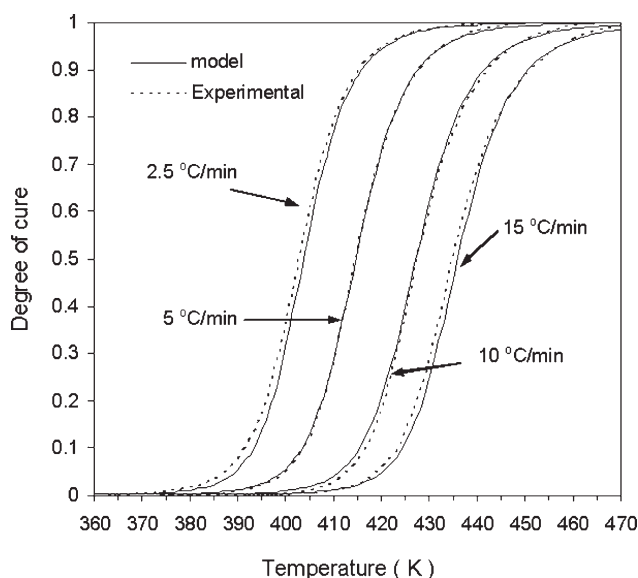
agreed well with the experimental data at all heating rates, and the best agreement was observed at 5 and 10°C/min.

Once we had the curves of  $\alpha$  versus temperature, the dependence of  $d\alpha/dT$  on temperature was easily determined by the differentiation of  $\alpha$  with respect to the temperature. With eq. (4),  $d\alpha/dt$  versus temperature was calculated. The predicted results, along with the experimental values, are shown in Figure 5.

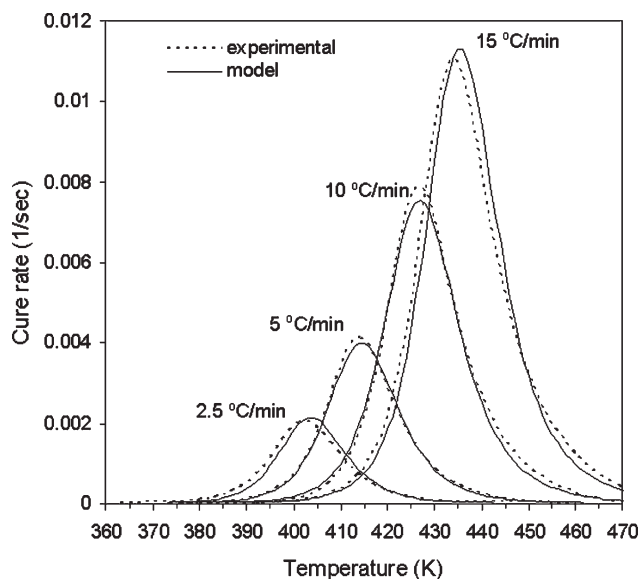
In this section, the whole curing process was studied with another method, which was based on the Borchardt and Daniels approach,<sup>21</sup> in which all four parameters  $A$ ,  $m$ ,  $n$ , and  $E_a$  were obtained simultaneously. The combination of eqs. (2) and (3) yields:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) \alpha^m (1-\alpha)^n \quad (14)$$

Equation (14) can be solved by multiple nonlinear regression. Because  $d\alpha/dt$  is an exponential function of the reciprocal of  $T$ , it is difficult to get a good solution. The fitting results showed that significant



**Figure 4**  $\alpha$  as a function of the temperature, calculated with the method based on the Kissinger and Ozawa approach (model) and determined experimentally at different heating rates (2.5, 5, 10, and 15°C/min).

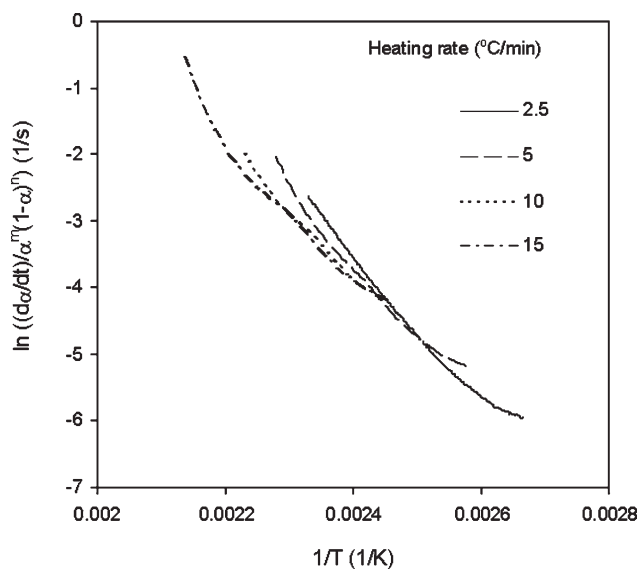


**Figure 5**  $d\alpha/dt$  as a function of the temperature, calculated with the method based on the Kissinger and Ozawa approach (model) and determined experimentally at different heating rates (2.5, 5, 10, and 15 °C/min).

errors existed for  $A$  and  $E_a$  determined by this method. The reaction orders  $m$  and  $n$  obtained by the multiple nonlinear regressions are given in Table IV. The variations of  $m$  and  $n$  with the heating rate were small. Compared to the average values of 0.80 and 1.58 previously obtained for  $m$  and  $n$ , the average values determined by this method were 0.76 and 1.63, respectively. The apparent values of  $A$  and  $E_a$  had big standard errors (not shown in Table IV). Therefore, it was necessary to redetermine the apparent values of  $A$  and  $E_a$  to reduce the magnitudes of the standard errors. Once the orders of the cure reaction  $m$  and  $n$  were determined,  $A$  and  $E_a$  were determined with small standard errors by the Barrett<sup>22</sup> method. Equation (14) can be rearranged to yield

$$\frac{\left(\frac{d\alpha}{dt}\right)}{\alpha^m(1-\alpha)^n} = Ae^{-(E_a/RT)} \quad (15)$$

Equation (15) shows that there is a linear relationship between the logarithm of  $(d\alpha/dt)/[\alpha^m(1-\alpha)^n]$



**Figure 6** Plots of the logarithm of  $(d\alpha/dt)/[\alpha^m(1-\alpha)^n]$  versus the reciprocal of  $T$  at heating rates of 2.5, 5, 10, and 15 °C/min.

and  $1/T$ ; therefore, the apparent values of  $A$  and  $E_a$  could be determined from the intercept and slope of line obtained from eq. (15). The plots are shown in Figure 6. A main portion of the curve in the range  $\alpha = 5\text{--}95\%$  exhibited linear behavior. By fitting to the linear part of the curve, we determined the apparent values of  $A$  and  $E_a$ . These are given in Table IV. The apparent values of  $A$  and  $E_a$  increased with increasing heating rates. This method is interesting because it provides enough information with a single dynamic DSC test. However, the results obtained for the cure of thermoset resins usually overestimate the value of the kinetic parameters with respect to the isothermal data and the Ozawa and Kissinger methods.<sup>23</sup> The average values of the cure kinetic parameters obtained by the three different methods are given in Table V. The lowest  $E_a$  values (76.8 kJ/mol) were obtained with the Kissinger method, whereas the highest value (87.9 kJ/mol) was obtained with the Borchardt–Daniels approach.  $A$  varied from  $0.095 \times 10^9$  to  $2.60 \times 10^9 \text{ s}^{-1}$ . It was interesting that the overall reaction order found with these three methods was almost constant ( $\cong 2.4$ ). Our results

**TABLE IV**  
Apparent Dynamic Kinetic Parameters Obtained by the Borchardt–Daniels Method

Parameter	Heating rate (°C/min)			
	2.5	5	10	15
$A$ (1/s)	$1.86 \times 10^9$	$2.00 \times 10^9$	$2.22 \times 10^9$	$4.30 \times 10^9$
$E_a$ (kJ/mol) <sup>a</sup>	86.3	86.8	87.9	90.4
$m$	0.75	0.75	0.76	0.78
$n$	1.59	1.59	1.64	1.69

<sup>a</sup> The average value was 87.9 kJ/mol.

TABLE V  
Average Cure Kinetic Parameters Obtained by the Kissinger, Ozawa, Borchardt–Daniels, and DSC Isothermal Methods

Method	$E_a$ (kJ/mol)	$A$ ( $s^{-1}$ )	$m$	$n$	$m + n$
Kissinger	76.8	$0.095 \times 10^9$	0.82	1.55	2.37
Ozawa	83.7	$0.688 \times 10^9$	0.80	1.58	2.37
Borchardt–Daniels	87.9	$2.60 \times 10^9$	0.76	1.63	2.39
Isothermal method <sup>a</sup>	94.8	$17.5 \times 10^9$	0.65	1.46	2.11

<sup>a</sup> The data were taken from Hayaty et al.<sup>7</sup>

were in agreement with the results of other authors<sup>8–14</sup> who studied DICY-cured epoxy resins. The  $E_a$  values reported in the literature were in the range 75–100 kJ/mol.

With all of the kinetic parameters in eq. (14) known,  $\alpha$  can be calculated through the solution of the differential equation. The substitution of eq. (4) into eq. (14) and rearrangement yields an ordinary differential equation the same as eq. (13). Matlab software was used again to find the numerical solution. The calculated results (model) at different heating rates are plotted in Figure 7. The model predictions were in good agreement with the experimental values at different heating rates. By differentiating  $\alpha$  with respect to  $T$ , we obtained  $d\alpha/dt$  with eq. (4). The plots of the calculated  $d\alpha/dt$  versus  $T$  are given in Figure 8. At each heating rate, the model predictions were in good agreement with the experimental values. As shown in Figures 4, 5, 7, and 8, the best agreement between the experimental data and the model in both methods were found at lower heating rates, especially at 5°C/min.

Finally, the results were tested by a standard cure cycle, which is generally composed of dynamic heat-

ing and isothermal holding segments. The prepreg was cured at a constant heating rate, 2.7°C/min, and with isothermal holding at 125°C. The model eq. (13) was solved numerically with the Matlab software. The solver used was ode45, which was based on the Runge–Kutta (4, 5) algorithm. With the same kinetic parameters of the Kissinger, Ozawa, and Borchardt methods obtained at 2.5°C/min for the dynamic section of the cure cycle and the kinetic parameters of the isothermal cure study mentioned in Table V for the isothermal part of the cure cycle, the predicted conversions were compared with the DSC experimental data, as shown in Figure 9. There was good agreement between all of the methods with the experimental data. However, as shown, the best agreement with the experimental data was found with the Ozawa kinetic parameters, and the most deviation was found with the Borchardt kinetic parameters.

## CONCLUSIONS

The cure behavior of a commercial glass/epoxy prepreg, HexPly 1454, was investigated by a dynamic DSC technique. The lowest  $E_a$  (76.8 kJ/mol) was obtained with the Kissinger method, whereas the highest value (87.9 kJ/mol) was obtained with the

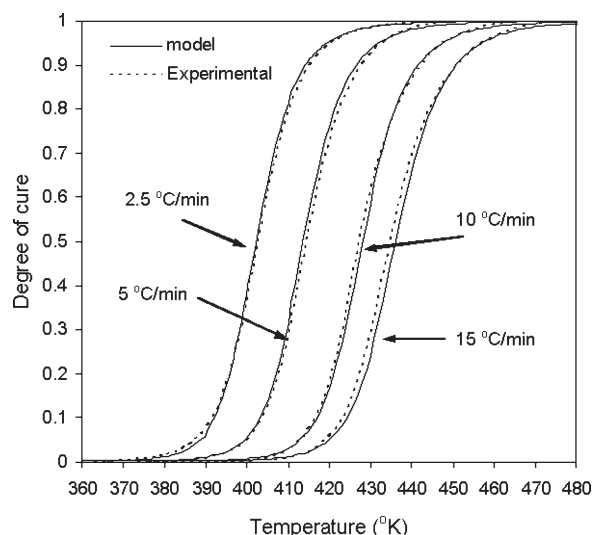


Figure 7  $\alpha$  as a function of the temperature, calculated with the Borchardt–Daniels method and determined experimentally at heating rates of 2.5, 5, 10, and 15°C/min.

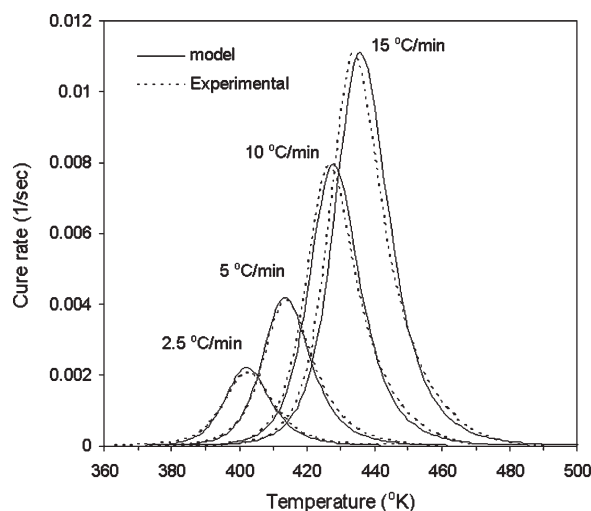
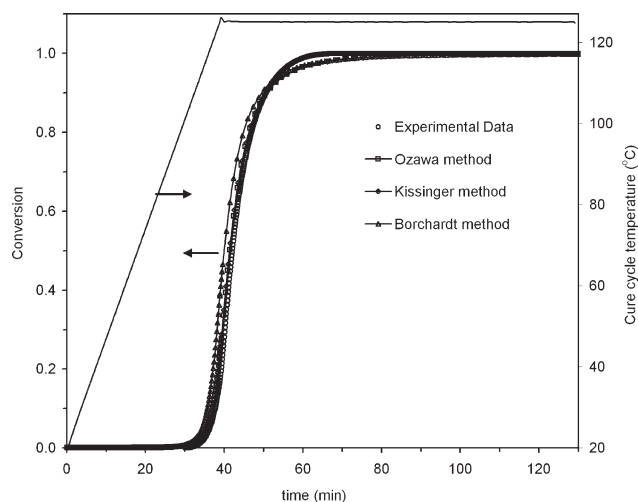


Figure 8  $d\alpha/dt$  as a function of the temperature, calculated with the Borchardt–Daniels method and determined experimentally at heating rates of 2.5, 5, 10, and 15°C/min.



**Figure 9** Prediction of the conversion with the isothermal kinetic parameters and dynamic kinetic parameters obtained by three methods versus DSC experiments as a function of the time for a standard cure cycle (2.7°C/min with holding at 125°C).

Borchardt–Daniels approach.  $\bar{A}$  varied from  $0.0947 \times 10^9$  to  $2.60 \times 10^9 \text{ s}^{-1}$ . The orders of the cure reaction changed a little with the heating rate; thus, the effect of the heating rate on the reaction order was not significant. The overall reaction order with these three methods was almost constant ( $m + n \cong 2.4$ ). With the kinetic parameters obtained by both the Ozawa and Borchardt–Daniels methods, good agreement between the experimental and the theoretical values was observed.

The Borchardt–Daniels method was the most rapid of the three methods studied because, with a single DSC run, it was feasible to calculate the kinetic parameters. All three methods studied had the same disadvantage: they gave a single value of  $E_a$  for the overall process, whereas in a complex system, such as the epoxy/DICY/Monuron system, this parameter changes with the curing time. However, the Ozawa and Kissinger methods were suitable for application in thermosetting resins because these models are not affected significantly by the baseline

shift. Also, these methods include simplicity and applicability to many types of reactions. There was good agreement between all of the methods with the experimental data. However, the best agreement with the experimental data was found with the Ozawa kinetic parameters, and the most deviation was observed with the Borchardt kinetic parameters.

## References

1. Tanaka, Y.; Bauer, R. S. In *Epoxy Resins Chemistry and Technology*; May, C. A., Ed.; Marcel Dekker: New York, 1988.
2. Kim, D. S.; Han, M. J.; Lee, J. R.; Chang, J. Y. *Polym Adv Technol* 1994, 5, 287.
3. Hill, D. J. T.; George, G. A.; Rogers, D. G. *Polym Adv Technol* 2001, 12, 169.
4. Yang, S. S.; Hsieh, T. H.; Bi, H. T.; Ho, K. S.; Ho, T. H.; Chen, H. R.; Ye, S. H.; Chang, Y. C. *J Appl Polym Sci* 2009, 114, 2373.
5. Karkanias, P. I.; Partridge, I. K. *J Appl Polym Sci* 2000, 77, 1419.
6. Sun, L.; Pang, S. S.; Sterling, A. M.; Negulescu, I. I.; Stubblefield, M. A. *J Appl Polym Sci* 2002, 86, 1911.
7. Hayaty, M.; Beheshty, M. H.; Esfandeh, M. *Polym Adv Technol*, DOI: 10.1002/pat.1607.
8. Sacher, E. *Polymer* 1973, 14, 91.
9. Schnider, N. S.; Sprouse, J. F.; Hagnauer, G. L.; Gillham, J. K. *Polym Eng Sci* 1979, 19, 304.
10. Son, P.; Weber, C. D. *J Appl Polym Sci* 1973, 17, 1305.
11. LaLiberte, B. R.; Bornstein, J.; Sacher, R. E. *Ind Eng Chem Prod Res Dev* 1983, 22, 261.
12. Abolafia, O. R. *SPE Annu Tech Conf Proc* 1969, 15, 610.
13. Olcese, T.; Spelta, O.; Vargiu, S. *J Polym Sci Polym Symp* 1975, 53, 113.
14. Miller, R. L.; Oebser, M. A. *Thermochim Acta* 1980, 36, 121.
15. Gonis, J.; Simon, G. P.; Cook, W. D. *J Appl Polym Sci* 1999, 2, 1479.
16. Yang, F.; Yao, K. D.; Koh, W. *J Appl Polym Sci* 1999, 73, 1501.
17. Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
18. Ozawa, T. *J Therm Anal Calorim* 1970, 2, 301.
19. Yang, F.; Yao, K. D.; Koh, W. *J Appl Polym Sci* 1999, 73, 1501.
20. Dupuy, J.; Leroy, E.; Maazouz, A. *J Appl Polym Sci* 2000, 78, 2262.
21. Borchardt, H. J.; Daniels, F. *J Am Chem Soc* 1956, 79, 41.
22. Riccardi, C. C.; Adabbo, H. E.; Williams, R. J. *J Appl Polym Sci* 1984, 29, 2481.
23. Alonso, M. V.; Oliet, M.; Perez, J. M.; Rodriguez, F.; Echeverria, J. *Thermochim Acta* 2004, 419, 161.