

Cure Kinetics of an Epoxy/Liquid Aromatic Diamine Modified with Poly(ether imide)

Mohammed Naffakh, Michel Dumon, Jérôme Dupuy, Jean-François Gérard

Laboratoire des Matériaux Macromoléculaires/Ingénierie des Matériaux Polymères, Unité Mixte de Recherche, Centre de la Recherche Scientifique 5627, Institut National des Sciences Appliquées de Lyon, Bâtiment Jules Verne, 20 avenue Albert Einstein, 69621 Villeurbanne Cedex, France

Received 19 April 2004; accepted 19 July 2004

DOI 10.1002/app.21495

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The cure kinetics and mechanisms of an epoxy oligomer based on diglycidyl ether of bisphenol A (DGEBA), polymerized with a liquid aromatic diamine based on diethyl toluene diamine (DETDA 80), and its blends with poly(ether imide) (PEI) at concentrations of 0–15 wt % were studied with differential scanning calorimetry under dynamic and isothermal conditions. The kinetic analyses were performed with a phenomenological approach. The reaction mechanism of the blends remained the same as that of the neat epoxy. However, the addition of PEI had a marked effect on the cure kinetics in the DGEBA/DETDA 80 system. The rate of reaction decreased with an

increase in the thermoplastic content. Diffusion control was incorporated to describe the cure behavior of the blends in the latter stages. Greater diffusion control was observed as the PEI concentration increased and the cure temperature decreased. Polymer blends based on this epoxy/liquid aromatic diamine had not been previously studied from a kinetic viewpoint. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 660–672, 2005

Key words: differential scanning calorimetry (DSC); curing; kinetics; modeling; blends

INTRODUCTION

Epoxy resins are an important class of thermosetting polymers widely used for many technical applications, such as composite matrices, coatings, potting compounds, encapsulants, and structural adhesives.^{1–3} Such materials are desirable because they possess various excellent properties, such as high tensile strength and modulus, easy processing, good thermal and chemical resistance, and dimensional stability. However, the further growth of these materials in engineering applications is limited because such good properties in an epoxy resin require a high level of crosslinking, which usually results in brittle behavior.^{1,4}

Although epoxy resins can be substantially toughened by the addition of reactive liquid rubbers,^{4–7} improvements in toughness are inevitably accompanied by the lowering of other good properties, such as the glass-transition temperature (T_g) and thermal and oxidative stability. Therefore, an alternative approach has emerged in which epoxy resins are toughened by

physical blending with high-performance engineering thermoplastics, such as poly(ether sulfone),^{5–7} polysulfone,^{8,9} poly(ether ether ketone),^{10,11} poly(ether imide) (PEI),^{12–14} and polyimide.¹⁵ Studies have revealed that blending with these thermoplastics can enhance the fracture toughness of epoxy resins without sacrificing the strength, stiffness, T_g , or any other desirable properties. Because of the close relationship between the network structure, mechanical properties, and reaction kinetics, it is important to understand the reaction kinetics of the epoxy resins in these blends, whatever process is used. However, introducing a thermoplastic modifier may create further complexities because of specific interactions between the thermoplastic and epoxy resin, which may influence the cure process. For this reason, a clear understanding of the curing mechanism and the ability to develop suitable kinetic models to simulate the curing reaction are essential for predicting and controlling the end properties of the crosslinked materials.

The aim of this work was to investigate the cure behavior of an epoxy system containing diglycidyl ether of bisphenol A (DGEBA) and diethyl toluene diamine (DETDA 80) as a curing agent modified with a high-performance thermoplastic PEI. This blend system was chosen to be processed by resin transfer molding (RTM), the thermoplastic being inserted directly into the mold. First, cycloaliphatic diamines (4,4'-diamino-3,3'-dimethyl dicyclohexylmethane

Correspondence to: M. Dumon (michel.dumon@insa-lyon.fr).

Contract grant sponsor: European Commission (through the Research Training Networks program under the name Polynetset); contract grant number: HPRN-CT-2000-00146.

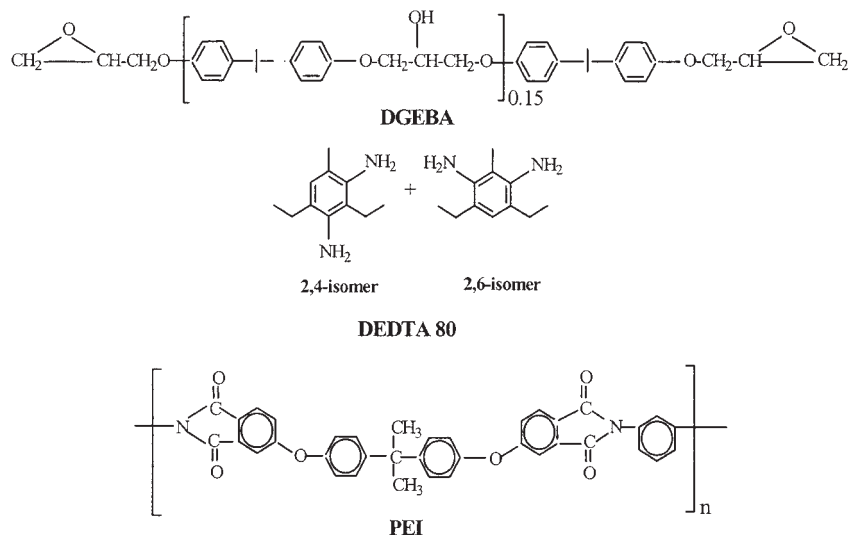


Figure 1 Chemical formulas of the epoxy prepolymer DGEBA, the liquid aromatic diamine DETDA 80, and the thermoplastic PEI.

(3DCM), 3 aminomethyl 1-3,5,5 trimethylcyclohexylamine (IPD), and 1,8 diamine p. methane (MNDA) were tested for their capacity for dissolving PEI on a timescale compatible with RTM, that is, before reacting.¹⁶ None of these amines were suitable for this purpose. Then, an aromatic diamine was proposed, and DETDA 80 was selected to be a less reactive system with an epoxy resin, giving time for thermoplastic dissolution before gelation.^{17,18} Thus, epoxy-diamine/PEI blends were generated by reaction-induced phase separation after the dissolution of PEI. The ultimate goal was to create a multiphase morphol-

ogy able to induce toughening mechanisms to prevent delamination and crack propagation in the crosslinked epoxy resin.

EXPERIMENTAL

Materials

The epoxy resin used in this work was DER 330 (DGEBA, Dow Chem Deutschland, Rheinmunster, Germany), with a molar mass of 383.1 g mol^{-1} ; it was kindly supplied by Dow Chemical Co. The neat epoxy

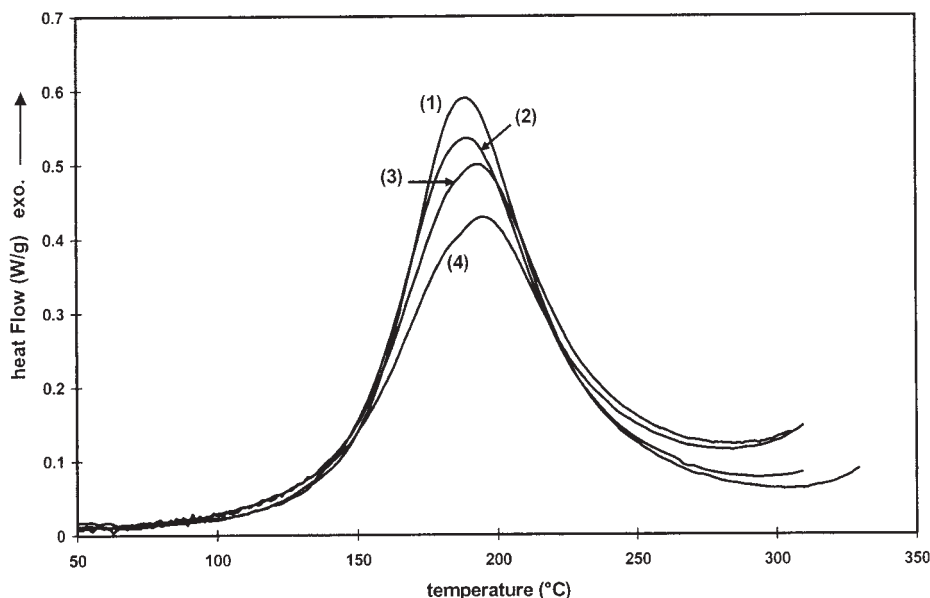


Figure 2 Dynamic thermograms of the PEI-modified DGEBA/DETDA 80 system at a heating rate of 5°C min^{-1} : (1) 0, (2) 5, (3) 10, and (4) 15 wt % PEI.

TABLE I
 ΔH_T , T_p , and $T_{g\infty}$ for Neat and PEI-Modified DGEBA/
 DETDA 80 Obtained During Dynamic
 DSC Measurements

V_h (°C/min)	PEI (wt %)	T_p (°C)	ΔH_T (J/g)	$T_{g\infty}$ (°C)
5	0	189	394	172
	5	189	390	172
	10	193	370	167
	15	194	346	161
10	0	210	385	172
	5	209	367	165
	10	214	300	160
	15	216	340	163

resin and its blend with PEI (GE Ultem 1000), the mass-average molar mass of which was $50,000 \text{ g mol}^{-1}$, were cured with a liquid aromatic diamine (DETDA 80, Lonza, Switzerland). The hardener was a mixture of two DETDA 80 isomers (77–81% 3,5-diethyltoluene-2,4-diamine and 18–22% 3,5-diethyltoluene-2,6-diamine) manufactured by Lonza, with a molar mass of $178.28 \text{ g mol}^{-1}$ and a manufacturer purity value greater than 97.5% according to the supplier. All the components were commercial products and were used as received without purification. The chemical formulas of the epoxy resin, hardener, and thermoplastic are shown in Figure 1.

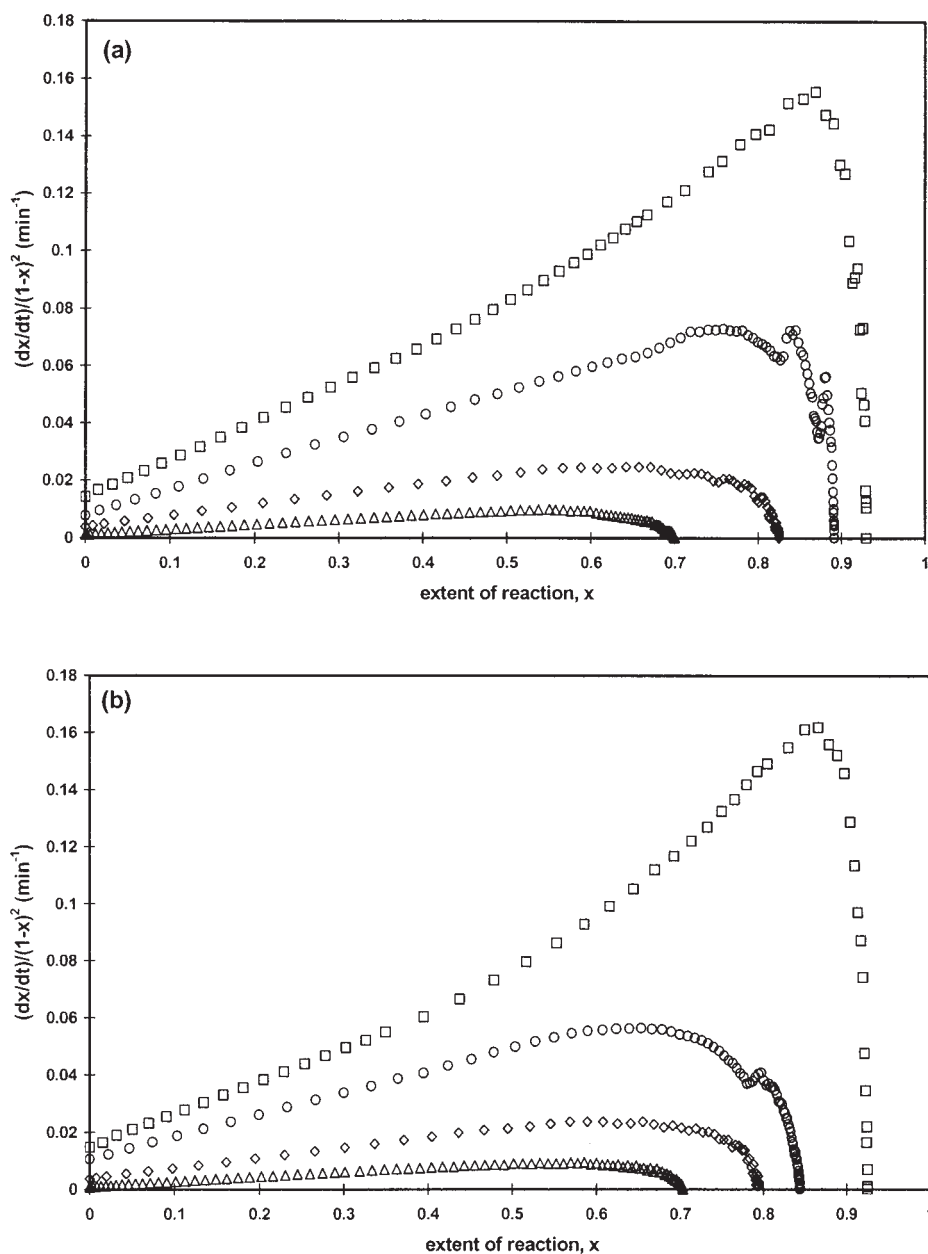


Figure 3 Reduced reaction rate $[(dx/dt)/(1-x)^2]$ versus x for blends, with (a) 5 and (b) 10 wt % PEI, cured at different temperatures: (Δ) 100, (\diamond) 120, (\circ) 140, and (\square) 150°C.

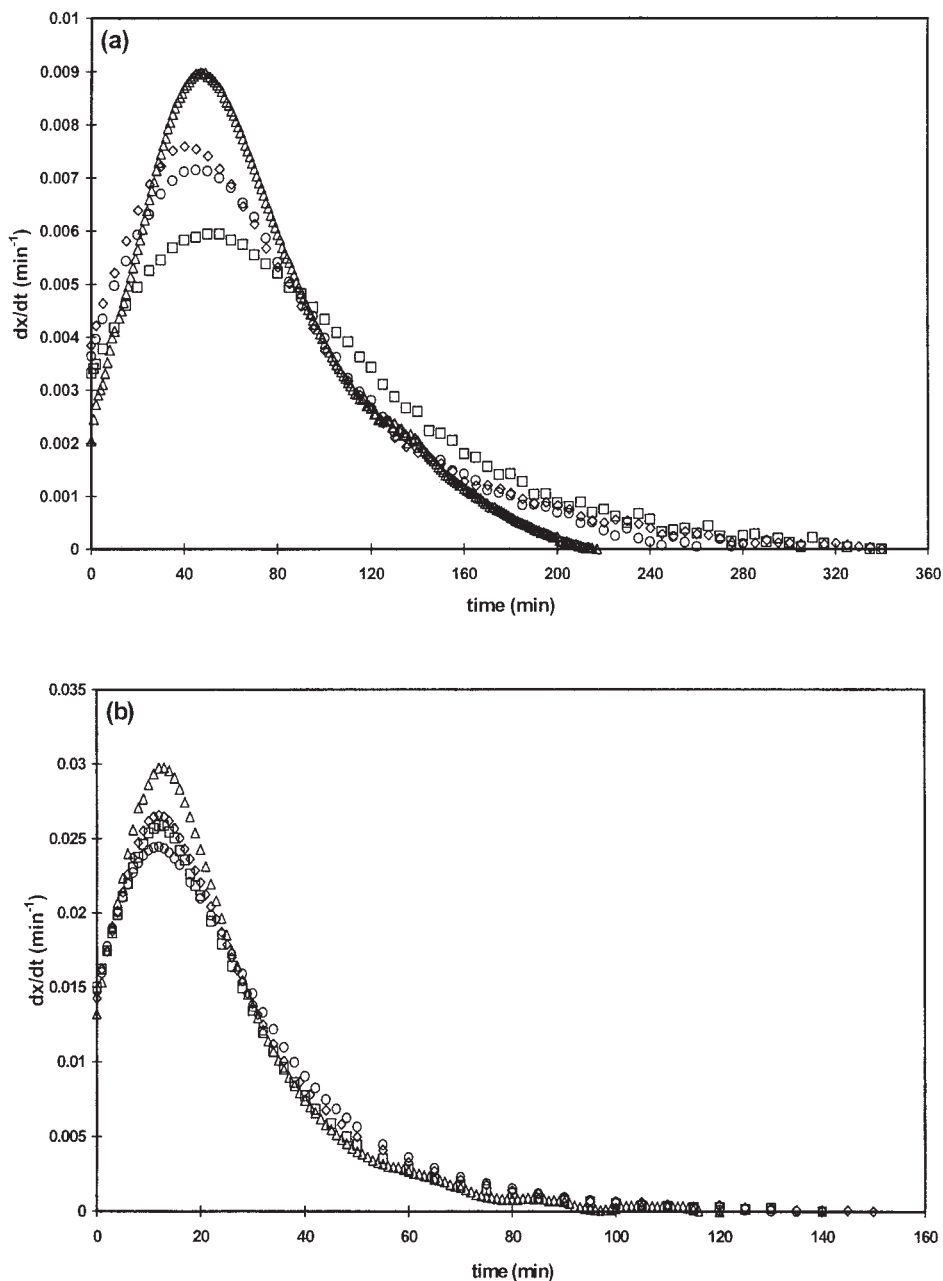


Figure 4 dx/dt versus the time for blends cured at (a) 120 and (b) 150°C: (Δ) 0, (\diamond) 5, (\circ) 10, and (\square) 15 wt % PEI.

The thermoplastic modifier was first dissolved in the epoxy resin at 150°C with constant stirring. The curing agent was dissolved in the blend at 150°C in less than 1 min to minimize the curing reaction during the mixing. Blends with 0, 5, 10, or 15 wt % thermoplastic were prepared. The amine/epoxide ratio was 1 in all cases.

Differential scanning calorimetry (DSC)

A Mettler TA 3000 differential scanning calorimeter equipped with a DSC-30 oven and a PerkinElmer DSC7 instrument were used to analyze the reaction

kinetics of the blends; proportionality was assumed between the heat that evolved during the cure and the extent of the reaction (x). Calibration was regularly performed with indium standards for each experiment performed.

For dynamic DSC scans, samples (20–25 mg) were sealed in aluminum pans and heated under an argon atmosphere. The first heating was performed at rates of 5 and 10°C min^{-1} from -80 to 350°C to measure the total heat of the curing reaction (ΔH_T) corresponding to $x = 1$. The value of T_g for the full conversion ($T_{g\infty}$) was determined during the second scan after rapid cooling.

TABLE II
 ΔH_i and x_f of DGEBA/DETDA 80/PEI Blends
 Cured at Different Temperatures

PEI (wt %)	T (°C)	ΔH_i (J/g)	x_f
0	100	297	0.75
	120	319	0.81
	140	351	0.89
	150	365	0.93
5	100	276	0.70
	120	325	0.83
	140	351	0.89
	150	367	0.93
10	100	278	0.71
	120	313	0.79
	140	332	0.84
	150	365	0.93
15	100	279	0.71
	120	315	0.80
	140	332	0.84
	150	348	0.88

For isothermal cures, small quantities of the samples (5–10 mg) were placed in sealed aluminum pans, and the experiments were then conducted at 100, 120, 140, or 150°C under a nitrogen atmosphere to obtain both the cure rate and the extent of the cure as functions of time. The time required to attain the maximum reaction extent at the temperature considered was determined from the thermograms when they leveled off at the baseline close to the initial baseline. The areas of the peak under the isothermal curve were used to calculate x at various times. x at time t was defined as $x = \Delta H_t / \Delta H_T$, where ΔH_t is the heat of cure at time t .

In this study, ΔH_T was obtained from dynamic DSC experiments.

RESULTS AND DISCUSSION

The aim of a kinetic investigation of a curing epoxy resin system is generally the construction of a kinetic model, either phenomenological or mechanistic, able to predict characteristic features of the curing system, such as the rate of reaction (dx/dt), x , or T_g for a given time–temperature profile. DSC is the most popular technique that permits the measurement of both dx/dt and x . As a result, DSC measurements provide the kinetic variables required for the solution of heat/mass-transfer equations: the heat flow (proportional to dx/dt) and the heat generation (proportional to x or the conversion). Information on the kinetics of the cure reaction allow the proper design of the cure and post-cure cycles, which play a key role in the optimization of processing parameters and the quality of the end properties.

Dynamic kinetic analysis

Dynamic experiments were performed from -80 to 350°C at different heating rates for the DGEBA/DETDA 80 matrix and for the modified mixtures with 5, 10, and 15 wt % PEI. Figure 2 shows the dynamic thermograms for the PEI-modified epoxy blends. The curves have been normalized to 1 g of the network component (DGEBA and DETDA 80). The integrated area of the exothermic curves was used to calculate

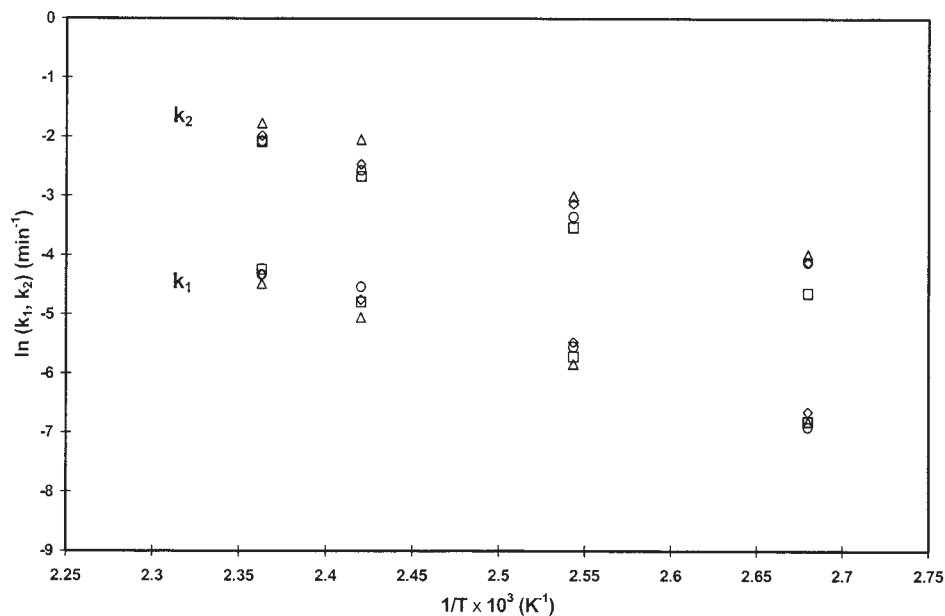


Figure 5 Arrhenius plots of k_1 and k_2 from eq. (2) for blends with (Δ) 0, (\diamond) 5, (\circ) 10, and (\square) 15 wt % PEI.

TABLE III
Kinetic Parameters for the Cure Process of PEI-Modified DGEBA/DETDA 80

PEI (wt %)	T (°C)	$k_1 \times 10^2$ (min ⁻¹)	$k_2 \times 10^2$ (min ⁻¹)	E_{a1} (kJ/mol)	E_{a2} (kJ/mol)	$A_1 \times 10^{-5}$ (min ⁻¹)	$A_2 \times 10^{-5}$ (min ⁻¹)
0	100	0.11	1.87	60	59	2.45	37.50
	120	0.29	4.97				
	140	0.64	12.90				
	150	1.13	17.10				
5	100	0.13	1.63	60	55	3.18	7.39
	120	0.42	3.60				
	140	0.86	8.51				
	150	1.32	13.82				
10	100	0.10	1.63	69	53	53.50	4.06
	120	0.39	3.50				
	140	1.07	7.68				
	150	1.32	12.62				
15	100	0.11	0.97	67	66	23.01	144.76
	120	0.33	2.93				
	140	0.83	6.92				
	150	1.44	12.45				

ΔH_T . These values and the peak temperature (T_p) are listed in Table I for different PEI concentrations.

The exothermic T_p tended to rise with an increasing concentration of the modifier and was accompanied by a slight reduction of ΔH_T . This fact indicates that PEI delayed the curing reaction rate of the DGEBA/DETDA 80 matrix. This kind of dependence has also been observed by many authors during the addition of a thermoplastic to a neat epoxy resin.¹⁹⁻²¹ The reduction of ΔH_T was also correlated to a decrease in T_g values observed during the second DSC scan, and this indicated vitrification effects. However, during a third scan, T_g of the epoxy-amine phase reached final T_g values close to the neat matrix (i.e., 172°C). Also, the glass transition of PEI in the blends was observed around 215°C ($T_g = 219^\circ\text{C}$ for neat PEI). In general, it is accepted that a delay in a polymerization reaction is mainly associated with physical factors, such as dilution effects and viscosity increases due to thermoplastic addition.^{7,11,12,14,20,22} However, in comparison with results in the literature,^{19,21} the differences observed in our system were not so pronounced.

On the basis of the dynamic DSC results, the isothermal DSC measurements of the modified epoxy/liquid aromatic diamine with PEI were conducted between 100 and 150°C, a temperature range suitable for the mold filling of the RTM process (Fig. 2). ΔH_T for the neat epoxy system was taken to be 394 J g⁻¹, as calculated in our previous work,¹⁸ and corresponded to a reaction enthalpy normalized to the number of epoxy groups [epoxy equivalent (ee)] of 93 kJ ee⁻¹, which is typical of epoxy-amine reactions.^{23,24} This value was used for calculating x at time t .

Isothermal kinetic analysis

The kinetic model used in this work is a phenomenological approach first developed by Kamal and Sour-

our.^{25,26} In this model, a general equation is widely used for the curing reaction of many epoxy-amine systems:²⁷⁻²⁹

$$\frac{dx}{dt} = (k_1 + k_2 x^m)(1 - x)^n \quad (1)$$

where k_1 and k_2 are the rate constants for the reaction, m and n are the kinetic exponents of the reaction, and $m + n$ provides the overall reaction order. Both k_1 and k_2 depend on the temperature according to an Arrhenius law:

$$k_i = A_i \exp\left(-\frac{E_{ai}}{RT}\right) \quad (2)$$

where A_i is the pre-exponential constant, E_{ai} is the activation energy, R is the gas constant, and T is the absolute temperature.

An earlier study by Horie et al.³⁰ was the first important investigation of the curing kinetics of epoxy-amine addition. The approach assumed that the two main epoxy-amine reactions (primary and secondary amines) had the same reactivity and led to the well-known dimensionless velocity equation:

$$\frac{dx}{dt} = (k_1 + k_2 x)(1 - x)(B - x) \quad (3)$$

where B is the initial ratio of amine groups to epoxide groups. For a stoichiometric mixture with $B = 1$, the model becomes a special case of eq. (1) for which m is 1 and n is 2. Nevertheless, the etherification reaction between reacted and unreacted epoxy groups is not taken into consideration in this model.

To test the applicability of this kinetic model to the description of the curing behavior of DGEBA/DETDA

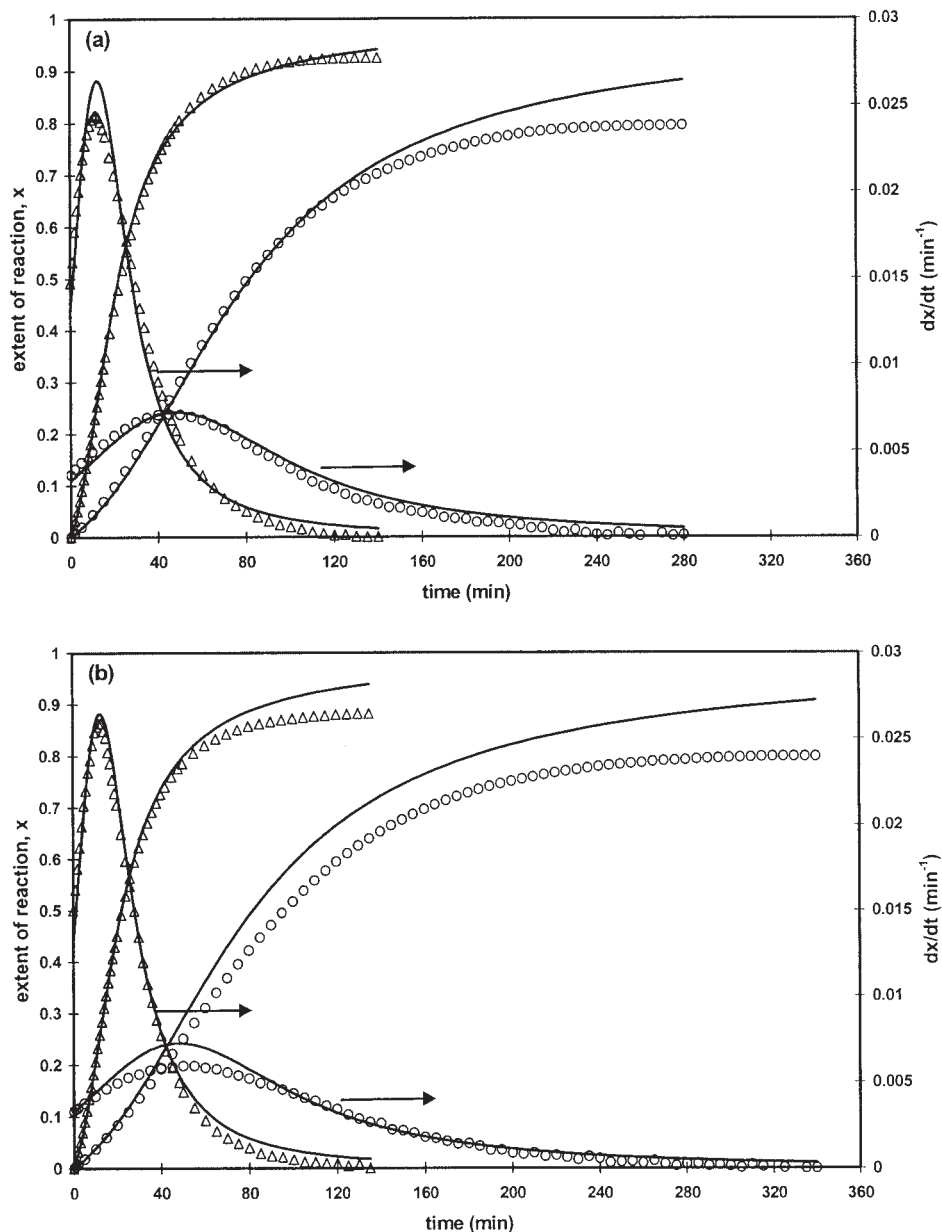


Figure 6 Comparison of the experimental data with (—) kinetic model predictions, with values of E_{ai} and A_i from Table III, for blends with (a) 10 and (b) 15 wt % PEI: x and dx/dt versus the time at curing temperatures of (○) 120 and (△) 150°C.

80/PEI blends, we plotted $(dx/dt)/(1-x)^2$ versus x , for example, at cure temperatures of 100, 120, 140, and 150°C for two concentrations of PEI (5 and 10 wt %), as shown in Figure 3. The straight lines for the low conversions justify the assumption of the values of kinetic exponents m and n . These values are independent of the cure temperature and the amount of the thermoplastic polymer. The linear regions of the curves with intercept k_1 and slope k_2 are followed by maxima and sharp declines toward zero. This deviation from eq. (1) can be attributed to vitrification, that is, the time at which T_g of the reactive system reached the cure temperature.^{22,31,32}

The neat resin and its blends with 5, 10, and 15 wt % PEI were cured at different temperatures. dx/dt versus

time is shown in Figure 4. A maximum rate can be observed after the start of the reaction and shows its autocatalytic effect. These results also demonstrate that the presence of PEI in the epoxy resin did not vary the cure mechanism of the DGEBA/DETDA reaction. However, the maximum dx/dt value of epoxy did decrease with an increase in the PEI concentration and also with a decrease in the isothermal cure temperature.

Detailed values of the heat of reaction (ΔH_i) and final conversion (x_f) at each cure temperature are listed in Table II. The calculation of ΔH_i for the blends was based on the net weight of DGEBA/DETDA 80 in the blends, with the weight of PEI in the epoxy blends being discounted. Our results

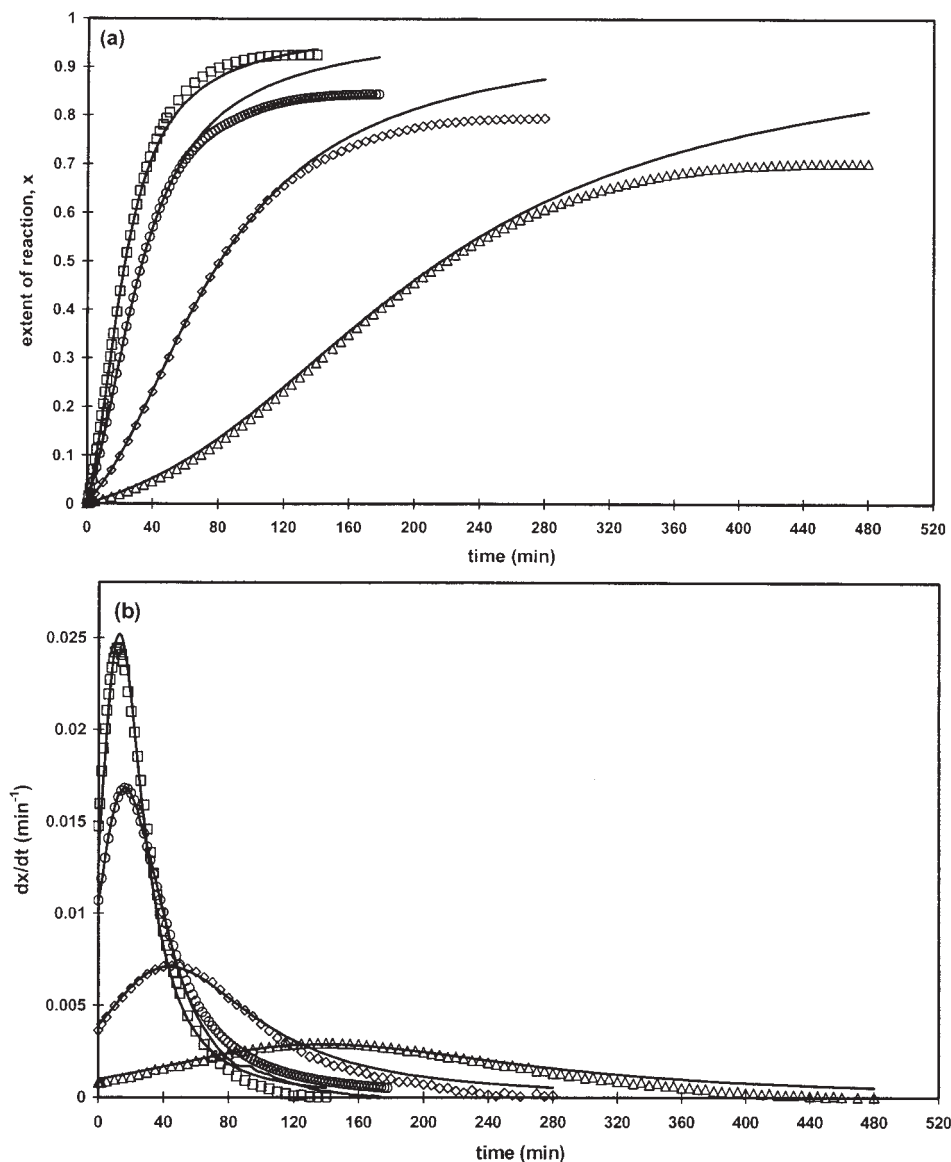


Figure 7 Comparison of the experimental data with (—) kinetic model predictions, with values of E_{ai} and A_i from Table III, for blends with 10 wt % PEI: (a) x and (b) dx/dt versus the time at curing temperatures of (\square) 100, (\diamond) 120, (\circ) 140, and (\triangle) 150°C.

demonstrate that for lower cure temperatures, ΔH_i and x_f decreased, and this corresponded to incompletely cured networks.

The kinetic parameters for DGEBA/DETDA 80 and its blends with PEI were determined with the proposed kinetic mechanism. Because there were two rate constants (k_1 and k_2) and two E_{ai} 's (E_{a1} and E_{a2}), they were obtained by the plotting of $\ln k_1$ and $\ln k_2$ versus $1/T$. The slopes of these plots were then used to calculate E_{a1} and E_{a2} , respectively. Fits of eq. (2) to the pure system and blends are shown in Figure 5, whereas the detailed individual values of the rate constants are listed in Table III. In our study, k_1 and k_2 were determined from eq. (1) without any constraints on them. Equation (2) well fits the linear plots of

Figure 5 from which the E_{ai} values were determined for the epoxy and its blends (Table III). Considering the low concentrations of PEI used in the blends (0–15 wt %), we found that E_{ai} for k_1 of the epoxy blends was apparently higher ($E_{a1} = 60\text{--}69\text{ kJ mol}^{-1}$) than that for the neat epoxy ($E_{a1} = 60 \pm 3\text{ kJ mol}^{-1}$). However, for E_{ai} for k_2 of the modified epoxy, this fact was observed only at a higher PEI concentration (15 wt %).

The phenomenological kinetic model and the rate constants obtained (listed in Table III) were used to calculate the theoretical conversion curves of the cure reaction of the epoxy blends at four RTM cure temperatures. With the four-order Runge Kutta integration technique, it was possible to plot x and dx/dt of the blends versus time. As a first approximation, the

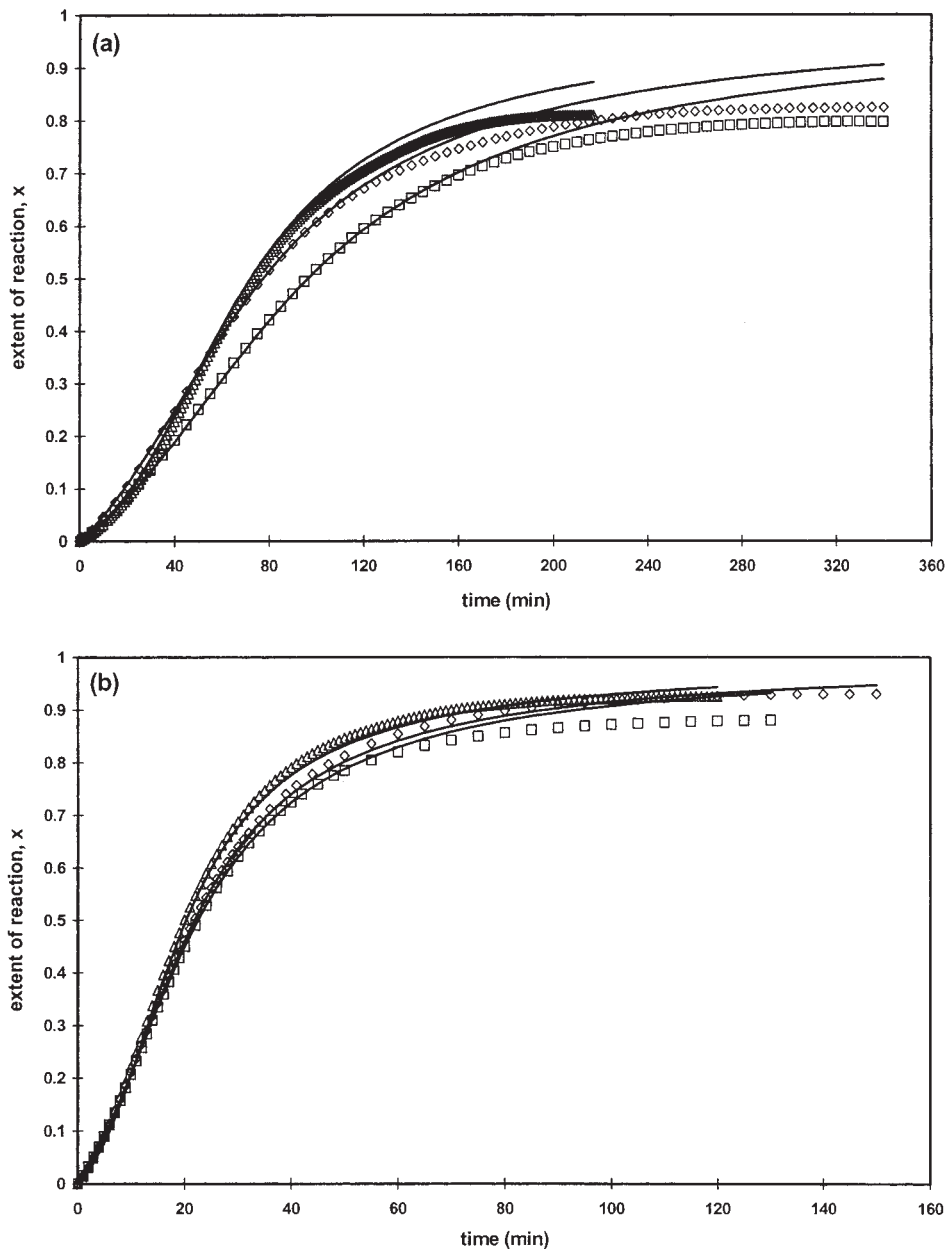


Figure 8 Comparison of the experimental data with (—) kinetic model predictions, with values of E_{ai} and A_i from Table III, for blends cured at (a) 120 and (b) 150°C: x versus the time for PEI concentrations of (Δ) 0, (\diamond) 5, and (\square) 15 wt %.

kinetic parameters of eq. (2), including E_{ai} and A_i for the blends could be considered linear regression values for all data plotted in Figure 5. Thus, dx/dt for epoxy modified with PEI could be given by the following form:

$$\frac{dx}{dt} = \left[\left(9.9 \times 10^5 \exp\left(-\frac{64}{RT}\right) + 20.1 \right) \times 10^5 \exp\left(-\frac{58}{RT}\right)x \right] [1-x]^2 \quad (4)$$

To test the applicability of this approximation for the description of the curing behavior, we plotted x

and dx/dt versus time at cure temperatures of 120 and 150°C for two concentrations of PEI (10 and 15 wt %), as shown in Figure 6. A good agreement was observed when the experimental x data for the blend with 10 wt % PEI were compared with those calculated from model predictions. However, for the blend with 15 wt % PEI cured at 120°C, both x and dx/dt appeared to diverge from the theoretical data.

For a better understanding of the cure behavior of the blends, the model predictions were based on the kinetic parameter values listed in Table III for each blend system. Plots of the experimental data and the data obtained from the kinetic model for a blend

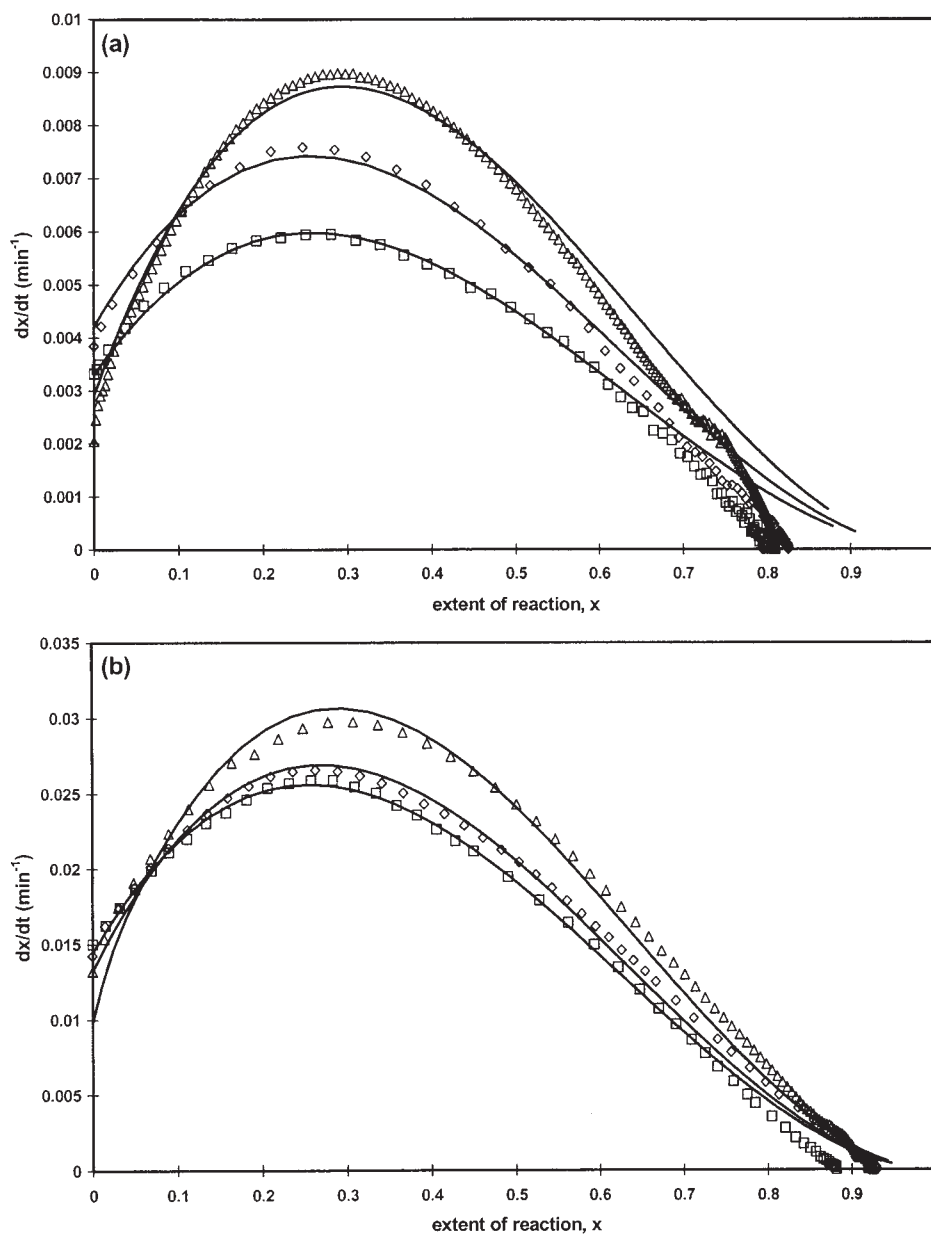


Figure 9 Comparison of the experimental data with (—) kinetic model predictions, with values of E_{ai} and A_i from Table III, for blends cured at (a) 120 and (b) 150°C: dx/dt versus x for PEI concentrations of (Δ) 0, (\diamond) 5, and (\square) 15 wt %.

with 10 wt % PEI cured at different temperatures are presented in Figure 7. In this case, the E_{ai} and A_i values of the cure reaction were $E_{a1} = 69 \text{ kJ mol}^{-1}$, $E_{a2} = 53 \text{ kJ mol}^{-1}$, $A_1 = 53.50 \times 10^5 \text{ min}^{-1}$, and $A_2 = 4.04 \times 10^5 \text{ min}^{-1}$, as listed in Table III. The model prediction curves agreed well with the experimental data for the modified epoxy with PEI. However, at higher conversions, the predicted values were too high in comparison with the experimental data. This behavior was likely a result of the vitrification phenomena of the system. The differences from the experimental data were greater at lower cure temperatures, at which the reaction became diffusion-controlled earlier.

Comparisons between the neat epoxy and its blends were developed. Figure 8 shows the variation of the experimental and theoretical data of x versus time for the modified epoxy cured at two temperatures. To avoid crowding the diagrams, we plotted only the curves for the neat epoxy resin and its blends with 5 and 15 wt % PEI. dx/dt decreased with increasing PEI concentration because of the diluent effect of the thermoplastic. This fact was also manifested when the data of dx/dt versus x were plotted for different concentrations of PEI (Fig. 9). The curves showed a maximum in dx/dt , a typical indication of autocatalytic reactions. This maximum was located in the same range, between conversions of 0.25 and 0.3, whatever the PEI concentration was.

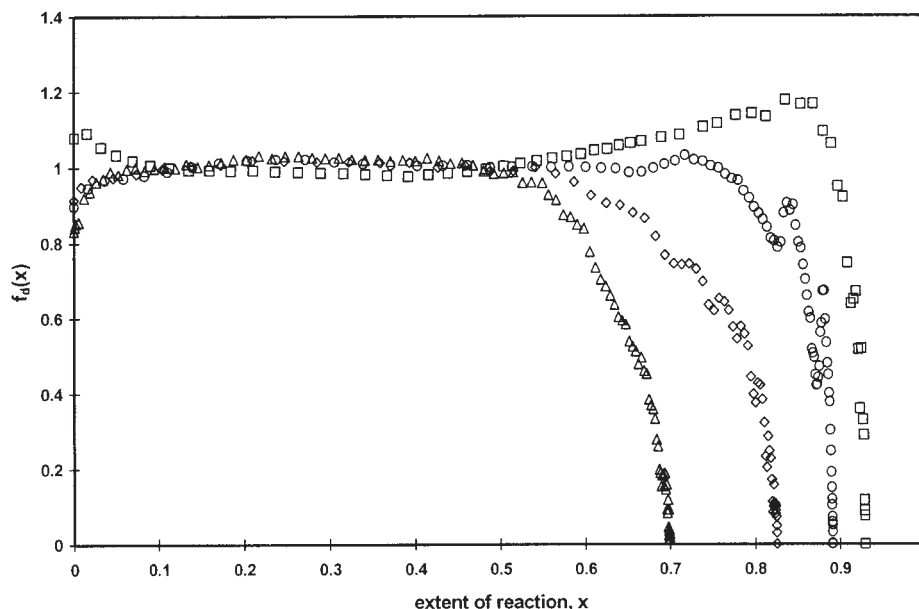


Figure 10 $f_d(x)$ versus x for blends, with 5 wt % PEI, cured at different temperatures: (Δ) 100, (\diamond) 120, (\circ) 140, and (\square) 150°C.

Diffusion control

To consider the diffusion effect, we used a modified kinetic model proposed by Chern and Poehlein³³ to calculate the critical values (x_c) at which diffusion became the controlling factor. Chern and Poehlein proposed a diffusion factor [$f_d(x)$] taking the form of a Williams–Landel–Ferry function:

$$\frac{dx}{dt} = (k_1 + k_2x)(1 - x)^2 f_d(x) \quad (5)$$

with

$$f_d(x) = \frac{1}{1 + \exp[C(x - x_c)]}$$

where C and x_c are curve-fitted variables. When the cure reaction was dominated by the chemical kinetic mechanism, $f_d(x)$ was 1. As the cure reaction became diffusion-controlled, $f_d(x)$ decreased exponentially. However, the change from chemical control to diffusion control was a gradual process, and so the calculation of x_c was difficult to determine with accuracy. An alternative approach was proposed by Fournier et al.³² $f_d(x)$ is given by an empirical function as follows:

$$f_d(x) = \frac{2}{1 + \exp[(x - x_f)/b]} - 1 \quad (6)$$

where x_f is the final conversion reached at the cure temperature chosen and b is an empirical parameter. $f_d(x)$ was determined, as the ratio of experimental dx/dt values to dx/dt values predicted by the kinetic

model in eq. (1), for all the compositions and cure temperatures, and an example is shown in Figure 10. During the early stages of cure, $f_d(x)$ was around 1, and this was indicative of a chemical kinetic mechanism. As the cure proceeded, $f_d(x)$ decreased markedly because of the onset of diffusion control. A similar trend was obtained for other blends. The values of b and x_f obtained by the application of nonlinear regression to $f_d(x)$ versus x are listed in Table IV. A good agreement was observed when these x_f data were compared with those listed in Table II. The influence of the PEI concentration on the curing reaction of the DGEBA/DETDA 80 system was also determined, as

TABLE IV
Values of x_f and b for DGEBA/DETDA 80/PEI Blends Cured at Different Temperatures

PEI (wt %)	T (°C)	b	x_f
0	100	0.029	0.763
	120	0.026	0.816
	140	0.021	0.899
	150	0.012	0.929
5	100	0.046	0.706
	120	0.032	0.829
	140	0.015	0.885
	150	0.010	0.933
10	100	0.047	0.715
	120	0.037	0.802
	140	0.035	0.849
	150	0.006	0.921
15	100	0.054	0.713
	120	0.045	0.809
	140	0.038	0.856
	150	0.028	0.886

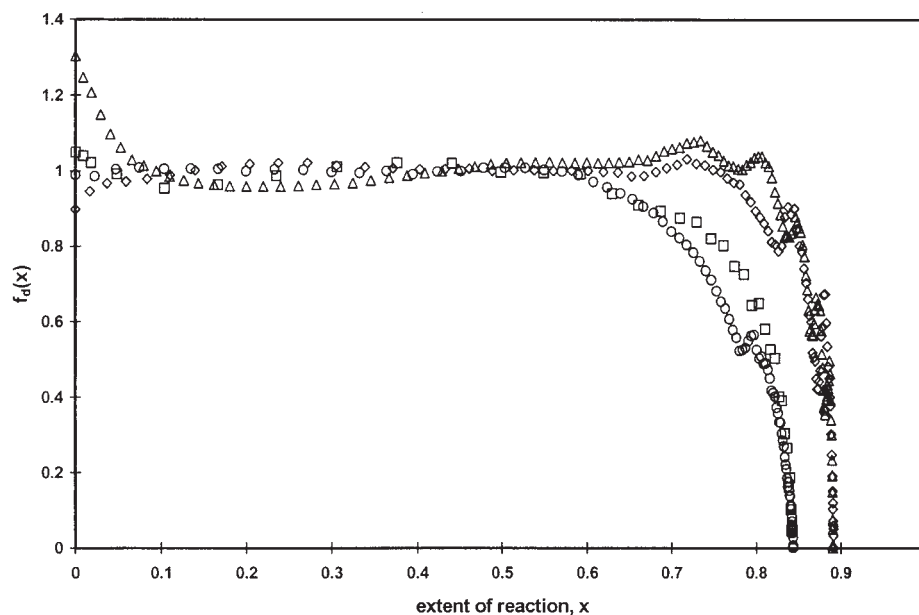


Figure 11 $f_d(x)$ versus x for blends cured at 140°C: (Δ) 0, (\diamond) 5, and (\square) 15 wt % PEI.

shown in Figure 11. $f_d(x)$ dropped away at lower cure conversions at higher PEI contents. The mechanism became more diffusion-controlled with an increasing concentration of PEI in the DGEBA/DETDA/PEI blends (because the T_g value of PEI was higher than that of the network matrix).

CONCLUSIONS

The addition of PEI to the diepoxy prepolymer/diamine system DGEBA/DETDA 80 reduced the curing rate, in both dynamic and isothermal kinetic studies, because of a diluent effect of PEI on the cure process. The DSC results were fitted with a well-known kinetic model based on two rate constants, k_1 , and k_2 , and a two-reaction order ($n = 1$ and $m = 2$) and provided a good description of the cure kinetics up to the point of vitrification. The reaction mechanism of the DGEBA/DETDA 80 system remained the same in the presence of PEI. dx/dt decreased with an increasing concentration of PEI in the blends and also with a decreasing cure temperature. E_{ai} was seemingly influenced by the PEI concentration. The apparent values, E_{a1} and E_{a2} , for a blend with a high concentration of PEI (15 wt %) were greater than the values for the neat system. To describe the cure in the later stages of reaction, we introduced a diffusion factor. Greater diffusion control was observed with an increasing PEI concentration. Satisfactory agreement was observed when the experimental data were compared with those calculated with a model prediction based on one linear regression procedure of the rate constants for all blends. An improved agreement was reached with the kinetic parameters for each blend at cure temperatures suit-

able for RTM blend processing with a novel hardener of epoxy resins able to dissolve a high- T_g thermoplastic.

References

1. May, C. A. *Epoxy Resins: Chemistry and Technology*, 2nd ed.; Marcel Dekker: New York, 1988.
2. Goulding, T. M. In *Handbook of Adhesive Technology*; Pizzi, A.; Mattal, K. L., Eds.; Marcel Dekker: New York, 1994; p 531.
3. Chen, M.; Ren, A. S.; Wang, J. F.; Lee, M. S.; Dalton, L. R.; Zhang, H.; Sun, G.; Steirer, W. H. *Polym Prepr* 1999, 40, 162.
4. Kinloch, A. J., Ed.; *Structural Adhesives, Development in Resins and Primes*; Elsevier: New York, 1996.
5. Min, H. S.; Kim, S. C. *Polym Bull* 1999, 42, 221.
6. Mimura, K.; Ito, H.; Fujikoa, H. *Polymer* 2000, 41, 4451.
7. Varley, R. J.; Hodgkin, J. H.; Simon, G. P. *Polymer* 2001, 42, 3847.
8. Mackinnon, A. J.; Pethrick, R. A.; Jenkins, S. D.; McGrail, P. T. *Polymer* 1994, 35, 5319.
9. Huang, P.; Zheng, S.; Huang, J.; Guo, Q. *Polymer* 1997, 38, 5565.
10. Guo, Q.; Huang, J.; Li, B.; Che, T.; Zhang, H.; Feng, Z. *Polymer* 1991, 32, 58.
11. Francis, B.; Poel, G. V.; Posada, F.; Croenincks, G.; Rao, V. L.; Ramaswamy, R.; Thomas, S. *Polymer* 2003, 44, 3687.
12. Girard Reydet, E.; Vicard, V.; Pascault, J. P.; Sautereau, H. *J Appl Polym Sci* 1997, 65, 2433.
13. Barral, L.; Cano, J.; Lopez-Bueno, I.; Nogueira, P.; Ramirez, C.; Torres, A.; Abad, M. J. *Thermochim Acta* 2000, 344, 137.
14. Bonnet, A.; Lestriez, B.; Pascault, J. P.; Sautereau, H. *J Polym Sci Part B: Polym Phys* 2001, 39, 363.
15. Cho, J. B.; Hwang, J. W.; Cho, K.; An, J. H.; Park, C. E. *Polymer* 1993, 34, 4832.
16. Naffakh, M.; Dumon, M.; Martin, O.; Perier-Camby, H.; Gérard, J. F. *e-Polymers* 2004, P025, 1–14.
17. Naffakh, M.; Dumon, M.; Martin, O.; Gérard, J. F. Presented at the 31st Annual Meeting of Young Researchers on Polymers, Bouvines, France, 2003.

18. Naffakh, M.; Dumon, M.; Gérard, J. F. *J Appl Polym Sci*, submitted.
19. Su, C. C.; Woo, E. M. *Polymer* 1995, 36, 2883.
20. Martinez, I.; Martin, M. D.; Eceiza, A.; Oyanguren, P.; Mondragon, I. *Polymer* 2000, 41, 1027.
21. Barral, L.; Cano, J.; Lopez, J.; Lopez-Bueno, I.; Nogueira, P.; Ramirez, C.; Abad, M. J.; Ramirez, C. *Polymer* 2000, 41, 2657.
22. Jenninger, W.; Schawe, J. E. K.; Alig, I. *Polymer* 2000, 41, 1577.
23. Rozenberg, B. A. *Adv Polym Sci* 1986, 75, 115.
24. Siddiqi, H. M.; Dumon, M.; Eloundou, J. P.; Pascault, J. P. *Polymer* 1996, 37, 4795.
25. Kamal, M. R.; Sourour, S. *Polym Eng Sci* 1973, 59, 13.
26. Kamal, M. R. *Polym Eng Sci* 1974, 14, 231.
27. Yousefi, A.; Lafleur, P. G.; Guavin, R. *Polym Compos* 1997, 18, 157.
28. Zvetkov, V. L. *Polymer* 2001, 42, 6687.
29. Zvetkov, V. L. *Polymer* 2002, 43, 1069.
30. Horie, K.; Hiura, H.; Sawada, M.; Mida, I.; Kambe, H. *J Polym Sci Part A1: Polym Chem* 1970, 8, 1357.
31. Wasylyshyn, D. A.; Johari, G. P. *J Polym Sci Part B: Polym Phys* 1988, 36, 2703.
32. Fournier, J.; William, S. G.; Duch, C.; Aldrige, G. A. *Macromolecules* 1996, 29, 7097.
33. Chern, C. S.; Poehlein, G. W. *Polym Eng Sci* 1987, 27, 782.