

# Application of the Kinetic Composite Methodology to Autocatalytic-Type Thermoset Prepreg Cures

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## SYNOPSIS

Using a commercial epoxy/carbon fiber prepreg as a model system, cure kinetics of an autocatalytic-type reaction were analyzed by a general form of conversion-dependent function first proposed for degradation kinetics of polymers and composites. The characteristic feature of conversion-dependent function was determined using a reduced-plot method where the temperature-dependent reaction rate constant was analytically separated from the isothermal data. Assuming two elementary reaction mechanisms that were expressed by the  $n$ th order and autocatalytic kinetic models, they were combined with a composite methodology capable of predicting overall kinetic behavior. The activation energies were determined and favorably compared for both isothermal and dynamic-heating differential scanning calorimetry experiments in the temperature region for standard epoxy cures at 177°C (350°F). Finally, the proposed model equation demonstrated excellent predictive capability and broad applicability in describing various types of thermoset polymer cure for both isothermal and dynamic heating conditions. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Kinetic characterization of thermoset resins is fundamental in understanding structure–property–processing relationships for high performance composite manufacturing and utilization. Differential scanning calorimetry (DSC) has been used extensively to characterize cure kinetics of thermosetting systems for a wide variety of application regarding shelf-life predictions and optimization of processing conditions. In particular, commercialized  $B$ -staged resins and prepreps contain a number of reacting/nonreacting materials such as catalysts, toughening additives, solvents, water, etc. affecting the curing kinetics as well as final performance. For example, salicylic acid has been shown to possess long shelf life and short cure times because the acid acts as a hydrogen donor that influences hydroxyl–epoxide reactions.<sup>1</sup> Moisture, which is usually absorbed by the prepreps during manufacturing and initial storage, was also found to accelerate the cure and has

been attributed to chain-extension reactions such as the hydroxyl–epoxide etherification reaction.<sup>2</sup> The mixture of these reacting/nonreacting components results in a complex curing behavior that may not simply be predicted by the properties of constituent materials.

In kinetic studies using a thermogravimetric analyzer (TGA), weight loss kinetics were extensively studied for polymer stability and high temperature reaction mechanisms in long-term utilization.<sup>3,4</sup> Traditionally TGA and DSC kinetic issues have been addressed quite independently because the temperature range of concern and the interest vary. However, it should be noted that the kinetic model equations have been clearly tested in TGA kinetic studies using more stable baselines and relatively slow and controllable reaction rates.<sup>3</sup> Incorporating multistage independent reaction rates and elementary reaction mechanisms in TGA weight-loss kinetic studies, we have developed a *composite degradation methodology* describing complex behavior of weight loss in both isothermal and dynamic-heating conditions.<sup>5,6</sup> In these studies, it was noted that the misused conversion-dependent function seemed to be one of the major causes of kinetic modeling

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failure. Verification was also required that the temperature-dependent function, generally represented by the activation energy, be consistent in both isothermal and dynamic-heating conditions.

In this study, using the developed composite methodology, a specific form of the conversion-dependent function was proposed and utilized to describe cure kinetics of seemingly complex epoxy-based prepreg systems in both isothermal and dynamic-heating conditions. TORAYCA T800H/3900-2, a newly developed toughened prepreg system, was chosen as a model system for kinetic model development. It was recently qualified on Boeing Material Specification (BMS 8-276) to be utilized for aircraft primary structures as well as a broad range of load bearing structures.<sup>7-10</sup> The developed modeling methodology demonstrates the versatility and consistency in describing curing kinetics of various thermosetting polymer systems exposed to different thermal histories.

## EXPERIMENTAL

DSC measurements were performed with a TA Instruments 910 DSC coupled to a TA Instruments 2100 controller. Isothermal and dynamic-heating experiments were conducted in a flowing air environment (100 mL/min) using epoxy prepreg samples of  $15 \pm 2.0$  mg size. For isothermal experiments, the instrument was preheated to the experimental temperature, ranging from 160 to 185°C with a 5°C temperature increment, and then the sample pan was quickly placed in the DSC cell. For dynamic-heating experiments, six different heating rates were investigated: 1.02, 2.04, 3.04, 5.06, 10.09, and 20.31°C/min in air atmosphere. Finally, simulating a standard composite cure cycle, the samples in the DSC cell were heated at 2.85°C/min (5.13°F/min) up to 177°C (350°F) and were held at that temperature for 2 h until the cure reaction was completed.

When the isothermal experiments were performed higher than 185°C, the reaction rate was so rapid that the real reaction exotherm was masked by the nonisothermal heating signal to reach the destination temperature. Therefore 185°C was considered as the maximum experimental temperature in which kinetic analysis was possible. In addition to the experimental difficulties, it should also be noted that the amine-epoxy cure mechanism is not necessarily the same over the entire temperature range even without degradation.<sup>11</sup> The faster and lower activated reaction regime is known as the addition of the primary amine to epoxy, and the slower

and more highly activated reaction is likely to be the homopolymerization and etherification of the epoxy.<sup>2,11-13</sup> The values of activation energy for these primary-amine addition and high temperature reactions were reported as 69.9 and 177.0 kJ/mol, respectively.<sup>2</sup> As a result of further FTIR analysis, the etherification reaction was found not to occur at least at temperatures below 200°C.<sup>14</sup> Accordingly, the reactions with the activation energy of 177.0 kJ/mol are not likely to occur in the temperature range below 177°C where the TGDDM/DDS based epoxies and composites are usually suggested to be cured. However, if the curing reaction is forced to be cured at higher temperatures, additional high temperature reactions may be activated resulting in different reaction rates and mechanisms that will influence the curing kinetics as well as the final morphology and performance. According to the experimental difficulty and practical perspective, the isothermal DSC experiments were performed between 160 and 185°C for the kinetic analysis.

The material investigated in this study as a model system was a unidirectional TORAYCA T800H/3900-2 prepreg. The basic formulation of the matrix resin contains the popular 177°C curable TGDDM/DDS system with 145 g/m<sup>2</sup> fiber areal weight and 35 wt % resin content.<sup>7,8</sup> Amorphous polyamide particles are selectively localized onto the surface of the prepreg forming a thin resin/particle film between prepreg layers in the composite laminate in order to improve the interlayer fracture toughness and compressive strength after impact. Further details on this prepreg system may be found elsewhere.<sup>7-10,15</sup>

## BACKGROUND

If one assumes that the extent of reaction ( $\alpha$ ) is proportional to the heat generated during reaction, the reaction rate can be expressed as a function of conversion and temperature, viz.:

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

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

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

where  $A$  is the pre-exponential factor, and  $E$  is the

activation energy. An integrated form of the above equation often appears in the literature as<sup>4</sup>

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T)t \quad (3)$$

where  $g(\alpha)$  is the integrated form of the conversion-dependent function.

The conversion-dependent function,  $f(\alpha)$  or  $g(\alpha)$ , can be determined by a master curve construction comparing the experimental data with model equations without the effect of isothermal experimental temperatures.<sup>6</sup> In this method, the reaction rate constant,  $k(T)$ , can be separated from the conversion-dependent function in an analytical treatment of the basic kinetic equation, so that the characteristic features of the reaction mechanism can be exhibited.

For master curve construction, the maximum reaction-rate time ( $t_m$ ) may be chosen as a reference time, and eq. (3) expressed as

$$g(\alpha_m) = k(T)t_m. \quad (4)$$

Eliminating the reaction constant  $k(T)$  from eqs. (1) and (4),

$$\frac{d\alpha}{dt_r} = g(\alpha_m)f(\alpha) \quad (5)$$

where  $t_r = t/t_m$ , which is generally termed "reduced time." As seen in this equation, when  $d\alpha/dt_r$  values for different temperatures fall into the same curve plotted as a function of  $\alpha$ , the form of  $f(\alpha)$  in eq. (5) can be determined by fitting this master curve using an appropriate  $f(\alpha)$  model equation. If an analytical form of  $g(\alpha)$  can be obtained by the integration of  $1/f(\alpha)$  with respect to  $\alpha$ , eq. (5) can be directly utilized to determine the kinetic parameters included in  $f(\alpha)$ . However, as with most kinetic models, the analytical form of  $g(\alpha)$  is not often obtained to calculate  $g(\alpha_m)$  in eq. (5). Therefore, in order to replace the  $g(\alpha_m)$  value with some measurable master curve values, the following additional procedure may be needed. Manipulating eq. (5) using the maximum reaction rate exhibited in the master curve,

$$\left(\frac{d\alpha}{dt_r}\right)_{\alpha=\alpha_m} = g(\alpha_m)f(\alpha_m). \quad (6)$$

Eliminating  $g(\alpha_m)$  from eqs. (5) and (6),

$$\left(\frac{d\alpha}{dt_r}\right) = \frac{(d\alpha/dt_r)_{\alpha=\alpha_m}}{f(\alpha_m)} f(\alpha). \quad (7)$$

Consequently,  $(d\alpha/dt)_{\alpha=\alpha_m}$  and  $\alpha_m$  can be directly read from the master curve, and eq. (7) can be used to determine the kinetic parameters included in the  $f(\alpha)$  and  $f(\alpha_m)$  functions by fitting the master curve.

In most epoxy systems, the rate observed by the heat of reaction has been found to exhibit a maximum when plotted as a function of time, referred to as autocatalytic reaction. Representing  $\alpha$  as the catalytic concentration (e.g., hydroxyl group) generally produced by the preceding reactions, and  $(1 - \alpha)$  as reactants of epoxide and amine hydrogen, one of the most common form of autocatalytic-type kinetic model may be obtained as<sup>16</sup>

$$\frac{d\alpha}{dt} = k(T)\alpha^m(1 - \alpha)^n \quad (8)$$

where  $k(T)$  is an Arrhenius type reaction rate constant, and  $m$  and  $n$  are reaction orders. However, it should be noted that the initial reaction rate of most epoxy systems is not zero, which is the case with the above model equation.

To correct this shortcoming, the following phenomenological model equation has been often utilized in kinetic studies of autocatalytic reactions, viz.<sup>17-22</sup>

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (9)$$

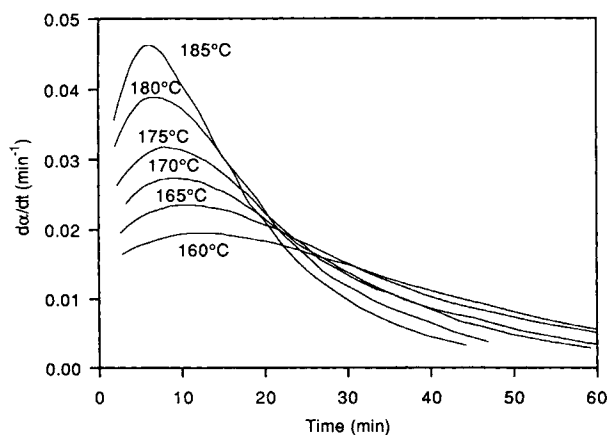
where  $k_1(T)$  and  $k_2(T)$  are reaction rate constants with two different activation energies and preexponential factors, and  $(m + n)$  are the overall reaction order, which is often assumed to be constant. Equation (9) exhibits the experimental observations of the maximum reaction rate at  $t > 0$  and a finite reaction rate at  $t = 0$ .

According to this model equation, the initial rate of reaction becomes  $k_1$  and may be directly determined as a function of temperature by the analysis of a DSC thermogram extrapolating the reaction rate ( $d\alpha/dt$ ) to  $t = 0$ .<sup>18</sup> However, it has been observed that the DSC experimental data usually show fluctuations in the initial period of reaction resulting in difficulties in extrapolation. Furthermore, for many epoxy systems, the extent of cure of the maximum reaction rate exhibits a constant value in a moderate range of isothermal experimental temperature. When the maximum rate appears at the same conversion for different temperatures, it may imply that only one activation energy is required in kinetic modeling, because there is no other characteristic dependence of reaction rate on temperature.<sup>6</sup> This can be easily demonstrated by the partial derivative

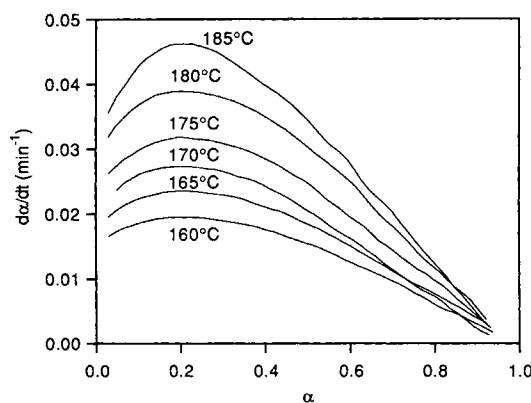
of eq. (9) with respect to  $\alpha$  setting to zero, viz.:  $\partial(d\alpha/dt)/\partial\alpha = 0$ . In this case, the activation energies of  $k_1$  and  $k_2$  must analytically be the same if the maximum rate of reaction is to appear at the same extent of reaction. As a result of this, the model parameters  $m$  and/or  $n$  were often obtained as a function of temperature in order to compensate for this abnormality.<sup>17-19</sup> In fact, it has been observed in the literature that these two activation energy values are often reported to be quite close in many kinetic studies.<sup>18,20-22</sup> Accordingly, the following model was proposed in this study.

## RESULTS AND DISCUSSION

Figure 1 shows the isothermal reaction rates of the model prepreg system obtained as a function of time at different temperatures exhibiting the maximum reaction rate, which is a typical feature of an autocatalytic reaction mechanism. The heat of reaction measured by isothermal experiments was  $127 \pm 7$  J/g and there was no apparent relation between the isothermal cure temperature and the heat of reaction observed within the experimental temperature range. As shown in Figure 2, the autocatalytic characteristics of the reaction can be more clearly seen in the  $d\alpha/dt$  versus  $\alpha$  plot, where the maximum reaction rates appear at the same conversion of 20% ( $\alpha_m$ ) regardless of the isothermal experimental temperatures up to 185°C. As can be seen, the extrapolated initial reaction rates could not be assumed to be zero, which is a requirement for using the kinetic model eq. (8).



**Figure 1** Isothermal reaction rate of model epoxy prepreg measured by DSC as a function of time for six different isothermal temperatures.



**Figure 2** Isothermal reaction rate of model epoxy prepreg measured by DSC plotted as a function of conversion for six different isothermal temperatures.

When several independent and/or competing reactions take place, the whole reaction process can be described by the composite methodology with an appropriate weighting factor.<sup>16</sup> Extending this methodology, the importance of each elementary reaction mechanism was successfully combined by an appropriate weighting factor to describe both isothermal and dynamic weight-loss kinetics of high temperature polymers.<sup>6</sup> According to this methodology, the overall conversion-dependent function can be described in a general form as

$$f(\alpha) = \sum_i y_i f_i(\alpha) \quad (10)$$

where

$$\sum_i y_i = 1.0 \quad (11)$$

and

$$f_i(\alpha) = \alpha^{m_i} (1 - \alpha)^{n_i} \quad (12)$$

Specific forms of  $f_i(\alpha)$  may be chosen by a rational model based on the basic physico-chemical aspects of a material reaction system, which should be finally verified by fitting the experimental data.<sup>3</sup>

For the epoxy-based systems, the first elementary reaction ( $R_1$ ) may be expressed by an  $n$ th order kinetic model if the reaction products do not affect the reaction rate, for example, primary amine-epoxide reactions:

$$f_{R_1} = (1 - \alpha)^p \quad (13)$$

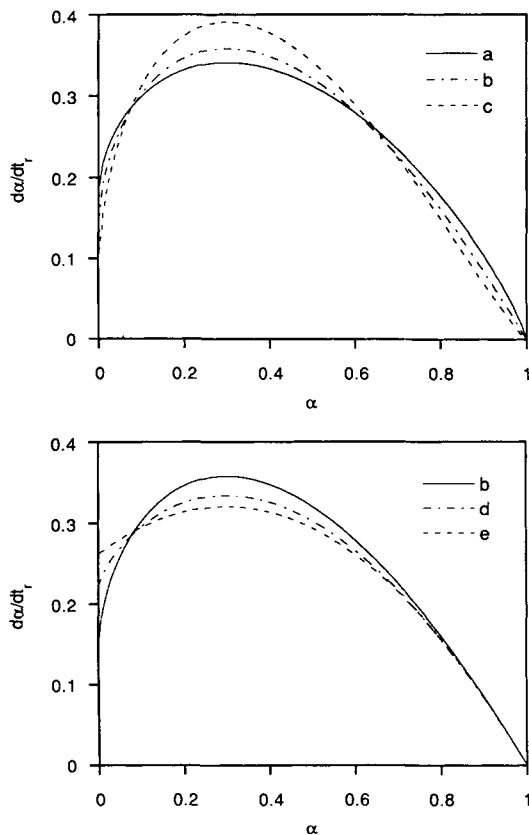
In fact, two principal reaction mechanisms of epoxy and primary amine are known to occur simultaneously in a random fashion to produce secondary and tertiary amines.<sup>16</sup> These two reactions are suggested as a first order reaction and they are very close in terms of activation energy: 58.2 and 56.1 kJ/mol for primary and secondary amine reactions, respectively.<sup>23</sup>

The second elementary reaction (R2) may be described by a general form of autocatalytic reaction model if the reaction rate is accelerated by reaction products:

$$f_{R2} = \alpha^m(1 - \alpha)^n. \quad (14)$$

Then, incorporating these two hypothetical elementary reactions by using the weighting factor, the model eqs. (10)–(12) can be specifically expressed for epoxy-based systems as:

$$\frac{d\alpha}{dt} = k[y_1(1 - \alpha) + y_2\alpha^m(1 - \alpha)^n] \quad (15)$$



**Figure 3** Model parameter effects of (a)  $n$  and (b)  $m$  on the characteristic features of reaction rate versus conversion master curve for a fixed  $\alpha_{\max} = 0.3$ . Plot is based on eq. (15) in text and values of Table I.

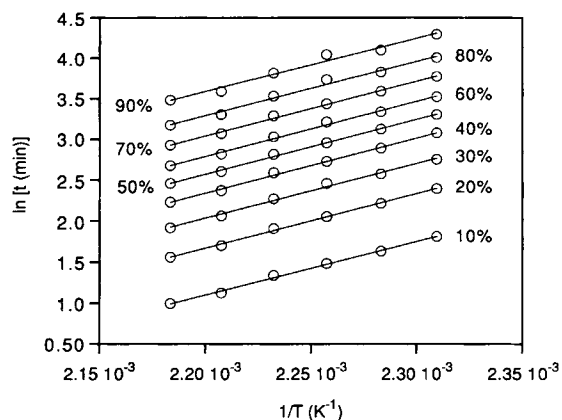
**Table I** Investigated Model Parameters for Predictions Shown in Figure 3

Curve	$m$	$n$	$y_1$	$g (\alpha_m = 0.3)$
a	0.6	0.8	0.238	0.766
b	0.6	1.0	0.163	0.899
c	0.6	1.2	0.0829	1.123
d	0.8	1.0	0.249	0.893
e	1.0	1.0	0.286	0.916

where  $y_1 + y_2 = 1.0$ . As seen in eqs. (2) and (15), there are five kinetic parameters to be determined by the expression to the experimental data:  $A$ ,  $E$ ,  $y_1$ ,  $m$ , and  $n$ . The activation energy,  $E$ , in the reaction rate constant  $k(T)$  is independently associated with the temperature effect on the reaction rates, which can be determined by many analytical techniques for both isothermal and dynamic-heating experiments.<sup>3,4</sup> On the other hand, comparing eqs. (1) and (15), the characteristic feature of the reaction mechanisms expressed by the conversion-dependent function  $f(\alpha)$  can be assumed independent of temperature. Consequently, the kinetic analysis can be performed independently on these two ideally independent parts by constructing a master cure curve.

In Figure 3, the characteristic features of the developed model eq. (15) were investigated by the master curves using the model parameters shown in Table I. For this parameter investigation,  $\alpha_m$  was fixed at 0.3, and  $m$  and  $n$  were chosen to change around 1.0. Under the constraints of  $\alpha_m = 0.3$  and two chosen values of  $m$  and  $n$ ,  $y_1$  should be analytically fixed by the model equation as shown in Table I. As seen in Figure 3(a), the reaction order,  $n$ , determines broadness of the master curve in a symmetrical fashion. On the other hand, Figure 3(b) shows that the parameter,  $m$ , affects the initial reaction rate significantly and controls asymmetry of the master curve. Conclusively, the proposed kinetic model demonstrates that various types of characteristic reaction shape can be described by appropriately choosing the model parameters of  $m$ ,  $n$ , and  $y_1$ .

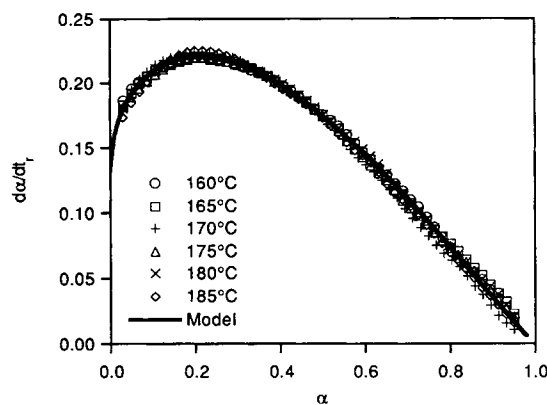
According to eqs. (2) and (3), the activation energy can be obtained in the isothermal case by plotting  $\log(t)$  versus  $T^{-1}$  at a constant conversion level assuming that the reaction mechanism is consistent at the same level of conversion within the temperature range being investigated. In this method, no additional assumption on the form of conversion-dependent function is needed to obtain the activation energy as a function of conversion. As shown



**Figure 4** Isothermal conversion time as a function of inverse temperature at constant conversion levels generated from isothermal DSC experiments of model epoxy prepreg. Data and calculated activation energies are summarized in Table II.

in Figure 4 and Table II, the activation energies were calculated from the slopes of the lines for every 10% conversion as  $55.5 \pm 1.0$  kJ/mol without any conversion dependence of the activation energy. Represented by a constant activation energy, the reaction mechanism of the model epoxy system may be the same throughout the whole conversion level in the experimental temperature range between 160 and 185°C. Analytically, the other parameter in the reaction rate constant, preexponential factor ( $A$ ), can be calculated from the intercept of the lines when the conversion-dependent function is known. Thus, the conversion-dependent function should be determined before the preexponential factor is calculated.

Corresponding to 20% of conversion ( $\alpha_m = 0.2$ ) of the model prepreg system, the times ( $t_m$ ) required for the maximum conversion rate was obtained from



**Figure 5** Reaction rate reduced-time plot (master curve) of model epoxy prepreg with the reference time of maximum conversion ( $\alpha_{\max} = 0.2$ ) compared with developed model eq. (7).

the experimental data in Figure 1. In order to construct a master curve, the  $d\alpha/dt$  values were multiplied by  $t_m$  to provide  $d\alpha/dt_r$ . Figure 5 shows  $d\alpha/dt_r$  as a function of  $\alpha$  for six isothermal experimental data. As seen in this figure, the experimental data fell into one master curve representing a characteristic feature of the cure reaction. It further demonstrates that there is only one activation energy process required to describe the whole curing reaction of the model prepreg system because the master curve constructed by the “ $t_m$ -manipulation” provides the merely conversion-dependent characteristics of reaction rate. As already seen in Figure 4 and Table II, the activation energy incorporated by  $t_m$  was determined as 55.3 kJ/mol for 20% of the maximum-rate conversion.

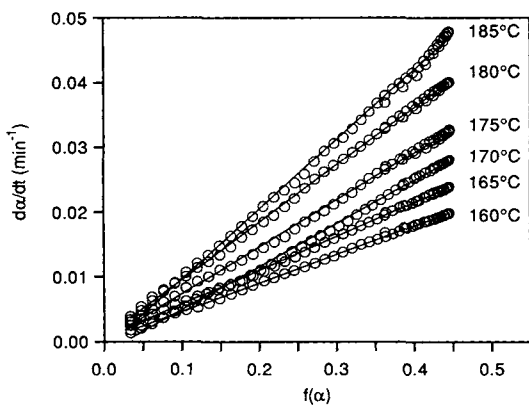
As mentioned earlier, determination of  $f(\alpha)$  function is another crucial point in kinetic analysis because the characteristic feature of the reaction

**Table II** Prepreg Isoconversion Time, Activation Energy, and Heat of Reaction at Full Cure From Isothermal DSC Experiments

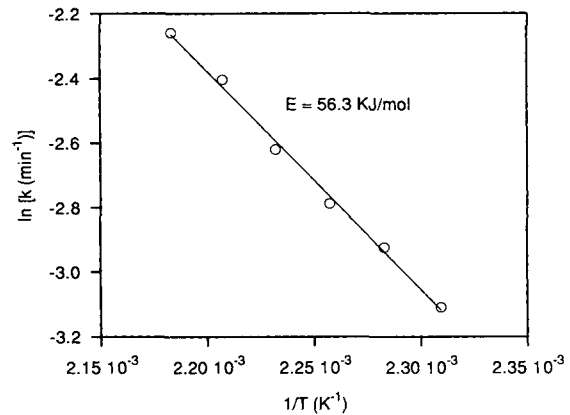
Temperature (°C)	Isoconversion Time (min)									$\Delta H$ (J/g)
	10%	20%	30%	40%	50%	60%	70%	80%	90%	
160	6.1	11.0	15.7	21.7	27.2	33.8	43.5	54.9	73.5	119.8
165	5.1	9.2	13.1	18.0	22.7	28.1	36.2	45.9	60.2	133.6
170	4.4	7.8	11.7	15.3	19.2	24.8	31.0	41.8	57.9	127.1
175	3.8	6.8	9.7	13.3	16.7	20.7	26.8	34.1	45.3	130.1
180	3.1	5.5	7.8	10.7	13.5	16.7	21.5	27.2	36.2	118.2
185	2.7	4.8	6.8	9.3	11.7	14.5	18.7	23.9	32.5	121.8
$E$ (kJ/mol)	54.1	55.3	55.6	55.9	55.8	56.2	55.8	55.8	54.9	—

process should be accounted for by the  $f(\alpha)$  function. When the reaction order  $p$  in the model eq. (13) is ascribed to the primary amine reaction, the reaction order may phenomenologically be assumed as 1. This assumption is not necessarily required for other material systems where the reaction is so complicated that an additional kinetic model parameter should be utilized to fit the experimental data. In this study, however, three kinetic parameters,  $m$ ,  $n$ , and  $y_i$ , were proved to be enough to describe the experimental data. As seen in Figure 5,  $\alpha_m = 0.2$  and  $(d\alpha/dt)_{\alpha=am} = 0.22$  were determined from the constructed master curve. A nonlinear data regression method was utilized to fit the experimental master curve providing  $m = 0.55$ ,  $n = 1.19$ , and  $y_1 = 0.27$ . The determined conversion-dependent function was compared with the master curve in Figure 5, showing an excellent description of experimental data.

According to eq. (1), if the conversion-dependent function is correctly determined, the reaction rate  $(d\alpha/dt)$  should show a linear relation with the conversion-dependent function providing the reaction rate constant from the slope. Using the determined model  $f(\alpha)$  function, the reaction rate constants were obtained from the slopes of the  $d\alpha/dt$  versus  $f(\alpha)$  plot for six different isothermal temperatures as shown in Figure 6. Then, the activation energy and preexponential factor can be determined by plotting the reaction constant versus inverse temperature according to the Arrhenius expression. In Figure 7, the activation energy and preexponential factor were determined from the slope and intercept:  $E = 56.4$  kJ/mol and  $A = 2.785 \times 10^5$  min<sup>-1</sup>. The activation energies determined in Figures 4 and 7 (55.5 and 56.4 kJ/mol, respectively) are favorably compared demonstrating the validity of the devel-



**Figure 6** Isothermal reaction rate as a function of conversion-dependence function  $f(\alpha)$  providing reaction rate constants from the slope of lines.



**Figure 7** Activation energy of model epoxy prepreg calculated from the slope of logarithmic value of reaction rate constant versus inverse temperature relation.

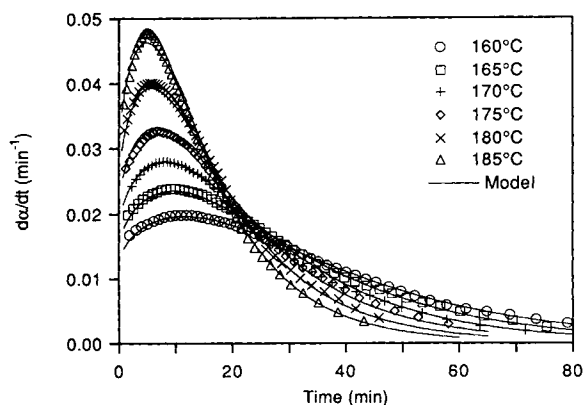
oped conversion-dependent function. From a viewpoint of kinetics modeling, any activation values obtained in this study can be utilized to describe the cure kinetics of the model prepreg system because the preexponential factor is usually determined by compensating the activation energy variance. Taking the activation energy determined in Figure 7 as a representative value of the model prepreg system, all the kinetic parameters of the proposed model are summarized in Table III.

These kinetic parameters were utilized for following model prediction to compare the DSC data under isothermal and dynamic-heating conditions. For the isothermal cure case, the model prediction is compared with the experiment in Figure 8. As can be seen, the developed kinetic model describes not only the characteristic shape but also the temperature effect of the reaction rates accurately.

For dynamic-heating analysis, two multiple heating rate kinetic methods were utilized: the Kissinger method<sup>24</sup> and the Flynn-Wall method.<sup>25</sup> According to the method of Kissinger, the activation energy is obtained from the maximum reaction rate where  $d(d\alpha/dt)/dt$  is zero under a constant-heating rate condition. The resulting relation can be expressed as

**Table III** Kinetic Model Parameters for Predictions Shown in Figures 8 and 10

$m$	$n$	$y_1$ ( $y_2$ )	$E$ (kJ/mol)	$A$ (min <sup>-1</sup> )
0.55	1.19	0.27 (0.73)	56.4	$2.785 \times 10^5$



**Figure 8** DSC isothermal reaction rate of model epoxy prepreg compared with the proposed model equation for six different temperatures.

$$\frac{d[\ln(q/T_m^2)]}{d(1/T_m)} = -\frac{E}{R} \quad (16)$$

where  $T_m$  is the maximum rate temperature and  $q$  is a constant heating rate. Therefore, a plot of  $\ln(q/T_m^2)$  versus  $1/T_m$  gives the activation energy without a specific assumption of the conversion-dependent function.

Based on the Doyle's approximation<sup>26</sup> an alternative method was developed by Flynn and Wall for calculation of activation energy, viz.:

$$\log[g(\alpha)] = \log\left[\frac{AE}{R}\right] - \log q - 2.315 - 0.457 \frac{E}{RT} \quad (17)$$

Starting with this equation, a more accurate value of activation energy can be obtained by iteration or least-squares techniques in order to improve the linear approximation on the temperature integration term.<sup>25,27,28</sup>

These two methods were applied to the dynamic-heating experimental data obtained at the heating rates between 1.02 and 20.31°C/min that were utilized in this study. As seen in Table IV, the heat of reaction was obtained as  $142 \pm 7$  J/g without an apparent relation with the heating rates adopted in this study. Without any assumptions on conversion-dependent functions, the Flynn-Wall method can provide activation energies for different conversion levels, but in this study it was only applied to the maximum rate where the DSC peak appears. As addressed by Prime, the measured DSC heat of reaction is not always consistent in isothermal and dy-

amic-heating experiments because of difficulties in baseline determination and additional heat of reaction in dynamic-heating cases as well as lack of instrument sensitivity.<sup>16</sup> Thus, several analytical methods were suggested to compensate the residual heat of reaction that may not be achieved by isothermal DSC scans.<sup>16,18,20</sup> As with this case, the heat of reactions measured in the constant-heating condition were found to be higher than those measured in the isothermal condition (142 and 127 J/g, respectively). In dynamic-heating experiments, the cure exotherm was often observed to proceed over 280–300°C, where the homopolymerization and etherification reactions could be activated affecting the heat of reaction and kinetic parameters. As a result, the maximum reaction rate  $(da/dt)_{\max}$  was given credence in kinetic analyses because it appears in a moderate temperature range and is obtained from the DSC experiments without integrating the exotherm peak with a hypothetical baseline.

Accordingly, applying the Flynn-Wall and Kissinger methods to the maximum reaction rates (peaks of DSC thermogram), the activation energies were determined by the slopes of the lines in Figure 9, where the data used to obtain this figure is summarized in Table IV. As can be seen, the slopes (or activation energies) were taken from the four slow heating rates because the two points obtained by fast heating rates seemed to deviate from the slow heating experimental data. The obtained activation energies were 57.8 and 57.6 kJ/mol for Flynn-Wall and Kissinger methods, respectively, that were also favorably compared with those obtained by isothermal kinetic analyses (55.5 and 56.4 kJ/mol). As seen in this figure, the peak temperatures obtained by the two fast heating rates of 10.1 and 20.3°C/min were 239 and 260°C, respectively, where the additional high temperature reactions, such as

**Table IV** Summary of Dynamic-Heating DSC Experiments Used in Activation Energy Calculations

$q$ (K/min)	$T_{\max}$ (°C)	$\ln(q/T_{\max}^2)$	$\log(q)$	$\Delta H$ (J/g)
1.02	173.0	-12.181	0.0086002	147.9
2.04	191.0	-11.567	0.30963	138.1
3.04	201.0	-11.211	0.48287	148.7
5.06	214.3	-10.756	0.70415	146.1
10.09	239.0	-10.165	1.0039	147.8
20.31	260.4	-9.547	1.3077	135.4

Calculations by Kissinger and Flynn-Wall methods.

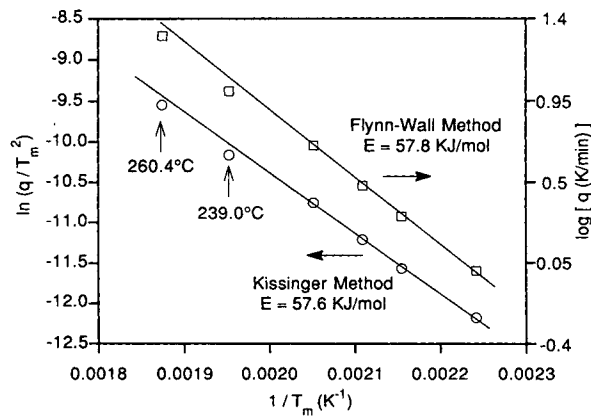


homopolymerization and etherification reactions, might be incorporated during the dynamic scans.

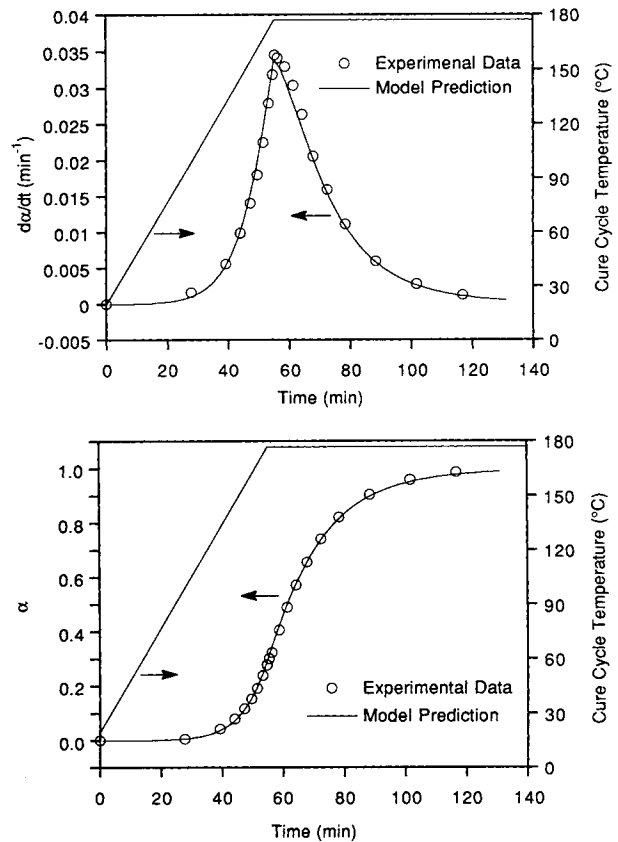
Finally, the developed model was tested by a standard cure cycle for most high performance epoxies, that is generally composed of a dynamic-heating and isothermal holding segments as high as 177°C (350°F). Based on the standard cure cycle, the proposed model equation<sup>15</sup> was solved numerically using the Hindmarsh's version of the Gear method.<sup>29-31</sup> Using the same model parameters shown in Table III, the predicted reaction rate and the conversion are compared with the DSC experimental data in Figure 10. The model prediction is in good agreement with the experiments when the prepreg is cured by a constant heating rate, 2.85°C/min (5.13°F/min), and isothermal holding at 177°C (350°F). It demonstrates that the developed model is capable of predicting both isothermal and dynamic-heating cure kinetics of autocatalytic-type thermosetting polymeric prepreps using the same model parameters without any additional assumptions.

## CONCLUSIONS

Based on a composite reaction methodology developed for TGA weight loss kinetics, a cure kinetic model was developed capable of describing a variety of characteristic shapes of autocatalytically reacting systems. Using a commercial complex epoxy-based prepreg as a model system, the developed model equation was thoroughly investigated and the parameters of the conversion-dependent function were determined by constructing an isothermal cure master curve.



**Figure 9** Activation energies obtained by Flynn-Wall and Kissinger methods exhibiting different reaction mechanisms in high temperature region.



**Figure 10** Kinetic model prediction of (a) reaction rate and (b) conversion compared with DSC experiments as a function of time for a standard cure cycle composed of dynamic-isothermal heating segments.

For both isothermal and constant-heating rate experiments, several analytical methods were utilized to compare the activation energies without assuming the form of conversion-dependent functions. The obtained activation energies were found to be in excellent agreement among different methods as well as different thermal conditions.

Finally, the developed kinetic model equations were tested by predicting both isothermal and dynamic-heating experiments using the same kinetic parameters without any additional assumptions. Demonstrating its versatility and broad applicability, the model prediction was in good agreement with the isothermal and dynamic experimental conditions likely to be encountered in actual cure processes.

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