

# Cure Kinetics of Neat and Carbon-Fiber-Reinforced TGDDM/DDS Epoxy Systems

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## SYNOPSIS

The cure kinetics of neat and carbon fiber-reinforced commercial epoxy systems, based on Tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) and 4,4'-diaminodiphenylsulfone (DDS) were studied by means of differential scanning calorimetry (DSC). Analysis of DSC data indicated that the presence of the carbon fibers has a very small effect on the kinetics of cure. A kinetic model, arising from an autocatalyzed reaction mechanism, was applied to isothermal DSC data. The effect of diffusion control was incorporated into the reaction kinetics by modifying the overall rate constant, which is assumed to be a combination of the chemical rate constant and the diffusion rate constant. The chemical rate constant has the usual Arrhenius form, while the diffusion rate constant is described by a type of the Williams-Landel-Ferry (WLF) equation. The kinetic model, with parameters determined from isothermal DSC data, was successfully applied to dynamic DSC data over a broad temperature range that covers usual processing conditions. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

In recent years, formulations consisting of epoxy resins and aromatic amines have been extensively studied as matrix materials for advanced fiber composites. Among these, tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) cured with 4,4'-diaminodiphenylsulfone (DDS) has been one of the most studied.<sup>1-23</sup> The growth of computer-aided design and manufacturing has resulted in increased interest in modeling the processing of these materials.<sup>24-27</sup>

There are several driving forces to model the process. Modeling helps one to better understand the effects of processing conditions, raw materials properties, and equipment size on process behavior. Modeling can lead to significant savings with respect to the amount of experimental work involved in determining the optimum processing conditions. Furthermore, the model may lead to the development of quantitative relationships between processing conditions, structure, and properties of the final

product. For thermoset matrices such as epoxy resins, probably the most important aspect of the model is an accurate description of the cure kinetics.<sup>18</sup>

As it is well known, the cure of thermoset resins involves conversion of liquid monomers or prepolymers into three-dimensional networks. The mechanism and kinetics of cure determine the network morphology, which, in turn, dictates the physical and mechanical properties of the cured product.<sup>12</sup> Chemical reactions that take place during cure are quite complex, and the cure kinetics are not always easily elucidated. Phenomena such as autocatalysis at early stages and effects of diffusion control at later stages of cure reaction can further complicate the analysis.

Curing kinetics of epoxy resins have been studied with different techniques, such as infrared spectroscopy (IR),<sup>28</sup> Fourier transform IR,<sup>2-4,6,9,12,21</sup> thermal analysis as differential scanning calorimetry (DSC),<sup>1,3,5,7,8,14-16,18-23,29</sup> and different approaches have been used to describe it. Due to the complex chemistry involved in the epoxy curing, a phenomenological approach is the most popular for these systems. Models arising from proposed kinetic mechanisms have been used as well, the most rele-

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vant being, perhaps, the one proposed by Horie et al.<sup>30</sup> In general, a good fit to experimental data was obtained in the early stages of the cure, but deviations were observed in the later stages, particularly near vitrification when the reaction is primarily diffusion controlled. Few mathematical treatments of this phenomenon have been reported,<sup>19,22,27,31-34</sup> but further efforts on the verification of developed model are needed.

The review of the literature shows that curing kinetics of the epoxy-amine systems was studied mostly in isothermal conditions. The modeling of the industrial processing usually requires a knowledge of the curing kinetics in nonisothermal conditions, in a broad temperature range. Very few efforts were made to check the prediction capability of the developed kinetic expressions arising from isothermal runs in nonisothermal conditions outside the range of temperature used for parameter fitting.

In the work to be described herein, the DSC technique was used to study the curing kinetics of commercial epoxy systems Hercules 8552, whose main components are TGDDM and DDS. The kinetic behavior of both neat resin and carbon fiber prepreg were analyzed and compared. The results of our initial phenomenological approach to describe the curing kinetics of the neat resin have been reported in the literature.<sup>22</sup> In this work, the Horie's mechanistic model,<sup>30</sup> adapted to account for diffusion control effects, has been used to describe kinetics of epoxy-amine cure in both isothermal and nonisothermal conditions. To our best knowledge, this is the first time that such model is applied to the cure of a TGDDM/DDS system.

## EXPERIMENTAL

### Materials

The materials studied were commercial epoxy systems based on Tetraglycidyl-4,4'-diaminodiphenylmethane and the primary amine curing agent 4,4'-diaminodiphenylsulfone. The samples were obtained from Hercules Inc. in the form of neat resin (Hercules 8552) and carbon fiber prepreg. The resin is reported to be toughened by thermoplastic additives at about 30% by volume. The prepreg contained unidirectional carbon-fiber reinforcement impregnated with Hercules 8552 resin to a nominal resin content of 35% by weight. The materials were used as received.

### Characterization

The cure of the neat resin and the prepreg was studied under both dynamic and isothermal conditions on a Mettler TA 300 differential scanning calorimeter operating in the temperature range between -100 and 500°C in a nitrogen atmosphere.

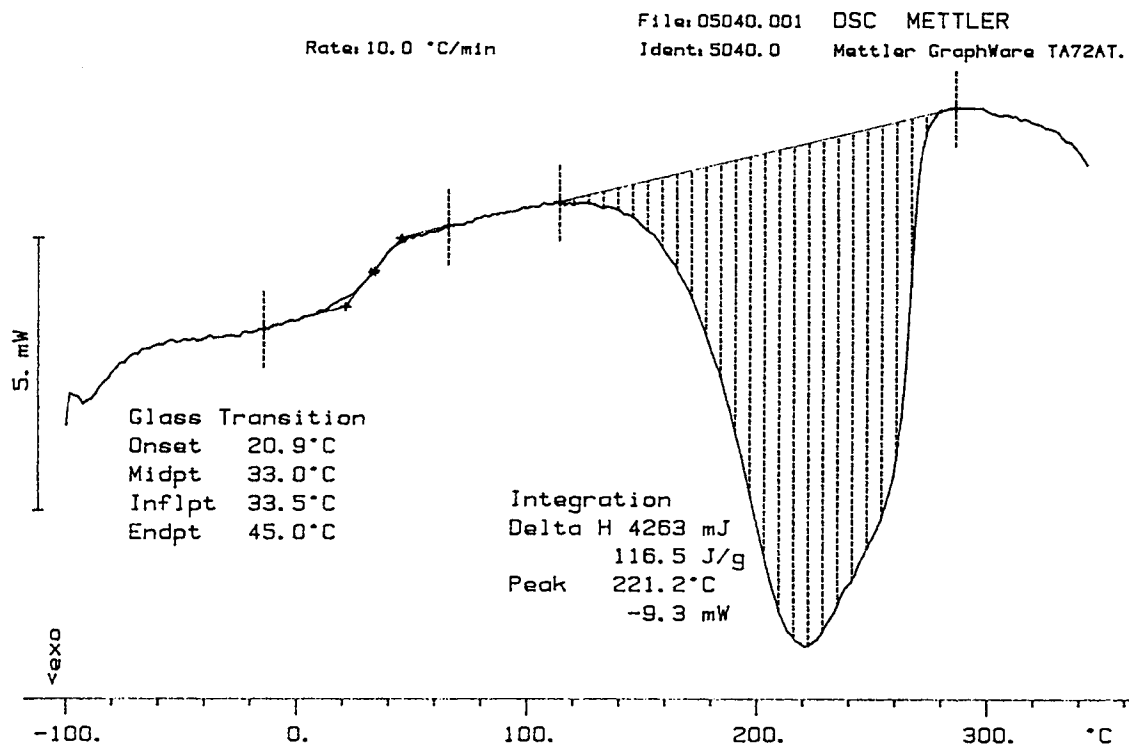
The dynamic DSC analysis was performed at three different heating rates: 5, 10, and 15°C/min. The sample was heated from room temperature to around 300°C, at which point some decomposition was observed. The total heat of reaction,  $H_T$ , was estimated by drawing a straight line connecting the baseline before and after the peak and integrating the area under the peak. An average value of 557 J/g was obtained. The temperature at which the exotherm peak maximum occurs was found to depend on the heating rate. The dispersion of the data was on the order of the experimental error, and no correlation can be established between the heat of reaction and the heating rate.

Isothermal DSC analysis was performed at temperatures ranging from 150 to 200°C in 10° increments. The reaction was considered complete when the rate curve leveled off to a baseline. The total area under the exotherm curve, based on the extrapolated baseline at the end of reaction, was used to calculate the isothermal heat of cure,  $H_i$ , at a given temperature. After each isothermal run the sample was cooled rapidly in the DSC cell to 30°C and then reheated at 10°C/min to 300°C in order to determine the residual heat of reaction,  $H_R$ .

The digitized data were acquired by a computer and transferred to an Apple Macintosh for further treatment.

### Measurements of the Glass Transition Temperature

In order to determine the glass transition temperature,  $T_g$ , as a function of fractional conversion, a series of samples of neat resin and the carbon-fiber prepreg were cured in the DSC cell at 130°C for various periods of time. After each isothermal run partially cured samples were cooled rapidly to -100°C and then subjected to a temperature scan from -100 to 300°C at 10°C/min, to determine the glass transition temperature and the residual heat of reaction. By means of the total heat of reaction and the residual heat of reaction,  $H_R$ , the corresponding fractional conversion was calculated. A typical DSC scan is shown in Figure 1.  $T_g$  appears as an endothermic shift over a temperature interval in the DSC scan. In this study,  $T_g$  was taken as the midpoint of the step transition. Dynamic DSC ex-



**Figure 1** A typical DSC scan (heat flow vs. temperature) of a partially cured sample. (Prehistory: Prepreg cured in DSC at 130°C for 50 min.)

periments were also performed to determine the glass transition temperature of an uncured and completely cured material. To determine the latter, the sample was heated from room temperature to 270°C at 10°C/min, then cooled rapidly in the DSC cell to room temperature and immediately reheated to 300°C at 10°C/min.

## RESULTS AND DISCUSSION

### Neat Resin Characterization

Typical dynamic and isothermal DSC curves showing heat flow,  $dH/dt$ , as a function of temperature or time are given in Figures 2 and 3.

In isothermal DSC, there is a brief period (1–2 min) of temperature stabilization after the sample is introduced into the instrument. Because of that, the data obtained at the beginning of the test are not very reliable. All isothermal curves have been corrected as shown in Figure 3 (the black portion of the thermogram), extrapolating the value of the heat flow to time = 0. The values of isothermal and residual heat of reaction, calculated according to the procedure described in the Experimental section, for investigated temperatures are shown in Table I. It

is seen that as the cure temperature is increased,  $H_i$  increases, while  $H_R$  decreases. Also, the sum of the  $H_i$  and  $H_R$  is comparable to the total heat of reaction obtained from dynamic tests (557 J/g). As will be shown later, these findings can be attributed to the influence of diffusion control on the reaction kinetics in the glass transition region.

The basic parameter governing the state of the material is the chemical conversion  $\alpha$ . Knowledge of the kinetic rate of curing and of how the rate changes with cure temperature is important and useful for predicting the chemical conversion achieved after a cure schedule.

In order to relate the heat evolution in the DSC experiment to the epoxide conversion, it is necessary to assume that the heat released on reaction of an epoxide group is the same regardless of the type of epoxy or the nature of the reaction. The results reported in the literature<sup>5,10,18</sup> support this assumption. The rate of reaction,  $d\alpha/dt$ , as a function of time,  $t$ , was calculated from the rate of heat flow measured in isothermal DSC experiments,  $dH/dt$ , by:

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

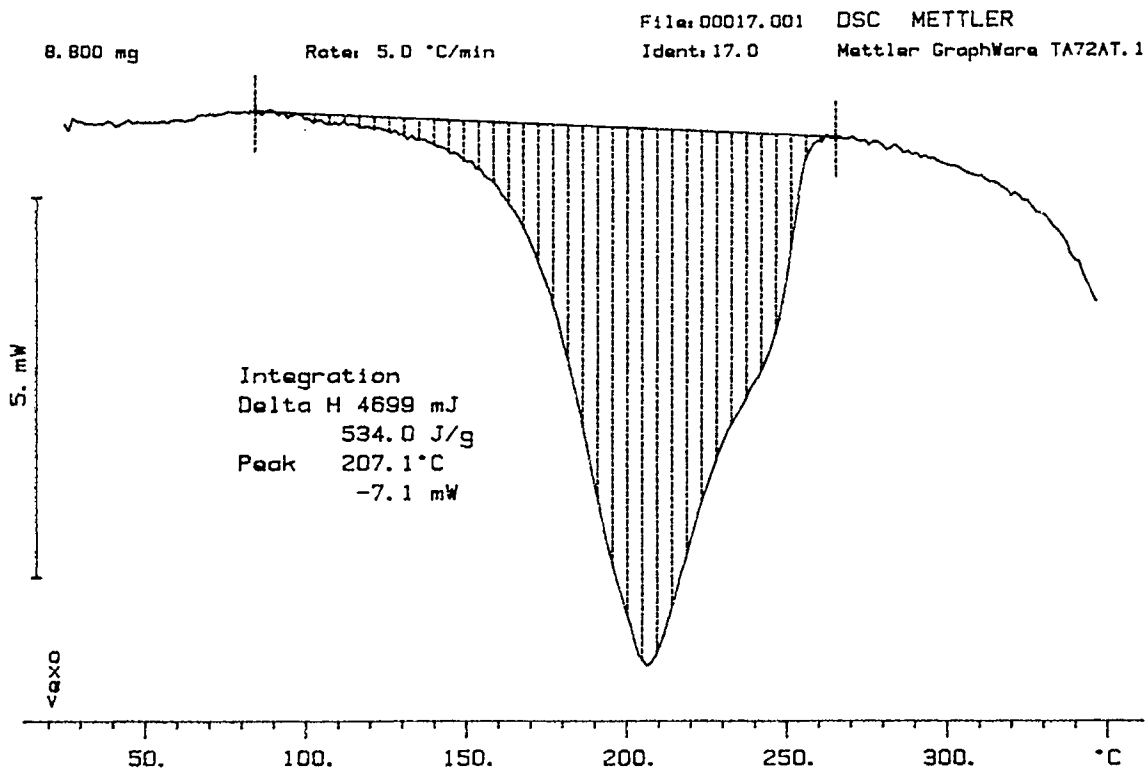


Figure 2 Dynamic DSC curve for neat resin at a heating rate of 5°C/min.

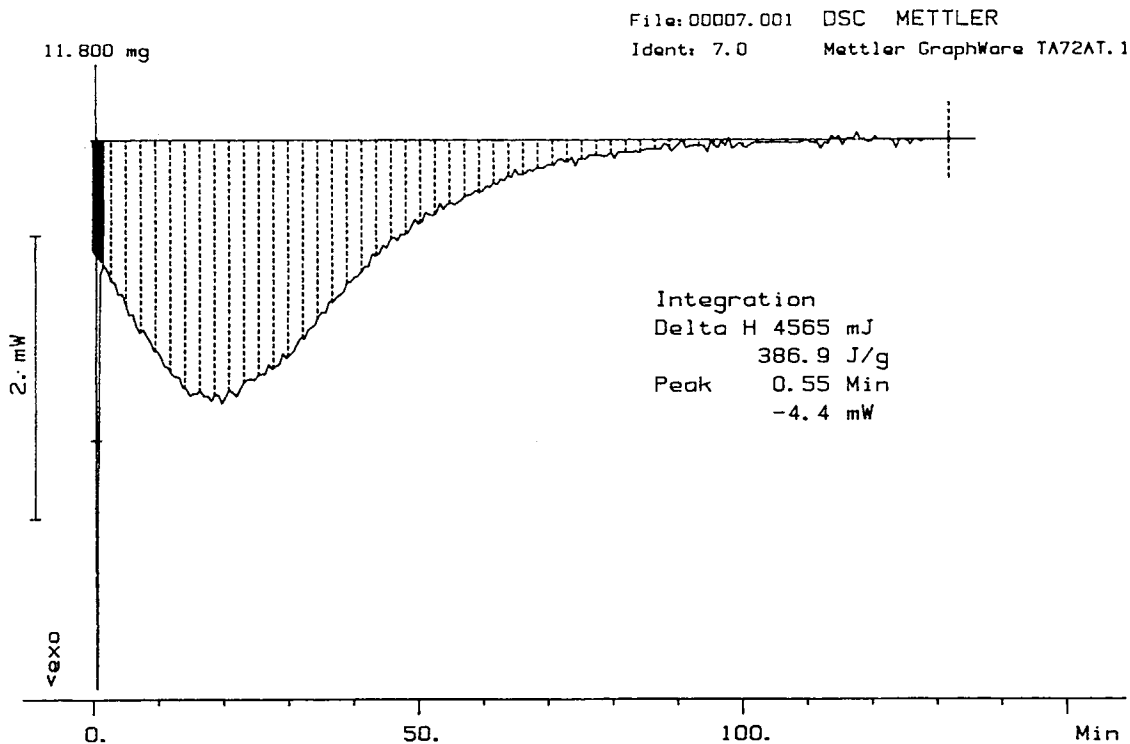


Figure 3 Isothermal DSC curve for neat resin at 160°C.

**Table I** Heat of Reaction Developed in Isothermal and Dynamic DSC Tests for Neat Resin

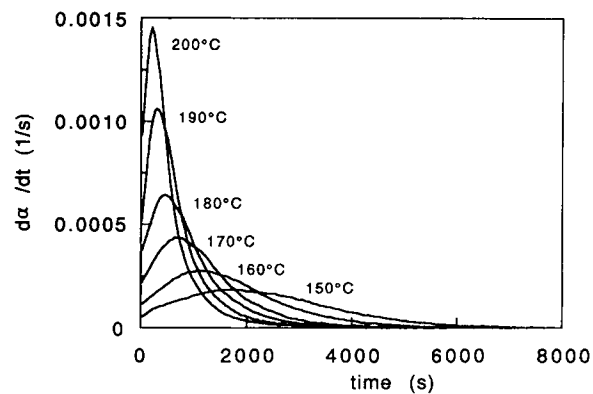
$T$ (°C)	$H_i$ (J/g)	$H_R$ (J/g)	$H_i + H_R$ (J/g)
150	361	155	516
160	385	124	509
170	415	98	513
180	456	70	526
190	521	47	568
200	533	18	551

The average value of the total heat developed during the dynamic DSC tests was taken as the basis for the ultimate fractional conversion,  $\alpha = 1$ . The rate of reaction as a function of time for different curing temperatures is shown in Figure 4. The maximum in the  $d\alpha/dt$  vs. time curve at  $t \neq 0$  is a characteristic of autocatalytic reactions. An increase in temperature increases the value of the reaction rate at the maximum and decreases the time required to reach the peak. By partial integration of the areas under the curves in Figure 4, the fractional conversion as a function of time was obtained (see Fig. 5):

$$\alpha = \frac{1}{H_T} \int_0^t \left( \frac{dH}{dt} \right) dt. \quad (2)$$

As expected from the results reported in Table I, at higher temperature higher fractional conversion is reached. The incomplete curing reaction obtained in isothermal conditions can be explained in terms of diffusion control effects in the vicinity of isothermal vitrification. Namely, the structural changes produced by the polymerization reactions are associated with an increase of the glass transition temperature,  $T_g$ , of the reactive system. When the increasing  $T_g$  approaches the isothermal cure temperature, the molecular mobility is strongly reduced, the reaction becomes diffusion controlled, and eventually stops. Subsequent exposure to temperatures greater than the previous isothermal cure temperature results in the increase of the molecular mobility of the polymer and further reaction as shown in Figure 6. The entire concept of vitrification has been described in a series of fine articles by Gillham.<sup>35,36</sup>

As described in the Experimental section, in order to determine the dependence of the glass transition temperature on the fractional conversion, a series of uncured, partially cured and completely cured

**Figure 4** Isothermal reaction rate as a function of time for neat resin at reported temperatures.

samples were subjected to another temperature scan. The fractional conversion of a partially cured sample was calculated as:

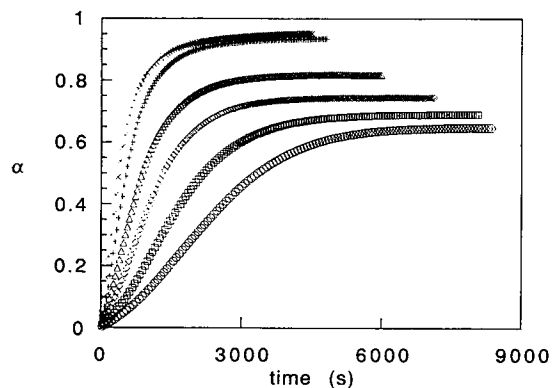
$$\alpha = \frac{H_T - H_R}{H_T} \quad (3)$$

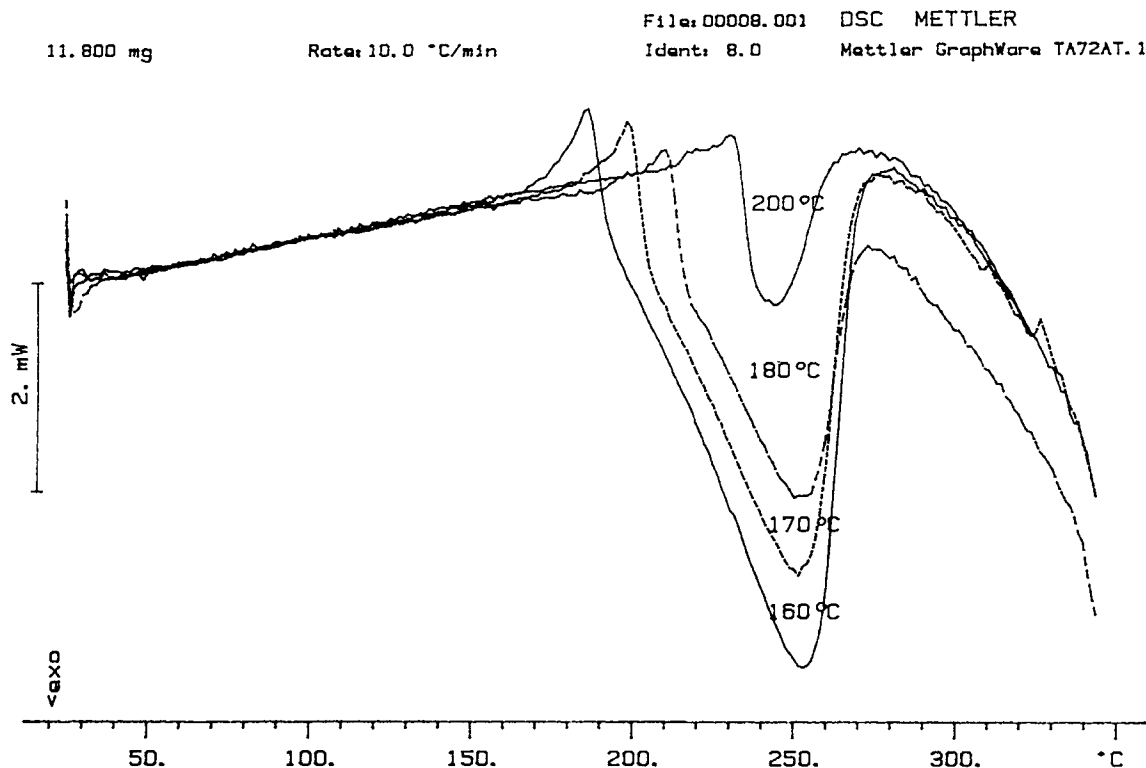
As Figure 7 shows, the glass transition temperature of the investigated system increases linearly with conversion:

$$T_g(\alpha) = 267.36 + 232.12\alpha \quad (4)$$

Among the numerous theoretical and empirical relations reported in the literature, most involve linear dependencies,<sup>37,38</sup> but exponential<sup>39,40</sup> or logarithmic<sup>41</sup> can also be found.

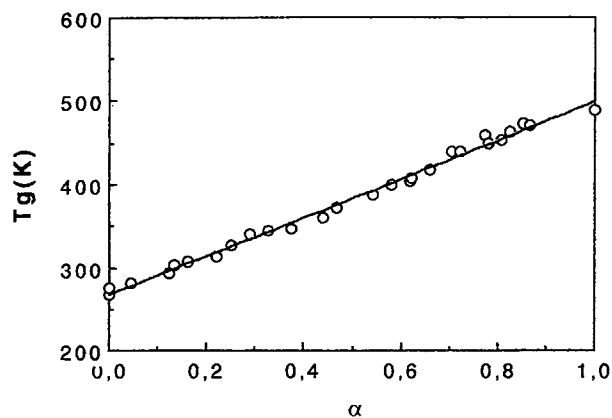
From eq. (4) the fractional conversion at vitrification,  $\alpha(T_g = T_{cure})$ , was calculated and compared with the final fractional conversion obtained during

**Figure 5** Isothermal fractional conversion as a function of time for neat resin at 150°C (○), 160°C (□), 170°C (◇), 180°C (△) 190°C (+), and 200°C (×).



**Figure 6** Dynamic DSC curves for neat resin recorded after isothermal runs at reported temperatures. Heating rate: 10°C/min.

isothermal cure,  $\alpha_{\max}$ , as given in Table II. In the temperature range between 150 and 180°C, comparable values of  $\alpha(T_g = T_{\text{cure}})$  and  $\alpha_{\max}$  were obtained, indicating that the diffusion control is already operative at isothermal vitrification. At 190 and 200°C,  $\alpha_{\max}$  is higher than  $\alpha(T_g = T_{\text{cure}})$ . This suggests that at isothermal vitrification at higher temperatures the reaction is still partly chemically controlled.



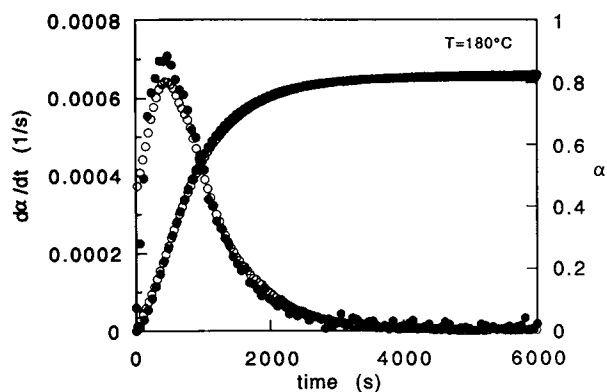
**Figure 7** Glass transition temperature as a function of fractional conversion.

### Prepreg Characterization

The carbon-fiber prepreg was characterized under the same conditions as the neat resin, and the obtained results were analyzed as already described. In Figure 8 the isothermal rate of reaction and the fractional conversion data of the prepreg are compared with the neat resin data. The rate of reaction profiles of the prepreg and of the neat resin obtained from dynamic DSC experiments at a heating rate of 5°C/min are compared in Figure 9. Results obtained under both isothermal and dynamic conditions suggest that the presence of the fibers has a

**Table II** Comparison of Final Fractional Conversion of Isothermal Cure with Fractional Conversion at Vitrification for Neat Resin

$T_{\text{cure}}$ (°C)	$\alpha_{\max}$	$\alpha(T_g = T_{\text{cure}})$ , Eq. (4)
150	0.647	0.671
160	0.690	0.714
170	0.745	0.757
180	0.818	0.800
190	0.935	0.843
200	0.956	0.886



**Figure 8** Comparison of isothermal DSC data for neat resin (○) and prepreg (●). Rate of reaction and fractional conversion as functions of time at 180°C.

very small effect on the kinetics of cure. In general, the isothermal reaction rate peaks are slightly lower for the neat resin, while the initial reaction rate is slightly higher for the resin. The conclusion about the effect of the carbon fibers on the reaction kinetics will be drawn later after the analysis of the DSC data by means of kinetic models.

#### Analysis of the Data by Means of an Autocatalytic Reaction Model

The essential step in the study of cure kinetics by DSC is fitting of the reaction rate profiles, obtained from isothermal and dynamic experiments, to a kinetic model. As already told, due to the complex nature of thermosetting reactions, phenomenological models are the most popular for these systems. However, they do not provide any information about the reaction path, which is important for understanding the network formation process. We have recently used a phenomenological model of the type

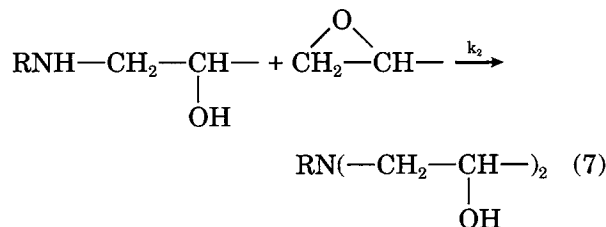
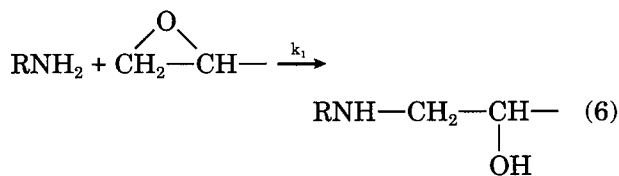
$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_{\max} - \alpha)^n \quad (5)$$

to analyze the curing kinetics of the Hercules 8552 neat resin<sup>22,42</sup> and prepreg.<sup>42</sup> Nonlinear regression analysis was used for the computation of the parameters of eq. (5), assuming an overall reaction order ( $m + n$ ) equal to 2<sup>42</sup> and 3.<sup>22</sup> Despite the experimentally observed similarity in the behavior of neat resin and prepreg, quite different values of their kinetic parameters were obtained.

In this work, a model<sup>33</sup> arising from the kinetic mechanism proposed by Horie et al.,<sup>30</sup> adapted to account for diffusion control effects, was applied to

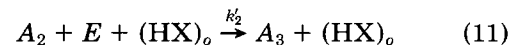
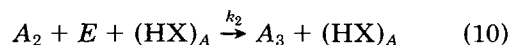
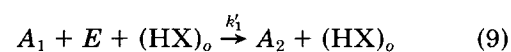
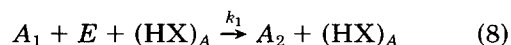
our data, and model predictions were compared to experimental results.

It is generally agreed that in the reaction between epoxides and amines the addition occurring in two stages is the most important:



These reactions are catalyzed by acids such as Lewis acids, phenols, and alcohols. The hydroxyl groups generated by the amine epoxide addition are active catalysts, so that the curing reaction usually shows an accelerating rate in its early stages, typical of auto catalysis.

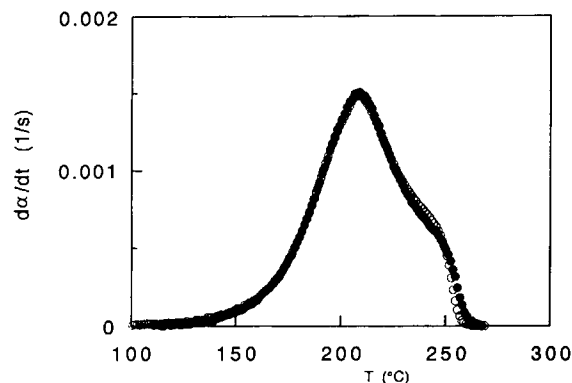
Horie et al.<sup>30</sup> have proposed the following scheme to describe the kinetics of the epoxy reaction with primary amine, taking into account the autocatalytic action of the hydroxyl groups formed during the reaction and assuming that some catalyst or impurity is initially present in the system:



where  $A_1$ ,  $A_2$ , and  $A_3$  are primary, secondary, and tertiary amine,  $E$  is epoxide,  $(\text{HX})_o$  is hydroxyl resident in the system as impurity or additive, and  $(\text{HX})_A$  is hydroxyl group formed in the amine-epoxide addition reaction. From this scheme an overall kinetic equation was derived:

$$\frac{dx}{dt} = (k'_1 c_o + k_1 x)(e_o - x)(a_1 + n a_2) \quad (12)$$

where  $x$  is the epoxide consumed at a given time,  $c_o$  and  $e_o$  are the initial concentrations of  $(\text{HX})_o$  and



**Figure 9** Comparison of dynamic DSC data for neat resin (○) and prepreg (●). Rate of reaction as a function of temperature at a heating rate of 5°C/min.

epoxide,  $a_1$  and  $a_2$  are the concentrations of primary and secondary amine and  $n = k_2/k_1 = k'_1/k'_1$ , the relative reaction rate of secondary and primary amine with epoxide. When the primary and secondary amines are of approximately equal reactivity, eq. (12) may be written in terms of the fractional conversion of epoxy groups<sup>33</sup>:

$$\frac{d\alpha}{dt} = k(\alpha + B)(1 - \alpha)(r - \alpha) \quad (13)$$

where  $k = k_1 e_o^2/2$  and  $B = k'_1 c_o/k_1 e_o$ , respectively.

From the rearranged eq. (13)

$$\frac{d\alpha/dt}{(1 - \alpha)(r - \alpha)} = k\alpha + kB \quad (14)$$

the parameters  $k$  and  $B$  can be determined by plotting  $(d\alpha/dt)/(1 - \alpha)(r - \alpha)$  vs.  $\alpha$ . The detailed composition of the resin was not disclosed by the producer. A stoichiometric mixture in which the number of epoxide rings is just sufficient to react with all the N—H bonds present, i.e.,  $r = 1$  was assumed. As Figure 10 shows, good correlation of  $(d\alpha/dt)/(1 - \alpha)^2$  vs.  $\alpha$  data was obtained for early stage of cure. At higher temperatures the deviation of the data from the straight line started at higher conversions. If the deviation is attributed to the change from chemically controlled to diffusion-controlled kinetics in the vicinity of isothermal vitrification, the observed linearity of the experimental  $(d\alpha/dt)/(1 - \alpha)^2$  vs.  $\alpha$  data suggests that there is no substitution effect (i.e.,  $k_2 = k_1 = 0.5$ ). Namely, in the derivation of eq. (13), equal reactivity of all amino hydrogens has been assumed.

The data corresponding to the chemically controlled regimes will be analyzed first. The values of

parameters  $k$  and  $B$  determined from the slope and intercept of the straight line are summarized in Table III. It is seen that the prepreg data compare very closely with the neat resin data. The nonzero value of  $B$  indicates the presence of initial trace catalyst accelerating the reaction in the system. This could be either a small amount of impurities of hydroxyl groups initially in the tetraepoxide monomer and/or those due to an initial extent of reaction occurring during mixing of the reactants. Apart from the data for the neat resin at 190 and 200°C, constant  $B$  is only a weak function of temperature, indicating that the rate constants  $k_1$  and  $k'_1$  have a similar temperature dependence.

As follows from eq. (13), the intercept of the straight line ( $\equiv kB$ ) correspond to the initial reaction rate. The reaction rate constant  $k$  and the initial reaction rate depend on the temperature following the Arrhenius relationship:

$$k = k_o \exp(-E_a/RT) \quad (15)$$

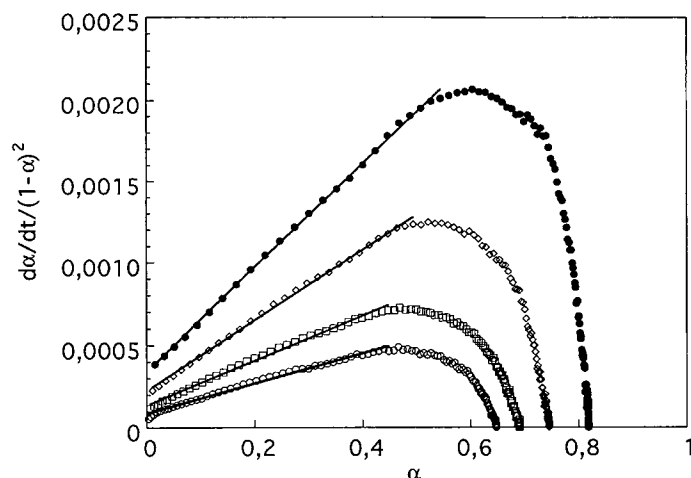
as shown in Figure 11. From Figure 8, one would expect lower values of the initial reaction rate for the prepreg in comparison with the neat resin. On the contrary, estimated values for the initial reaction rate, from the  $(d\alpha/dt)/(1 - \alpha)^2$  vs.  $\alpha$  plot, are comparable to those of the neat resin (see Fig. 11). Such findings are not very surprising. As already seen, the value of the heat flow at zero time of isothermal DSC experiments has been extrapolated, which implies an uncertainty in the value for the initial reaction rate. Therefore, the differences in the initial reaction rates seen in Figure 8 should not be explained as the effect of the carbon fibers on the cure kinetics.

From the linear least-square fit of  $\ln k$  vs.  $1/T$  data, the activation energy for the epoxy-amine reaction, catalyzed by newly formed hydroxyl groups, was determined. The plot of  $\ln(kB)$  vs.  $1/T$  was used to determine the activation energy for the reaction catalyzed by groups initially present in the resin. The Arrhenius parameters given in Table IV are comparable to those from the literature.<sup>18,29</sup> As seen, the activation energy for the epoxy-amine reaction catalyzed by newly formed hydroxyl groups is higher than the activation energy for the reaction catalyzed by groups initially present in the resin.

### Diffusion-Controlled Reaction Kinetics

It was shown that the chemical kinetics for the reaction of the investigated epoxy/amine system cannot be satisfactorily represented by the simple au-





**Figure 10** Plot of  $(d\alpha/dt)/(1-\alpha)^2$  as a function of  $\alpha$  for neat resin at 150°C (O), 160°C (□), 170°C (◇), and 180°C (●).

tocatalyzed kinetics throughout the entire conversion range because of the influence of diffusion control on the reaction kinetics, particularly in the glass transition region.

As suggested by Havlicek and Dusek,<sup>31</sup> the effect of the diffusion control can be incorporated into the kinetics of the reaction by modifying the rate constant using the Rabinowitch model<sup>43</sup> as follows:

$$\frac{1}{k_a(\alpha, T)} = \frac{1}{k_T(T)} + \frac{1}{k_d(\alpha, T)}, \quad (16)$$

where  $k_a$  is the overall rate constant,  $k_T$  is the rate constant of the chemically controlled reaction, and  $k_d$  is the diffusion rate constant. This equation shows that the overall rate constant is governed at one extreme by  $k_T$  and at the other extreme by  $k_d$ .

**Table III** Parameters of the Autocatalytic Kinetic Model, Eq. (13), in Chemically Controlled Region for Neat Resin and Prepreg

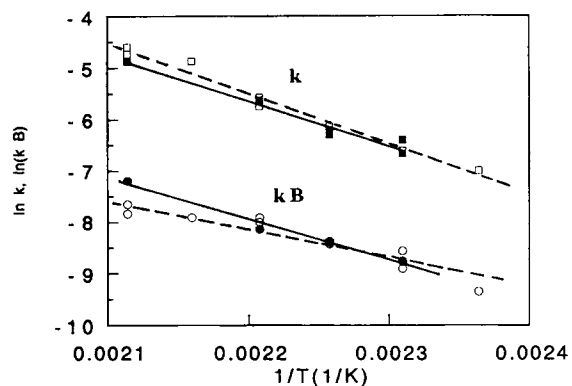
$T$ (°C)	Neat Resin		Prepreg	
	$k$ (s <sup>-1</sup> )	B	$k$ (s <sup>-1</sup> )	B
150	$9.092 \cdot 10^{-4}$	0.0954		
160	$1.353 \cdot 10^{-3}$	0.1000	$1.281 \cdot 10^{-3}$	0.1207
160			$1.667 \cdot 10^{-3}$	0.0938
170	$2.169 \cdot 10^{-3}$	0.1003	$1.830 \cdot 10^{-3}$	0.1265
170			$1.9372 \cdot 10^{-3}$	0.1161
180	$3.177 \cdot 10^{-3}$	0.1055	$3.605 \cdot 10^{-3}$	0.0810
180	$3.777 \cdot 10^{-3}$	0.0968		
190	$7.646 \cdot 10^{-3}$	0.0483		
200	$8.801 \cdot 10^{-3}$	0.0450	$7.674 \cdot 10^{-3}$	0.0987
200	$1.011 \cdot 10^{-2}$	0.0473		

From eq. (16) the diffusion rate constant is:

$$k_d = \frac{k_a k_T}{k_T - k_a}. \quad (17)$$

The rate constant of the chemically controlled reaction,  $k_T$ , is the same Arrhenius rate constant determined earlier (see Table IV). To evaluate  $k_d$ , the actual overall rate constant,  $k_a$ , was computed first for each isothermal temperature, according to the autocatalytic rate expression, eq. (13), using the experimental data for rate of reaction and fractional conversion:

$$k_a = \frac{d\alpha/dt}{(1-\alpha)(\alpha+B)} \quad (18)$$



**Figure 11** Arrhenius plots of isothermal reaction rate constants for neat resin (O, □, ---) and prepreg (●, ■, —) determined from the data analysis according to autocatalyzed reaction kinetics ([eq. (13)]).

**Table IV** Arrhenius Parameters for the Rate Constants of the Autocatalytic Kinetic Model, Eq. (13), for Neat Resin and Prepreg

	Rate		$E_a/R$ (K)	$E_a$ (kJ/mol)
	Constant (s <sup>-1</sup> )	ln $k_o$		
Neat resin	k	16.20	9861	82.0
	(k B)	5.17	6041	50.2
Prepreg	k	13.60	8747	72.7
	(k B)	9.43	7895	65.6

The data for  $k_T$  and  $k_a$  were substituted in eq. (17), and  $k_d$  as a function of  $\alpha$  was evaluated.

As proposed in the literature,<sup>33</sup> the  $k_d$  vs.  $\alpha$  dependence can be fitted to the following type of the Williams-Landel-Ferry<sup>44</sup> (WLF) equation:

$$\log k_d(T) = \log k_d(T_g) + \frac{C_1(T - T_g(\alpha))}{C_2 + (T - T_g(\alpha))}, \quad (19)$$

where  $T$  is the temperature of the experiment,  $k_d(T_g)$  is the diffusion rate constant at glass transition,  $C_1$  and  $C_2$  are constants.

Namely, according to the generally accepted view of relaxation processes controlled by diffusion of molecular chain segments in the glass transition region of amorphous polymers, the molecular relaxation time can be described by the WLF equation<sup>44</sup>:

$$\log(a_T) \equiv \log \frac{\tau(T)}{\tau(T_o)} = - \frac{C_1(T - T_o)}{C_2 + (T - T_o)}, \quad (20)$$

where  $T_o$  is an arbitrary reference temperature,  $C_1$  and  $C_2$  are constants,  $\tau(T)$  and  $\tau(T_o)$  are the polymer segmental relaxation times at the temperatures  $T$  and  $T_o$ , respectively, and  $a(T)$  is the time-temperature superposition factor. When  $T_o$  is chosen as the glass transition temperature, the value of  $C_1$  and  $C_2$  are generally found to be nearly constant and equal to 17.44 and 51.6°C, respectively, for many amorphous polymers.<sup>44</sup>

If it is supposed that the rate constant for the chemical reaction governed by the diffusion of chain segments,  $k_d$ , is proportional to the diffusion constant of the reactants, or equivalently, inversely proportional to the relaxation time of the polymer segments,<sup>45</sup> it can be expected that the dependence of  $k_d$  on  $\alpha$  and temperature could be described by eq. (19). If it is so, the plot of the logarithm of the computed  $k_d$  vs.  $(T - T_g(\alpha))/(C_2 + T - T_g)$  can be fitted to a straight line.

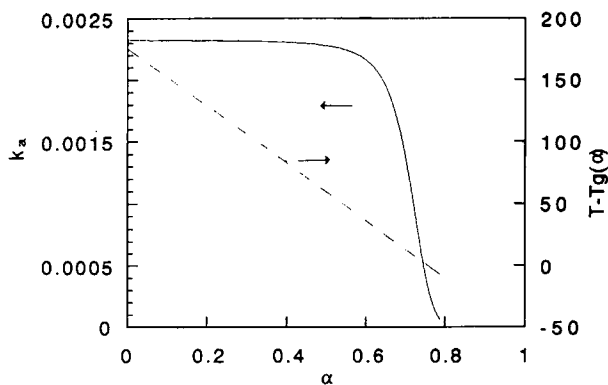
**Table V** Parameters for the Diffusion Rate Constants, Eq. (19), for Neat Resin, and Prepreg

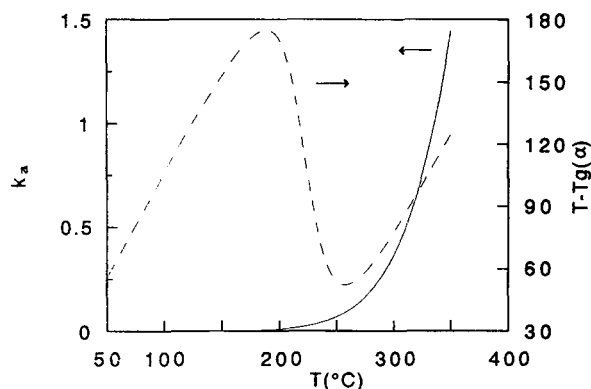
	$C_1$	$C_2$	ln $k_d(T_g)$
Neat resin	10.33	50	-78.090 + 0.1585 T
Prepreg	9.66	50	-77.806 + 0.1536 T

For constant  $C_2$  the value of 50°C was assumed, and the parameters  $C_1$  and  $k_d(T_g)$  were determined from the slope and the intercept of the obtained straight line. Similar results were obtained for both neat resin and prepreg as shown in Table V.  $C_1$  was found relatively insensitive to temperature, while ln  $k_d(T_g)$  vs.  $T$  data were fitted with straight lines.

It is worthwhile to note that in the study<sup>46</sup> of a modified multiphase epoxy (Hercules 8551-7), by means of dynamic mechanical analysis, the time-temperature superposition factor,  $a(T)$ , near and above the glass transition temperatures, was fitted to the WLF equation using  $T_g$  as the reference temperature. For  $C_1$  and  $C_2$ , values of 10.7 and 47.2 were obtained respectively, which are similar to our data.

The expression for diffusion rate constant,  $k_d$ , and the kinetic Arrhenius rate constant,  $k_T$ , are substituted in eq. (16) to evaluate the overall reaction rate constant  $k_a$ . As a consequence,  $k_a$  becomes a function of both the  $T_g$ , which varies with cure time, and the cure temperature. Depending on the interval between  $T_g$  and the cure temperature, the overall reaction rate constant allows for either chemical or diffusion control dominating the reaction kinetics. Figure 12 shows the dependence of the overall rate constant and of the difference between the reaction temperature and the glass transition temperature  $(T - T_g)$ , on the conversion of epoxy group at 170°C,

**Figure 12** Dependence of the overall reaction rate constant and of the difference between the reaction temperature and the glass transition temperature on fractional conversion for neat resin at 170°C.



**Figure 13** Dependence of the overall reaction rate constant and of the difference between the reaction temperature and the glass transition temperature, on temperature, at a heating rate of 10°C/min for neat resin

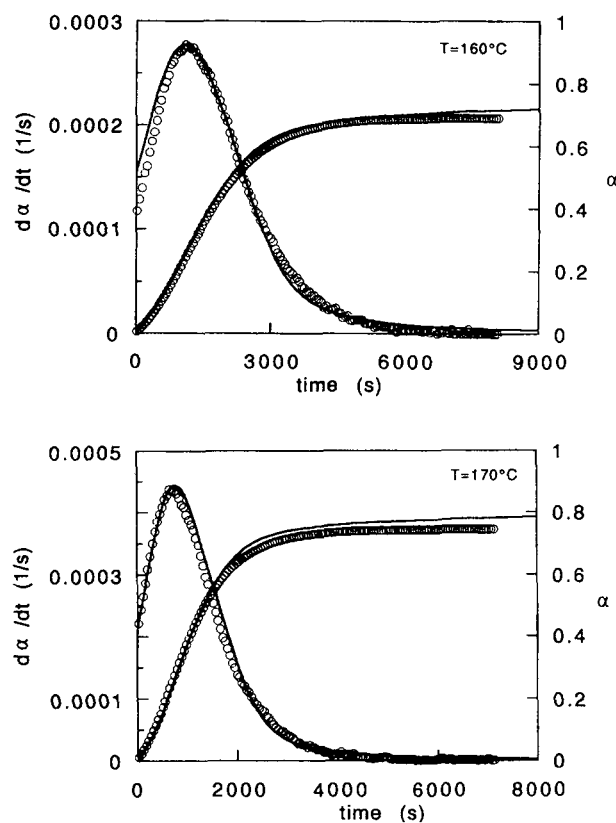
for the neat resin. Similar curves were obtained at other temperatures. A fall of the rate constant is observed at conversions close to the glass transition conversion. For a given isothermal cure temperature the Arrhenius rate constant,  $k_T$ , does not change with time. The value of  $k_d$ , on the other hand, depends on the difference between  $T_g$  and the temperature of cure. In the earlier stages of the reaction when  $T_g \ll T_{\text{cure}}$ ,  $k_d$  is much greater than  $k_T$  (e.g., at  $T_{\text{cure}} = 170^\circ\text{C}$  and  $T_g = 30^\circ\text{C}$ ,  $k_d = 0.94 \gg k_T = 2.33 \cdot 10^{-3}$ ). As a result,  $1/k_T \gg 1/k_d$ , and from eq. (16),  $k_a \approx k_T$ . Consequently, the reaction in the early stages is primarily chemically controlled. As the reaction proceeds,  $T_g$  rises and approaches  $T_{\text{cure}}$ . The value of  $k_d$  becomes smaller because  $(T - T_g)$  becomes less, whereas the value of  $k_T$  remains constant at the given cure temperature (e.g., at  $T_{\text{cure}} = 170^\circ\text{C}$  and  $T_g = 170^\circ\text{C}$ ,  $k_d = 4.77 \cdot 10^{-4} \ll k_T = 2.33 \cdot 10^{-3}$ ). Therefore,  $1/k_T \ll 1/k_d$ , and  $k_a \approx k_d$ , resulting in the reaction being dominated by diffusion-controlled kinetics.

Typical dependence of the difference between the reaction temperature and the glass transition temperature on temperature, during a nonisothermal cure at a constant heating rate, is given in Figure 13. For all investigated heating rates, the glass transition temperature of the reacting system never reached the cure temperature, i.e., the reaction proceeded to completion entirely in the rubbery state, without encountering vitrification or devitrification.

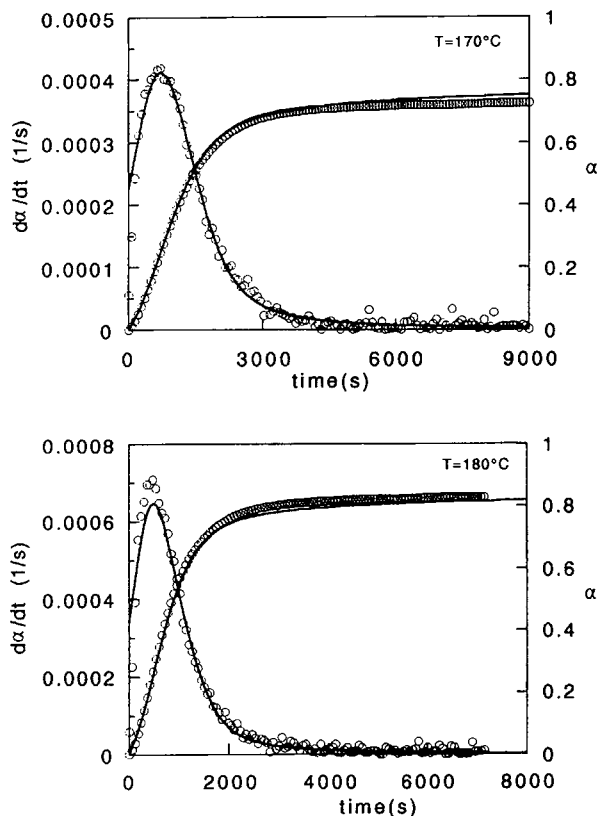
The expression for  $k_a$  was substituted in the autocatalytic rate expression, eq. (13), which was solved numerically by the Runge-Kutta method for each investigated temperature, to obtain the conversion and the rate of reaction as a function of time.

In Figures 14 and 15, the experimental isothermal profiles for the rate of reaction and fractional conversion of the neat resin and prepreg are compared to the kinetic model data. Good agreement between calculation results and the experimental data was obtained. Therefore, by modifying the rate constant of the mechanistic kinetic model, a model applicable to entire conversion range of isothermal cure was obtained. To our best knowledge this is the first time that such a model is applied to the cure of a TGDDM/DDS system.

In order to see if the kinetic expressions arising from isothermal runs are valid outside the range of temperature used for parameter fitting, the cure in dynamic conditions, at constant heating rates, was simulated as well. Comparisons between the experimental data obtained in dynamic DSC runs at three different heating rates and the model predictions are presented in Figure 16. The agreement between calculation results and the experimental data is very good in a broad temperature range. The kinetic model does not predict the shoulder in dynamic DSC thermograms, which appears at high temperatures.



**Figure 14** Comparison of experimental data (dotted curves) with the kinetic model data, (solid lines) for neat resin. Isothermal reaction rate and fractional conversion as functions of time at reported temperatures.



**Figure 15** Comparison of experimental data (dotted curves) with the kinetic model data (solid lines) for prepreg. Isothermal reaction rate and fractional conversion as functions of time at different temperatures.

It may suggest that at high temperatures some changes in reaction mechanism occur. As already seen, in the derivation of the kinetic model only primary amine-epoxy and secondary amine-epoxy reactions were taken into account. At high temperatures and high conversions etherification reactions probably occur as well. In spite of the mentioned limitation, it is very encouraging that the behavior under both isothermal and dynamic conditions can be described with the same model over a temperature range that covers the usual processing conditions.

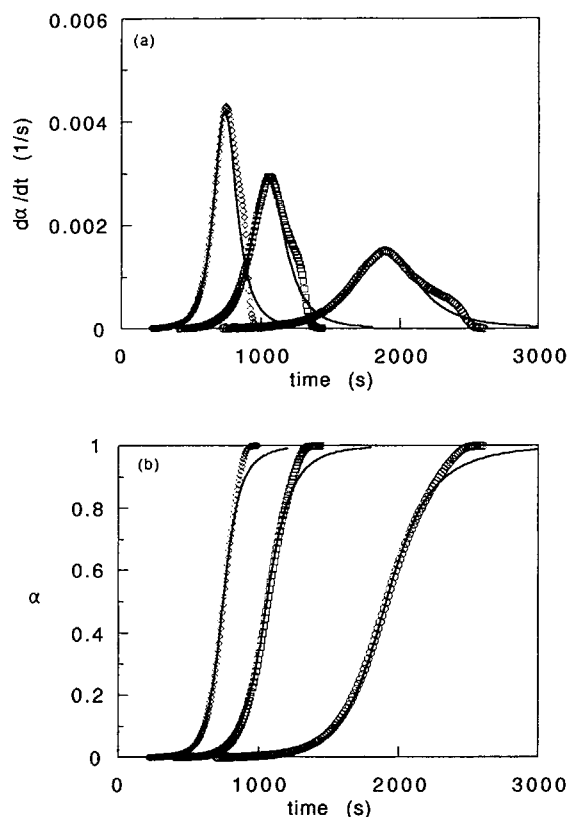
## CONCLUSIONS

The cure of a commercial toughened epoxy system, based on Tetraglycidyl-4,4'-diaminodiphenylmethane and the primary amine curing agent 4,4'-diaminodiphenylsulfone, in the form of neat resin and carbon-fiber prepreg, was studied using differential scanning calorimetry.

The heat of reaction developed during isothermal cure was found to be an increasing function of the

test temperature and lower than the heat of reaction evaluated from nonisothermal data. Subsequent exposure of samples to temperatures greater than the isothermal cure temperature resulted in further reactions. These findings were attributed to the influence of diffusion control on the reaction kinetics in the glass transition region. The variation of the glass transition temperature of the system during cure was adequately described by a linear relationship over the whole conversion range. Analysis of DSC data for both neat resin and prepreg indicated that the presence of the reinforcements (carbon fibers) has a very small effect on the kinetics of cure.

A kinetic model, arising from an autocatalyzed reaction mechanism, was applied to DSC data. The effect of diffusion control was successfully incorporated into the mechanistic model by modifying the overall rate constant, which is assumed to be a combination of the chemical rate constant and the diffusion rate constant. The chemical rate constant obeys the Arrhenius relationship, whereas the dif-



**Figure 16** Comparison of experimental data (dotted curves) with the kinetic model data (solid lines) for prepreg. Rate of reaction (a) and fractional conversion (b) as a function of time at three different heating rates: 5°C/min (○), 10°C/min (□), and 15°C/min (◇). Zero time corresponds to the temperature of 50°C.

fusion rate constant is assumed to be given by the WLF equation.

The kinetic model, with parameters determined from isothermal DSC data, was successfully applied to dynamic DSC data, over a broad temperature range. This is the first time that such model is applied to a TGDDM-DDS system.

Results indicate that in the investigated system the predominant reaction is the amine addition to the epoxy group. Over a temperature range that covers usual processing conditions there is no need to consider an etherification reaction. Also, results suggested that primary and secondary amine are equally reactive. The activation energy for the epoxy-amine reaction catalyzed by newly formed hydroxyl groups was found higher than the activation energy for the reaction catalyzed by groups initially present in the resin.

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