

# Blends of Thermotropic Liquid Crystalline Polymer and *O*-Cresol Formaldehyde Epoxy Resin. II. Curing Kinetics

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**ABSTRACT:** Curing kinetics of *O*-cresol formaldehyde epoxy resin and its blends with a liquid crystalline block copolymer (PDBH) cured with linear phenol–formaldehyde resin were studied by the nonisothermal differential scanning calorimetry (DSC) and isothermal DSC methods. The parameters of nonisothermal curing kinetics were obtained according to the Kissinger method, and those of isothermal curing kinetics were deduced on the basis of the *n*-order mechanism proposed by Kamal. The curing reaction is considered 1-order reaction as shown by the nonisothermal and isothermal results. The model gave a good description of

curing kinetics up to the onset of vitrification. A diffusion factor has been introduced in the latter stage of reaction to describe the degree of conversion over the whole range. The obtained *n*-order model modified by diffusion-controlled factor is consistent with the experimental data almost over the whole range of conversion. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1269–1276, 2006

**Key words:** *O*-cresol formaldehyde epoxy resin; liquid crystalline polymer; curing kinetics

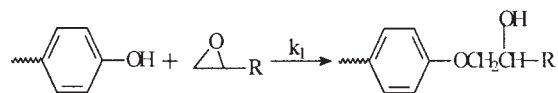
## INTRODUCTION

*O*-Cresol formaldehyde epoxy resin (*O*-CFER) is an important thermosetting polymer, which was exploited in 1970s to cater to the rapid development of semiconductors and electron industries.<sup>1</sup> However, its highly crosslinked structure results in significant brittleness and limits its applications. Efforts have been made to modify this weakness. Thermotropic liquid crystalline polymer (TLCP), as a novel toughening agent, has attracted people's considerable interest in the aspect of modifying epoxy resin, which can not only improve the toughness and the strength of epoxy resin but can also modify its heat resistance.<sup>2–4</sup>

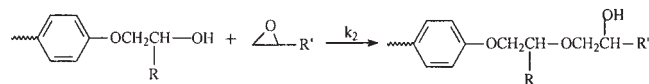
Generally, the properties of a thermosetting polymer are related to the degree of curing reaction. Knowledge of curing kinetics and the mechanism involved are critical for understanding the structure-property relationship of a polymer. Description of curing kinetics is usually based on the experimental data from DSC and Fourier transform infrared spectroscopy (FTIR) methods. For the autocatalysis model, the initial stage of curing reaction tends to show the feature of self-acceleration. For the *n*-order model, the curing reaction rate decreases with increasing the conversion excluding autocatalyst. In the later stage, the deviation of experimental data from the model is ap-

parent because of the onset of gelation. When curing proceeds and the resin crosslinks, the glass transition temperature,  $T_g$ , of the cured resin increases. For curing temperature well over  $T_g$ , the rate of reaction between the epoxy and the reactive groups of curing reagent is chemically kinetically controlled, and the experimental data fit the curing model on the whole. With a further rise in  $T_g$ , the curing reaction becomes diffusion-controlled, and the reaction rate is very slow. At this time, the obtained model must be modified according to the diffusion-controlled effect for satisfying the experimental data.<sup>5–7</sup>

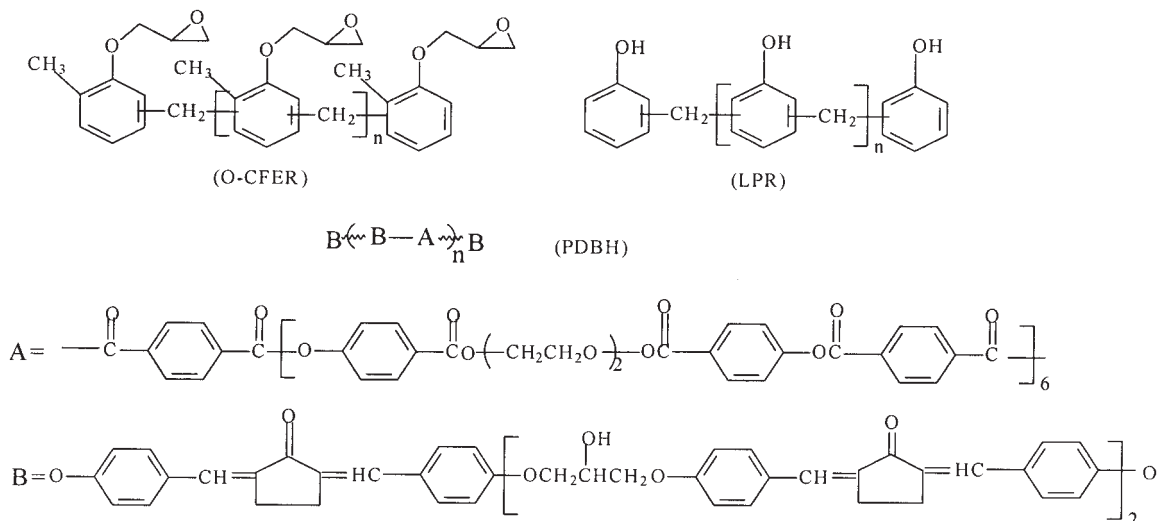
Although epoxy–hydroxy reactions are rather complicated, depending on the reaction conditions, it was generally accepted that there is one important addition reaction, namely primary phenol–OH:



The second type of reaction that occurs to a certain extent at a later stage is alcohol–OH etherification, which is a reaction between an epoxy group and the alcohol–OH group of the intermediate products from the previous phenol–OH addition:



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**Scheme 1** The chemical structures of O-CFER, LPR, and PDBH.

hol-OH is much lower than that of the phenol-OH, depending on the structural hindrance effect of the phenol-OH or the presence of solvents. Moreover, the reaction of alcohol-OH and epoxy group in the later stage may be terminated by gelling network. As a result, the curing kinetics has to be determined by the formed epoxy network structure. Changes of epoxy network structure, for example, by adding other polymers or alternating curing temperature and time, might influence the reaction kinetics.<sup>8,9</sup>

In this study, the curing kinetics of an epoxy system containing O-CFER and LPR as the curing agent were investigated by differential scanning calorimetry (DSC) via nonisothermal and isothermal dynamic methods. A thermotropic liquid crystalline block copolymer (PDBH) was added to improve the toughness of the epoxy system. To date, the curing kinetics of this curing system has rarely been reported. For further understanding of the curing mechanism, it is very important to study the curing kinetics.

## EXPERIMENTAL

O-CFER (each 100 g epoxy resin contains 0.49 mol epoxy group) was supplied by Yueyang Detrochemicals Company of China. LPR (each 100 g resin contains 0.98 mol hydroxy group) was supplied by Zhongdianhuawei Electron Limited Company of China. PDBH, a thermotropic liquid crystalline polyester, was synthesized in our laboratory by condensation reaction in solution.<sup>2</sup> The molecular structures of O-CFER, LPR, and PDBH are listed in Scheme 1.

DSC measurements were performed with a Perkin-Elmer DSC 7 supported by a Perkin-Elmer Computer for data acquisition. Before the experiments, O-CFER, LPR, and PDBH were dissolved in the mixed solution

of methylene chloride and acetone, and then the solvent was removed under reduced pressure at room temperature. The DSC was precalibrated with high purity indium. DSC nonisothermal data were obtained with 8 mg sample in nitrogen atmosphere at a heating rate of 5–20°C/min from 60 to 300°C. The instrument is capable of reaching the designated isothermal temperature at the fastest heating rate (500°C/min) and then equilibrating to the target temperature when the isothermal curing experiment starts. Thus, the heat of reaction that was lost (and thus not recorded) during the transient ramping was virtually negligible, which ensured the accuracy of the kinetics analysis. The completion of reaction was considered when the isothermal DSC thermogram leveled off to the baseline. The total area under the exothermic curve, which was based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure,  $\Delta H_o$ . After the cure reaction was completed in the calorimeter, the sample was cooled to 40°C. To determine the residual heat of reaction,  $\Delta H_R$ , the samples after curing were scanned at 20°C/min from 40 to 280°C. The sum of the isothermal heat ( $\Delta H_o$ ) and the residual heat of the reaction ( $\Delta H_R$ ) was taken to represent the total heat of cure ( $\Delta H_T$ ). The isothermal conversion at time  $t$  was defined as  $\alpha(t) = \Delta H_o / \Delta H_T$ .

## RESULTS AND DISCUSSION

### Models of curing kinetics

A general equation for autocatalytic curing reactions of epoxy is given as follows:<sup>10–14</sup>

$$r = d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (1)$$

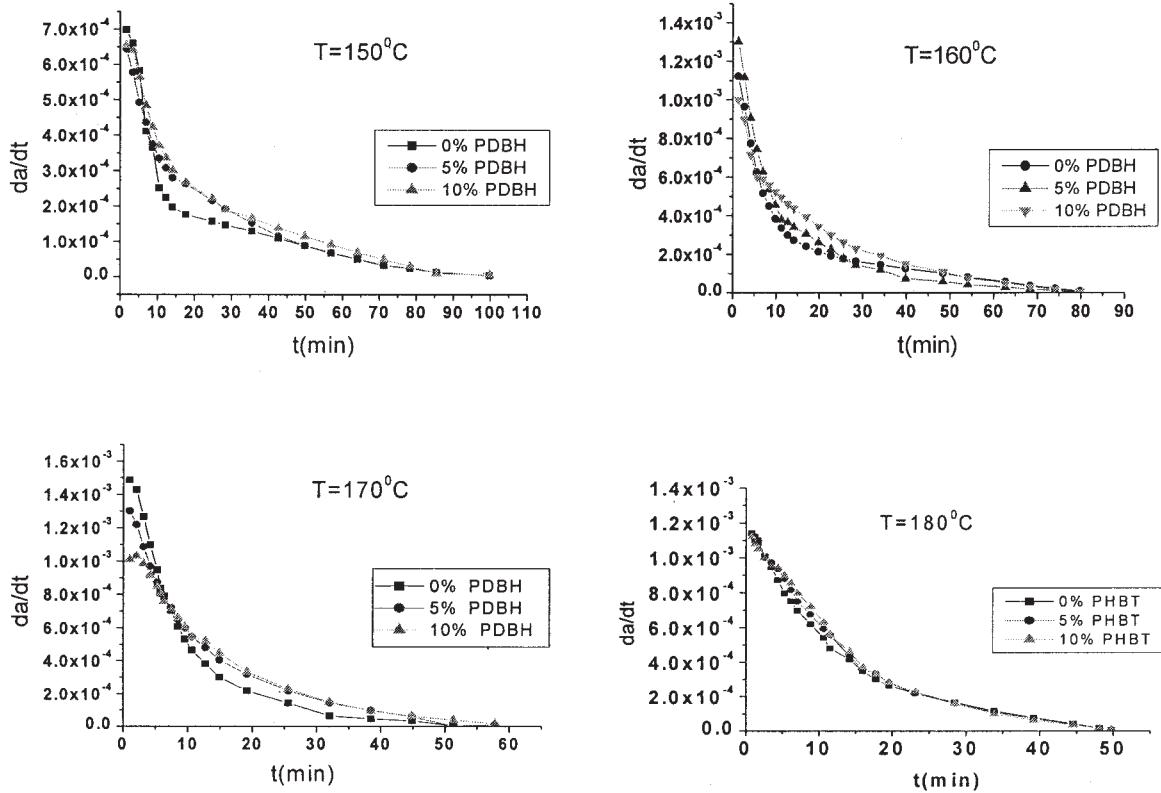


Figure 1 Plot of the reaction rate  $d\alpha/dt$  vs. time  $t$  for *O*-CFER/LPR/PDBH system.

where  $\alpha$  is the conversion,  $k_1$  and  $k_2$  the apparent rate constants,  $r$  the reaction rate, and  $m$  and  $n$  the kinetic exponents of the reactions. These parameters can be calculated according to the nonlinear fitting method proposed by Chean.<sup>9</sup> The two kinetic constants,  $k_1$  and  $k_2$ , are assured to be of the Arrhenius form, i.e.

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

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

To obtain the isothermal reaction activation energy,  $E_a$ , eq. (2) is modified:

$$\ln k = \ln A - E_a/RT \quad (3)$$

If the plot of  $\ln k$  against  $1/T$  is linear, the activation energy and the pre-exponential constant can be obtained from the slope and intercept of the corresponding straight line, respectively.

For an  $n$ -order curing reaction, the data from nonisothermal DSC measurements are analyzed by the following equation. Since  $T = T_o + \beta t$  and  $dT = \beta dt$ ,

$$r = d\alpha/dt = \beta d\alpha/dT = A \exp\{-E_a/RT\}(1 - \alpha)^n \quad (4)$$

where  $T$  is the temperature,  $T_o$  the starting temperature,  $t$  the heating time,  $\alpha$  the conversion and  $\beta$  the heating rate. Since the maximum rate takes place when  $dr/dt$  is zero, differentiating eq. (4) with respect to time and equating the resulted expression to zero give the following equation:

$$\beta \frac{E_a}{RT_p^2} = An(1 - \alpha)_p^{n-1} \exp\{-E_a/RT_p\} \quad (5)$$

where  $T_p$  is the peak temperature of the DSC exothermic curve and it is also the temperature where the maximum reaction occurs. Equation (5) can be written in the natural logarithm form as shown below:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{An(1 - \alpha)_p^{n-1}R}{E_a}\right) - \frac{E_a}{RT_p} \quad (6)$$

#### Kinetics analysis of the blends of *o*-CFER with PDBH

Isothermal cure reactions of the blends containing 0, 5, and 10 wt % PDBH were investigated at 150, 160, 170, and 180°C, respectively, and their kinetics analyses were performed using the aforementioned kinetics methods. Figure 1 shows the relation diagrams of the curing rate and curing time of neat epoxy resin and its blends with 5 and 10 wt % PDBH. These rate curves

conform distinctly to  $n$ -order model in nature, because the maximum rate, the symbol of the autocatalytic model, is not seen after the start of the reaction regardless of the reaction temperatures. In this context, the isothermal curing kinetics equation should use  $n$ -order reaction kinetics referring to the eq. (1):

$$d\alpha/dt = k_{(T)}(1 - \alpha)^n \quad (7)$$

Neglecting the parameters of  $m$  and  $k_2$ , the results, shown in Figure 1, also demonstrate that the presence of PDBH in epoxy resin has no effect on the nature of the  $n$ -order model. However, the reaction rate of the epoxy resin is slightly altered. As shown in Figure 1, the initial reaction rate of the epoxy blends is slower than that of the neat epoxy owing to the long relaxation time of PDBH, but subsequently, the reaction rate of the blends is higher than that of the neat epoxy until they are almost equal finally.

To obtain the reaction order  $n$ , eq. (7) is modified to give the following form:

$$\ln(d\alpha/dt) = \ln(k_{(T)}) + n \ln(1 - \alpha) \quad (8)$$

The  $n$  and  $k$  values can be determined from the slope and intercept of the linear regression of  $\ln(d\alpha/dt)$  vs.  $\ln(1 - \alpha)$ , respectively. Figure 2 illustrates the plots of  $\ln(d\alpha/dt)$  against  $\ln(1 - \alpha)$  of neat epoxy and its blends according to the eq. (8) at various curing temperatures. From the linear parts shown in Figure 2 for the conversion lower than 80%, the reaction order  $n$  and reaction rate constant  $k_1$  are determined for the neat epoxy resin and its blends, which further proves the curing reaction to be the  $n$ -order reaction at low conversion. The values of  $n$ ,  $k_1$ , and other kinetics parameters including  $A$  and  $E_a$  are shown in Table I. The obvious deviation from linearity at high conversion should contribute to the diffusion effect, which will be discussed later.

The relationship of curing time  $t$  and conversion  $\alpha$  at various curing temperatures is shown in eqs. (9) and (10) from integral of eq. (7).

$$t(\alpha,1) = -\frac{1}{A} \exp\left\{\frac{E_a}{RT}\right\} \ln(1 - \alpha) \quad (n = 1) \quad (9)$$

$$t(\alpha,n) = \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)A} \exp\left\{\frac{E_a}{RT}\right\} \quad (n \neq 1) \quad (10)$$

As shown in Table I, most of the  $n$  values are nearly unity. Figure 3, referring to the data of 5 wt % PDBH, shows the relation plot of curing time  $t$  versus conversion  $\alpha$  or curing temperature  $T$  according to eq. (9). Analyzing the curves in Figure 3, we may conclude that the curing time  $t$  increases rapidly with increasing the conversion  $\alpha$  when the conversion  $\alpha$  is over 90% at

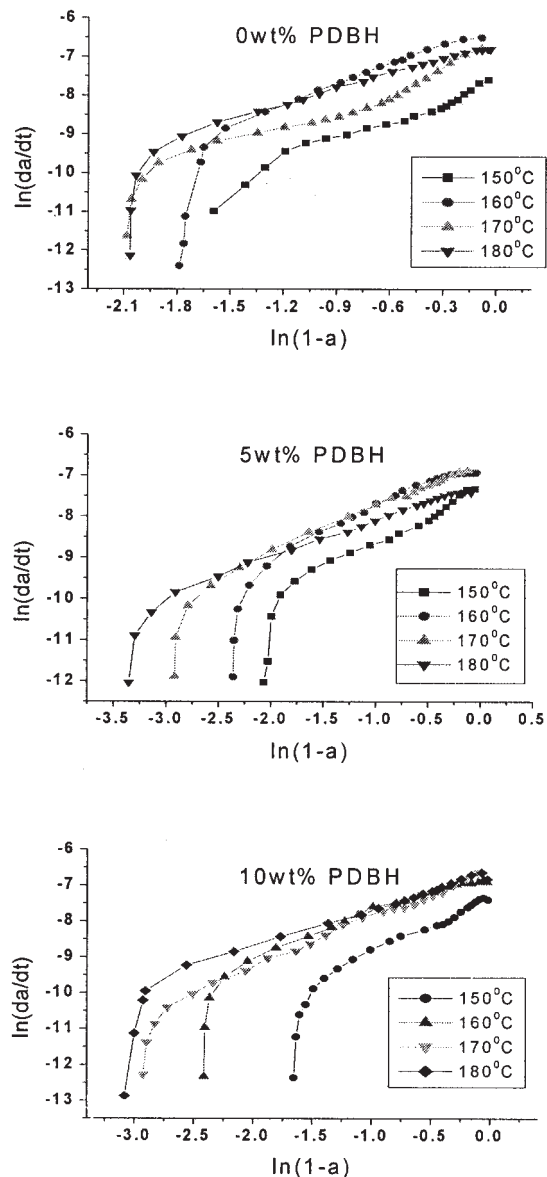


Figure 2 Plot of  $\ln(d\alpha/dt)$  vs.  $\ln(1 - \alpha)$  for O-CFER/LPR/PDBH system.

certain temperature  $T$ , and the curing time  $t$  rapidly decreases with increasing the curing temperature  $T$  when the curing temperature  $T$  is under  $170^\circ\text{C}$ . Therefore, the curing reaction should be carried out over  $170^\circ\text{C}$  for the sake of reducing the curing time.

To further study how the conversion  $\alpha$  changes with the addition of PDBH, we plotted conversion  $\alpha$  vs. curing time  $t$  in Figure 4. As shown in Figure 4, the conversion  $\alpha$  gradually increases with the content of PDBH for certain curing time, indicating that the addition of PDBH to the epoxy matrix enhances not only the reaction rate but also the conversion  $\alpha$ .

The values of  $\Delta H$ ,  $\alpha$ , and other kinetics parameters are also listed in Table I, which shows that the total heat of reaction  $\Delta H$  ( $\Delta H_I + \Delta H_R$ ) is slightly influenced

**TABLE I**  
 Values of  $n$ ,  $k$ ,  $C$ , and  $\alpha_c$  at Different Temperatures

Temperature (°C)	$n$	$\ln(k)$	$E_a$ (KJ/mol)	$\ln(A)$	$\Delta H_R$	$\Delta H_I$	$\alpha$	$C$	$\alpha_c$
Neat EP									
150	1.14	-8.10	81.24	14.96	157.29	613.73	0.796	26	0.70
160	1.30	-7.59			126.54	626.65	0.832	29	0.78
170	1.25	-7.20			90.81	624.24	0.873	51	0.85
180	1.19	-6.53			90.08	630.54	0.875	71	0.86
5 wt % PDBH									
150	1.19	-8.04	74.50	13.16	142.99	605.64	0.808	27	0.83
160	1.28	-7.52			64.59	615.29	0.905	110	0.87
170	1.21	-6.98			42.67	624.12	0.936	43	0.92
180	1.13	-6.67			34.90	611.34	0.946	70	0.94
10 wt % PDBH									
150	1.44	-7.93	71.23	12.33	86.33	593.45	0.873	23	0.75
160	1.26	-7.46			59.27	599.28	0.910	75	0.89
170	1.21	-6.91			29.19	605.36	0.954	117	0.93
180	1.17	-6.63			22.52	620.92	0.965	107	0.94

by adding PDBH. Since the calculation of the heat of reaction for the blends was based on the net weight of the epoxy-phenol resin in the blends without the weight of PDBH, the decrease of  $\Delta H$  with increasing the amount of PDBH should not be taken as a result of the PDBH weight in the blends because the addition of PDBH will decrease the epoxy value of per gram blend system, which should not attribute to the change of reaction mechanism in the presence of PDBH in the blends. Since the data in the Table I show that the reaction order  $n$  of different curing systems at different curing temperatures approach to 1, indicating that the curing reaction is 1-order reaction, eq. (6) is rearranged as follows:

$$\ln(\beta/T_p^2) = \ln(AR/E_a) - E_a R/T_p \quad (11)$$

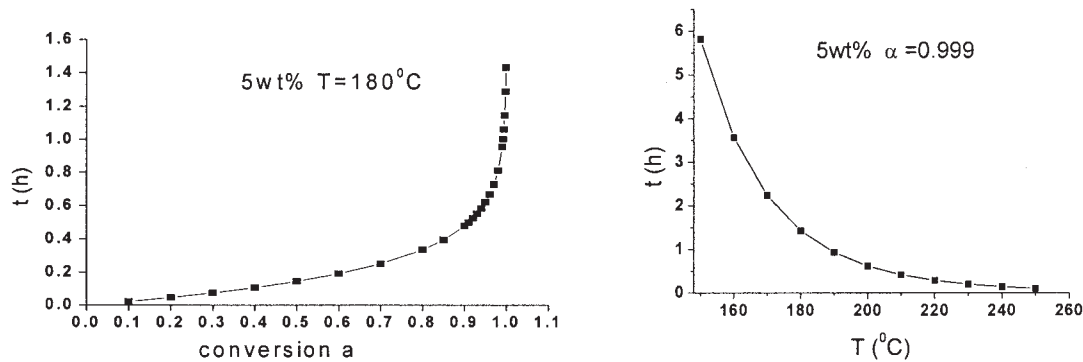
This is the famous Kissinger formula describing the nonisothermal curing kinetics reaction. If the plot  $\ln(\beta/T_p^2)$  against  $(1/T_p)$  is linear, the activation energy can be obtained from the slope of the corresponding straight line.<sup>15</sup> For the 1-order model, the frequency

factor  $A$  can be obtained from the intercept based on the above equation, being independent of the conversion  $\alpha$ . The values of nonisothermal  $E_a$  are shown in the Table II.

The initial  $T_{i'}$ , peak  $T_p$ , and final  $T_f$  are obtained from the intercepts of Figure 5 that describes the relation of curing temperature and heating rate  $\beta$  based on 5 wt % PDBH blend system. The results of its and other blends are shown in the Table II as well. For the experimental convenience, the actual initial  $T_{oi'}$ , curing  $T_{op}$ , and final  $T_{of}$  are set at 150, 180, and 200°C, respectively, but the curing time is longer than the data shown in Figure 3 owing to the diffusion-controlled effect in the later stage.

To investigate the deviation of the experimental result from the  $n$ -order model, eq. (10) is rearranged as follow:

$$\alpha = 1 - [1 - (1 - n)kt_{(\alpha,n)}]^{(1/1-n)} \times (k = A \exp(-E_a/RT)) \quad (12)$$



**Figure 3** The relations of curing time  $t$  and curing temperature  $T$  or  $\alpha$ , according to eq. (9).

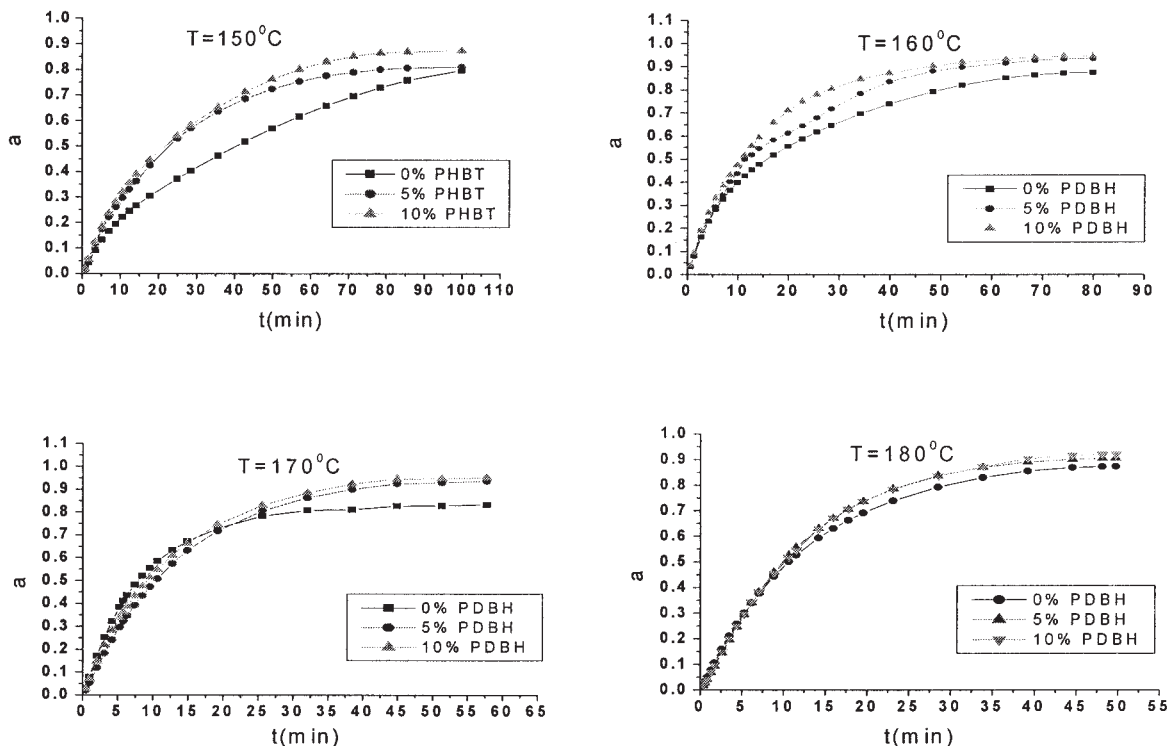


Figure 4 Plots of conversion  $\alpha$  and curing time  $t$  for neat EP and its blend at different temperature.

Comparisons between typical experimental DSC data at 180°C and the prediction of the  $n$ -order model on the basis of eq. (12), with values of model parameters determined in the Table I, are shown in Figure 6. In the initial stage, the experimental data are consistent with those obtained from  $n$ -order model. However, the predicted values from the  $n$ -order model are obviously higher than the experimental data in the later stage, which should be attributed to the diffusion-controlled effect owing to the existence of onset of gelation. With decreasing curing temperature, this phenomenon is much clear. The reason is that the viscosity of the curing system decreases gradually with increasing reaction temperature, so that the phenol-OH of the curing reagent is easy to approach to the epoxy group and further decreases the diffusion-controlled factor.

It is supposed that the conversion  $\alpha$  of curing reaction is proportional to the heat generated during the

TABLE II  
Nonisothermal Curing Kinetics Parameters

PDBH (wt %)	$n$	$E_a$ (KJ/mol)	$T_i$ (°C)	$T_p$ (°C)	$T_f$ (°C)
0	1.10	79.70	208	239	250
5	1.19	75.63	201	227	245
10	1.09	70.26	193	222	236

$T_i$ ,  $T_p$ , and  $T_f$  express initial, peak, and final curing temperatures, respectively.

reaction. The reaction rate  $r$  may be expressed as the function of temperature  $T$  and conversion  $\alpha$  given as follows:

$$d\alpha/dt = k_{(T)}f(\alpha) \quad (13)$$

where  $k(T)$  is the Arrhenius rate constant and  $f(\alpha)$  is a function depending on the reaction mechanism. To explain the diffusion-controlled effect in the curing reaction, Chern put forward a semiempirical relationship according to the free volume considerations.<sup>9</sup> When the reaction attains a certain critical value  $\alpha_c$ , the diffusion-controlled effect will play the primary role, whose reaction rate constant  $k_d$  is given as follows:

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \quad (14)$$

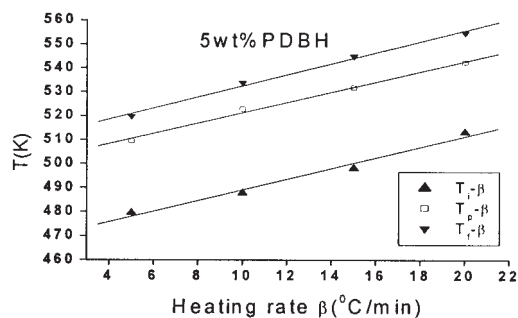
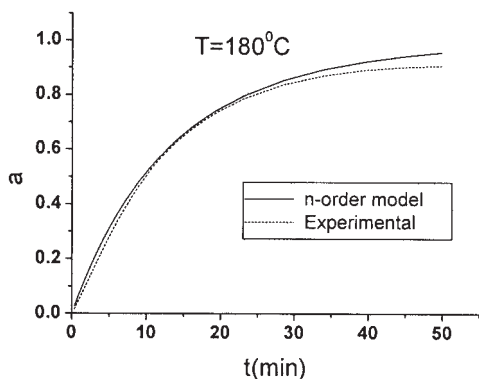


Figure 5 Plot of  $T_i$ ,  $T_p$ , and  $T_f$  vs. heating rate  $\beta$ .



**Figure 6** Comparison of experimental with  $n$ -order model predictions: conversion  $\alpha$  vs. time  $t$ .

where  $k_c$  is the rate constant for kinetic-controlled reaction and  $C$  is a constant. According to Rabinowich,<sup>16</sup> the overall effective rate  $k_e$  considering the chemical-controlled and diffusion-controlled factors can be given as

$$1/k_e = 1/k_d + 1/k_c \quad (15)$$

According to eqs. (14) and (15), the diffusion factor  $f(\alpha)$  can be defined as

$$f(\alpha) = \frac{k_e}{k_d} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (16)$$

where  $C$  and  $\alpha_c$  are two empirical parameters. By substituting the eq. (16) into eq. (13), eq. (17) can be obtained to describe the reaction rate of the diffusion-controlled effect:

$$\frac{d\alpha}{dt} = k_{(T)} \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (17)$$

When the conversion is much less than the critical value  $\alpha_c$ , the reaction is chemical kinetically controlled, neglecting the diffusion-controlled effect. With increasing the conversion  $\alpha$ , the chemical kinetic-controlled factor has to decrease gradually. Equation (17) corresponds to a rather abrupt onset of diffusion control at  $\alpha = \alpha_c$ . However, the onset is more gradual, and there is a region where both chemical and diffusion factors are controlling. When the conversion  $\alpha$  increases further, the diffusion-controlled effect will take over the reaction, neglecting the kinetic-controlled factor, but the effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by  $f(\alpha)$ .

Values of  $\alpha_c$  and  $C$  obtained according to eq. (17) are also shown in the Table I. An increase in  $\alpha_c$  with increasing curing temperature is observed, but for the coefficient  $C$ , no desirable trend is found. This is in

agreement with the studies of Cole et al. and Barral et al. on epoxy-amine systems.<sup>8,12</sup>

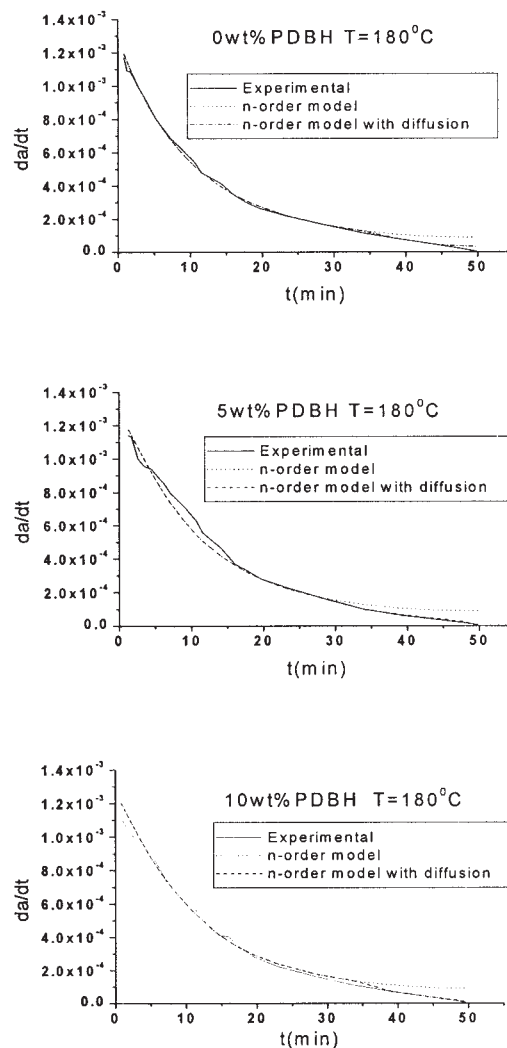
To further study the diffusion-controlled kinetics, eq. (18) is given as follows from the integration of the eq. (17):

$$r = \frac{1}{k_{(T)}} \left[ (\alpha - \alpha_c) + \frac{1}{C} (e^{C(\alpha - \alpha_c)} - 1) \right] + t_c \quad (18)$$

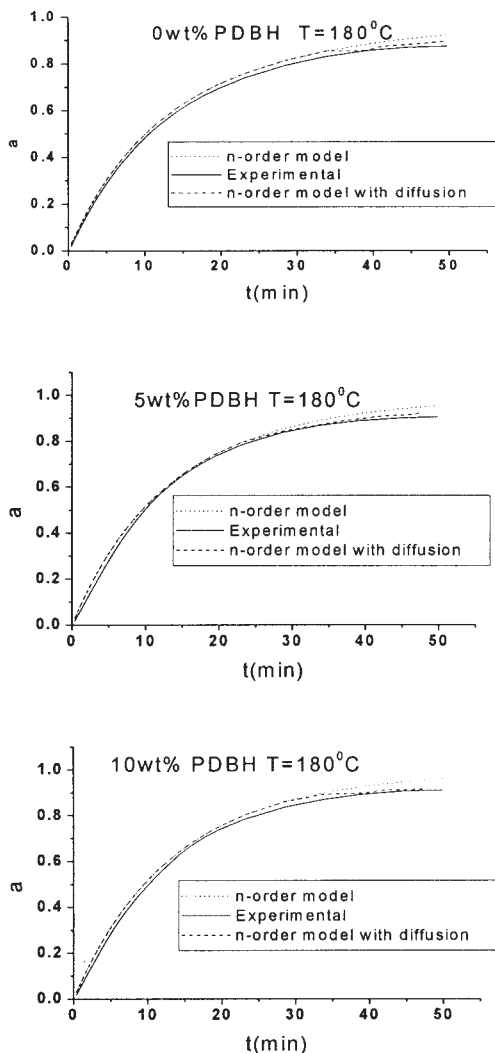
Figures 7 and 8 show the results for other curing systems at 180°C according to eqs. (17) and (18) where the experimental values of  $d\alpha/dt$  and  $\alpha$  vs. curing time ( $t$ ) are compared with those calculated by the  $n$ -order model based on eqs. (7) and (12), coupled with the diffusion factor according to eqs. (17) and (18). Excellent agreement is found almost over the whole curing temperature range.

## CONCLUSIONS

According to the data from nonisothermal DSC and isothermal DSC studies, a  $n$ -order curing model was



**Figure 7** Comparisons of experimental data with model predictions: reaction rate  $d\alpha/dt$  vs.  $t$ .



**Figure 8** Comparisons of experimental data with model predictions: conversion  $\alpha$  vs.  $t$ .

found to be able to describe the curing kinetics of O-CFER and its blends with a liquid crystalline block copolymer (PDBH).

In the first stage of the curing reaction, the experimental data show an  $n$ -order behavior, which includes two parameters of  $k$  and  $n$  fitting the experimental data well up to the vitrification point. The curing reaction is considered 1-order reaction because most of the  $n$  value approach 1. Moreover, the small amount addition of PDBH not only increases the reaction rate but also the conversion  $\alpha$ , so that the curing time  $t$  is shortened as compared with the neat epoxy resin system. From the data of 5 wt % PDBH, a curing craft-work condition is provided to satisfy the requirements of experiment.

To describe the cure in the latter stages of reaction (postvitrification region), a diffusion factor has been introduced. The obtained  $n$ -order model modified by diffusion-controlled factor can fit the experimental data almost over the whole range of conversion. The mechanism of LCP promoting the curing reaction and toughening EP will be discussed in our other paper.

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