

Curing Kinetics and Thermal Property Characterization of a Bisphenol-F Epoxy Resin and DDO System

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ABSTRACT: The curing kinetics of a bisphenol-F epoxy resin (BPFER)/4,4'-diaminodiphenyl oxide (DDO) system were studied with isothermal experiments via differential scanning calorimetry. Autocatalytic behavior was shown in the first stages of the cure for the system, which was well described by the model proposed by Kamal that includes two rate constants, k_1 and k_2 , and two reaction orders, m and n . The curing reaction at the later stages was practically diffusion-controlled because of the onset of gelation and vitrification. For a more precise consideration of the diffusion effect, a diffusion factor, $f(\alpha)$, was introduced into Kamal's equation. In this way, the curing kinetics were predicted well over the entire range of conversion, covering both previtrification and postvitrification stages. The glass-transition temperatures (T_g 's) of the BPFER/DDO system partially isothermally cured were determined by means of torsional braid analysis, and the results showed that T_g 's increased with conversion up to a constant value. The highest T_g was 376.3 K. The thermal degradation kinetics of cured BPFER were investigated with thermogravimetric analysis, which revealed two decomposition steps. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1586–1595, 2002

Key words: bisphenol-F epoxy resins; 4,4'-diaminodiphenyl oxide; cure reaction kinetics; diffusion; glass-transition temperature; thermal degradation kinetics

INTRODUCTION

Bisphenol-A epoxy resin (BPAER) is the most important epoxy resin widely used in the polymer industry, employed for coatings, adhesives, insulating materials, polymer matrices of composite materials, and so forth. Its widespread use, however, is limited in many applications because of its higher viscosity. Compared with BPAER, bisphenol-F epoxy resin (BPFER) has a lower viscosity and good processability. Therefore, it can be applied in the liquid state at a lower viscosity.¹ Because it is not necessary to add a reactive di-

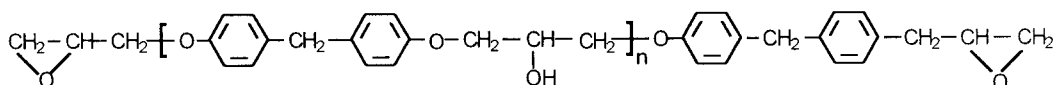
luculent or solvent to the BPFER reaction system, the thermal stability, chemical resistance, and corrosion resistance especially do not decrease. Furthermore, the overall properties of a BPAER system modified by BPFER are improved greatly.²

Studies of BPFER applications^{3,4} and physical properties⁵ of cured BPFER have been reported extensively in recent years. However, descriptions of the cure kinetics of the BPFER/amine system have been lacking until now. To provide a basis for curing process theory for applications of BPFER, we must conduct research on the curing kinetics of the BPFER/amine system. In our previous work, the curing kinetics of bisphenol-S/4,4'-diaminodiphenylmethane were studied with isothermal differential scanning calorimetry (DSC). Kamal's model,⁶ arising from an autocatalytic re-

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action mechanism, only describes the first stage of cure due to gelation and vitrification. In this article, the curing kinetics of 4,4'-diaminodiphenyl oxide (DDO)-cured BPFER were evaluated with isothermal DSC. The Kamal kinetic model was also applied to isothermal DSC data. For inclusion of the diffusion effect, the Kamal model was extended by the introduction of a diffusion factor, $f(\alpha)$. The glass-transition temperature (T_g) and thermal degradation kinetics were investigated with torsional braid analysis (TBA) and thermogravimetric analysis (TGA), respectively. The relationship between T_g and conversion was examined. TGA data were analyzed according to the literature.^{7,8} The structures of noncured and cured BPFER were investigated with Fourier transition infrared (FTIR) analysis.



where $n = 0-1$. The epoxy value was determined according to Jay¹⁰ to be 0.496 mol/100 g.

IR Measurements

The BPFER/DDO samples were prepared with a stoichiometric ratio of epoxy groups and hydrogen groups. Each sample was dissolved in acetone and then coated into a thin film on a potassium bromide plate. During the isothermal curing, an FTIS-40 IR spectrophotometer (BIO-RAD Co. Ltd.) was used for the investigation of the structural changes in the curing system.

DSC Method

Curing studies were carried out with a Shimadzu DT-41 differential scanning calorimeter (Shimadzu Co., Ltd., Japan). It was calibrated with high-purity indium; α -Al₂O₃ was used as the reference material. Isothermal and dynamic heating experiments were carried out according to Opalicki et al.¹¹ under a nitrogen flow of 40 mL/min.

BPFER and curing agent DDO were mixed homogeneously in a 1:1 equivalent ratio. Approximately 10-mg samples of the mixture were weighed accurately into an aluminum DSC sample pan and covered with an aluminum lid. The entire operation was carried out in a dry chamber.

Samples were placed in thermostatic baths at curing temperatures (T_c 's) between 110 and

EXPERIMENTAL

Materials

Bisphenol-F was recrystallized from toluene, and a crystal with a melting point of 162°C was obtained. Epichlorohydrin, NaOH, KOH, acetone, ethyl alcohol, hydrochloric acid, and curing agent diaminodiphenyl oxide were all analytically pure and were supplied by Beijing Chemical Reagent Co. (Beijing, P. R. China).

Synthesis of BPFER

The epoxy resin used in this work, based on bisphenol-F, was synthesized according to Rainer et al.⁹ The molecular structure of this resin had approximately the following form:

130°C in 5°C increments. The reaction was considered complete when the rate curve leveled off to a baseline. The total area under the exothermal curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure, ΔH_i , at a given temperature. After each isothermal run, the sample was quenched to 10°C and then reheated at 10°C/min to 300°C to determine the residual heat of reaction, ΔH_r . The total heat evolved during the curing reaction was $\Delta H_0 = \Delta H_i + \Delta H_r$.

TBA

Specimens, prepared by heat-cleaned glass fiber braid being dipped into an acetone solution of the BPFER/DDO system (an equivalent ratio of 1:1), were completely evaporated *in vacuo*. The air oven was first heated to a desired T_c of 383, 393, 398, 403, or 413 K and kept there for a certain period of time until the system reached the equilibrium state. Specimens were quickly set in the thermostatic baths for 5, 10, 20, 30, 60, 120, or 180 min and then taken out and cooled to room temperature; their T_g 's were determined with TBA with a heating rate of 2 K/min.

TGA Measurements

A sample of BPFER/DDO, mixed homogeneously in a 1:1 equivalent ratio, was cured at 403 K for

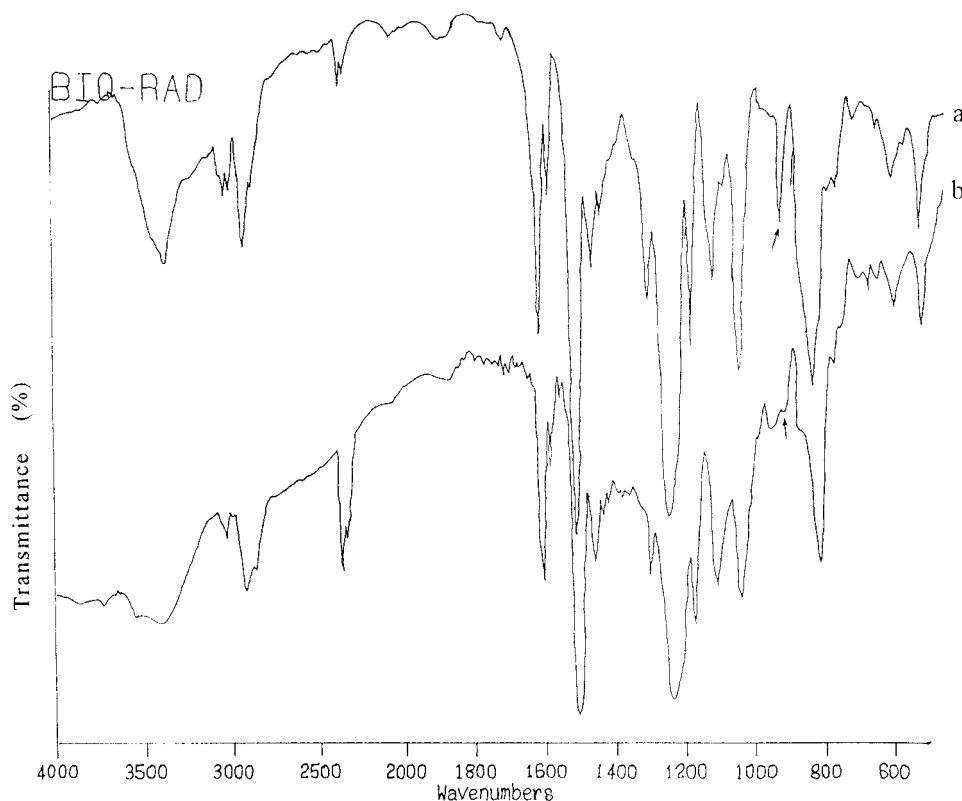


Figure 1 FTIR spectra of BPFER/DDO after curing at 130°C for (a) noncured BPFER and (b) BPFER cured for 600 min.

4 h. A thermal analysis was carried out on a Shimadzu DT-40 thermogravimetric analyzer under a static air atmosphere. About 3 mg of the sample was put into a platinum cell and placed on detector places, and then the furnace was heated to 700°C at a heating rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

Isothermal Curing

The FTIR spectra of the BPFER/DDO system before and after cure are shown in Figure 1. The most significant feature is the appearance of the epoxide group absorption at 914 cm⁻¹ (marked by an arrow): the absorption peak of DDO/BPFER cured for 2 h at 130°C becomes much lower than that of noncured BPFER.

The mechanisms of the curing reaction of thermosetting resins have two general kinetic models: *n*th-order kinetics and autocatalytic kinetics.¹² The reaction rate of *n*th-order kinetics can be expressed as

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

The reaction rate of autocatalytic kinetics can be defined as

$$\frac{d\alpha}{dt} = k' \alpha^m (1 - \alpha)^n \quad (2)$$

where α is the extent of the reaction and is given by $\alpha = \Delta H_t / \Delta H_0$, where ΔH_t is the partial area under a DSC trace up to time t ; m and n are the reaction orders, and k' is the kinetic rate constant.

To account for an autocatalytic reaction in which the initial reaction rate is not zero, Kamal⁶ proposed the following generalized expression:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \quad (3)$$

where k_1 and k_2 are specific rate constants that are functions of temperature. According to the

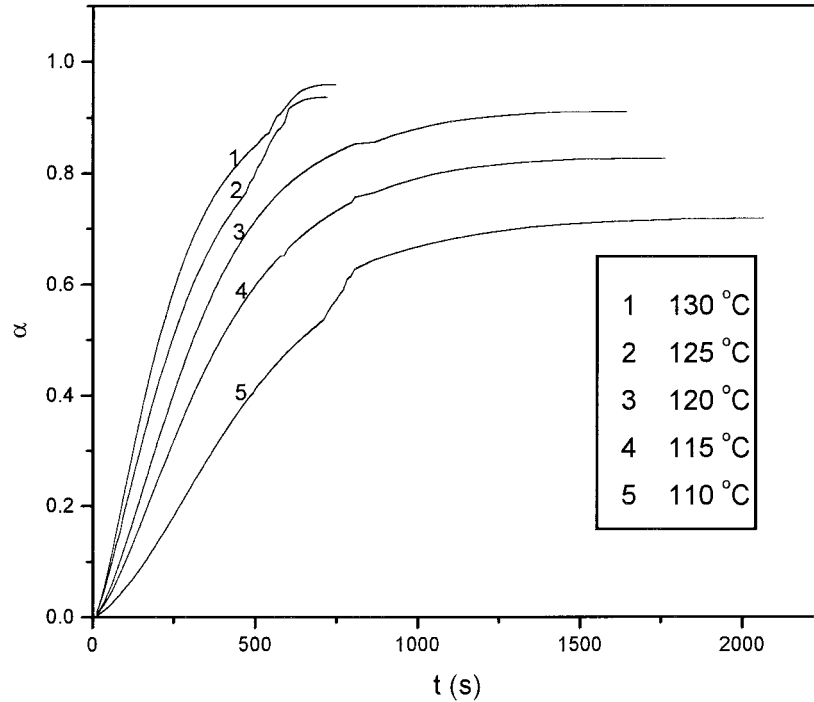


Figure 2 α versus t at different T_c 's.

n th-order kinetic model, the maximum reaction rate will be observed at $t = 0$, whereas the maximum reaction rate of the autocatalytic reaction will appear at some intermediate conversion.

During the curing reaction of the thermosetting resins, the heat of reaction released at any time is proportional to the number of moles reacted at that time;^{13,14} that is, the released heat is

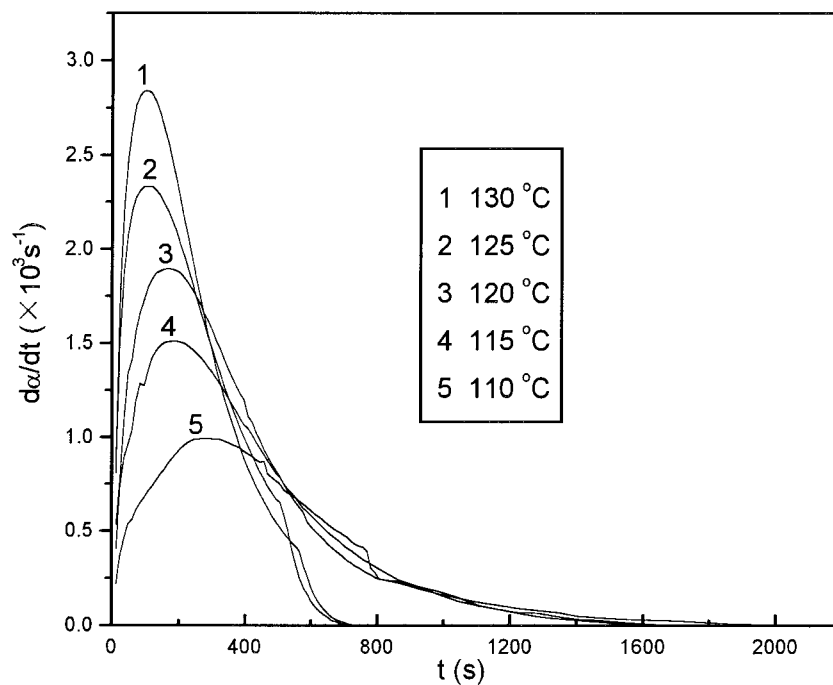


Figure 3 $d\alpha/dt$ versus t at different T_c 's.

Table I Kinetic Parameters for Isothermal Curing of BPFER/DDO

Parameter	T (°C)				
	110	115	120	125	130
$k_1 (\times 10^{-4})$	3.66	4.56	6.86	12.72	13.01
$k_2 (\times 10^{-3})$	4.80	5.09	5.94	5.69	7.42
m	0.83	0.65	0.69	0.66	0.66
n	2.19	1.78	1.52	1.45	1.41
$m + n$	3.02	2.43	2.21	2.11	2.07

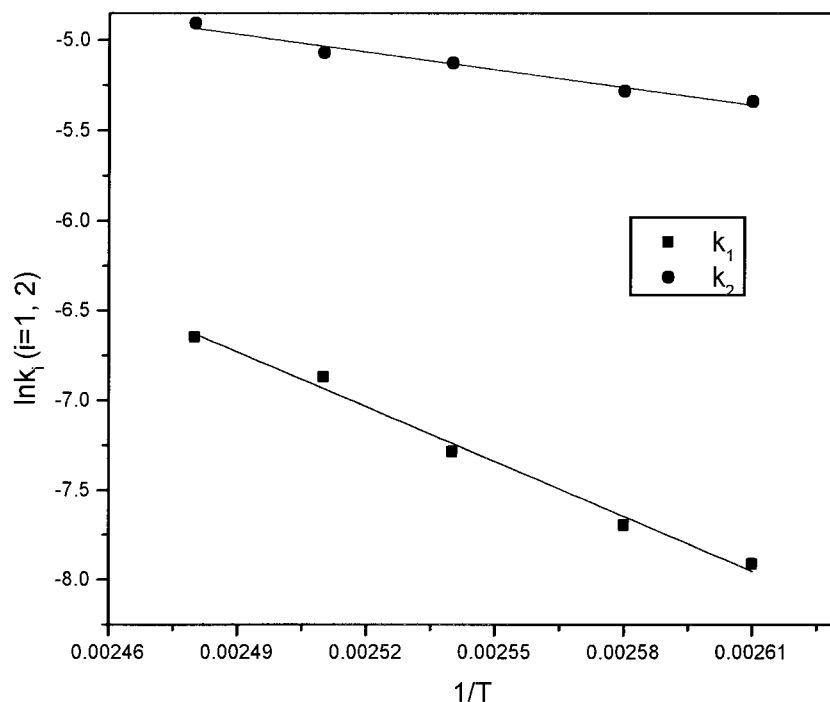
proportional to the extent of the reaction. If the cure reaction is the only thermal event, the reaction rate, $d\alpha/dt$, is proportion to the heat flow,¹² dH/dt :

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \quad (4)$$

Therefore, the curing kinetics were studied, and the kinetic data were determined.^{15,16}

Figure 2 shows plots of the curing reaction conversion α versus time t at different isothermal temperatures. A series of isothermal reaction rate curves, as a function of time, are shown in Figure 3. The reaction rate at any temperature increases

with time at the initial stage of cure and passes through a maximum. The peak of the reaction rate becomes higher and shifts to a shorter time with increasing T_c . The plots show a maximum reaction rate at $t > 0$, thereby negating simple n th-order kinetics. To compute kinetic parameters in eq. (3), several methods have been proposed.¹⁷⁻¹⁹ In this study, k_1 was graphically calculated as the initial reaction rate at $t = 0$, given by the intercept of Figure 3. Then, k_2 , m , and n were calculated through nonlinear regression according to eq. (3). The resulting data obtained from this method for all isothermal experiments are shown in Table I. As seen in Table I, the kinetic rate constants, k_1 and k_2 increase with T_c ,

**Figure 4** $\ln k_1$ and $\ln k_2$ versus $1/T$.

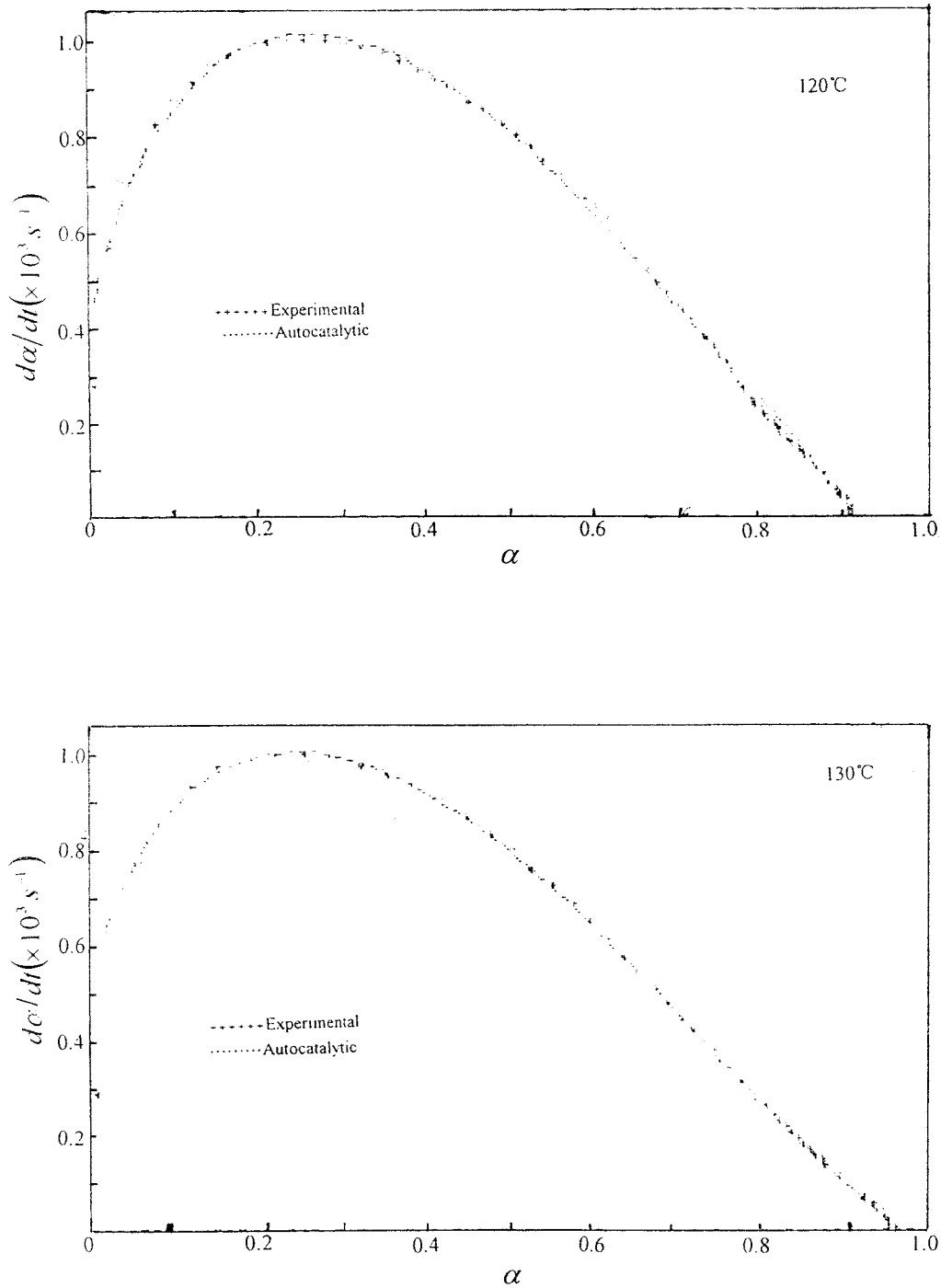


Figure 5 Comparisons of experimental data with theoretical values: $d\alpha/dt$ versus α at 120 and 130°C.

whereas the total reaction order, $m + n$, decreases with T_c .

The reaction rate constants, k_1 and k_2 , depend on the temperature and follow the Arrhenius relationship:

$$k_i = A_i \exp(-E_i/RT) \quad i = 1, 2 \quad (5)$$

where A_i is the pre-exponential constant, E_i is the activation energy, R is the gas constant, and T is the absolute temperature. The relationships be-

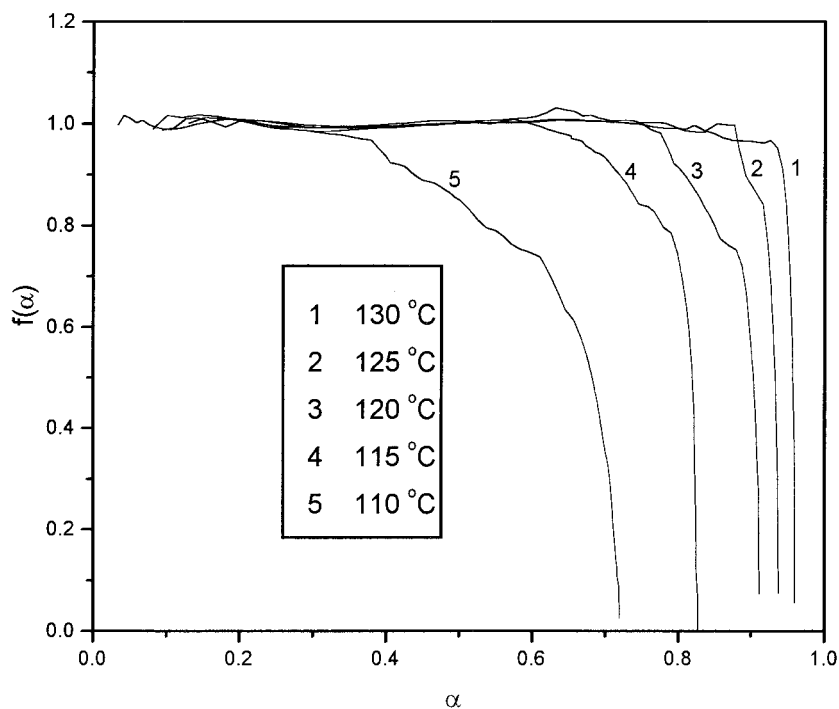


Figure 6 $f(\alpha)$ versus α at different T_c 's.

tween $\ln k_i$ and reciprocal temperature $1/T$ are shown in Figure 4. The activation energies E_1 and E_2 are 161.63 and 32.41 kJ/mol, respectively. The linear correlation coefficient for the k_1 value is 0.9874 and for k_2 is 0.9728.

Typical comparisons between the experimental DSC data and the autocatalytic model with previously determined parameters are shown in Figure 5. At early stages of cure, before gelation and vitrification, the reaction takes place in the liquid phase and is controlled by chemical kinetics. Therefore, the kinetic behavior described by this model coincides with the experimental data. As the reaction progresses, a deviation appears that is due to the onset of gelation and vitrification, where the mobility of reactive groups is hindered, and the rate of conversion is controlled by diffusion rather than kinetic factors.²⁰ Differences between model predictions and experimental data were observed at the same conversion. This can be interpreted by free-volume considerations:²¹ the free volume of materials decreased with temperature, and then the rate of diffusion of reactive groups was reduced, leading to a decreasing reaction rate.

To consider the diffusion effect more precisely, a semiempirical relationship, based on the free-volume consideration, was proposed by Chern

and Poehlein.²¹ In this relationship, $f(\alpha)$ was defined with two empirical parameters as follows:

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (6)$$

where C is the diffusion coefficient and α_c is the critical conversion depending on T_c . The plots of $f(\alpha)$ versus α at different T_c 's are shown in Figure 6. For $\alpha \ll \alpha_c$, $f(\alpha)$ approximately equals unity, and the effect of diffusion is negligible, so that the reaction is kinetically controlled. As α approaches α_c , $f(\alpha)$ begins to decrease, reaching a value of 0.5 at $\alpha = \alpha_c$. Beyond that point, it continues to decrease and approaches zero, which means that the reaction becomes very slow and effectively stops.

If we consider the diffusion effect, the reaction rate of cure can be expressed in the following form to account for the effects of diffusion:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \cdot \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (7)$$

Figure 7 shows a comparison between experimental values and those obtained from eq. (7). The

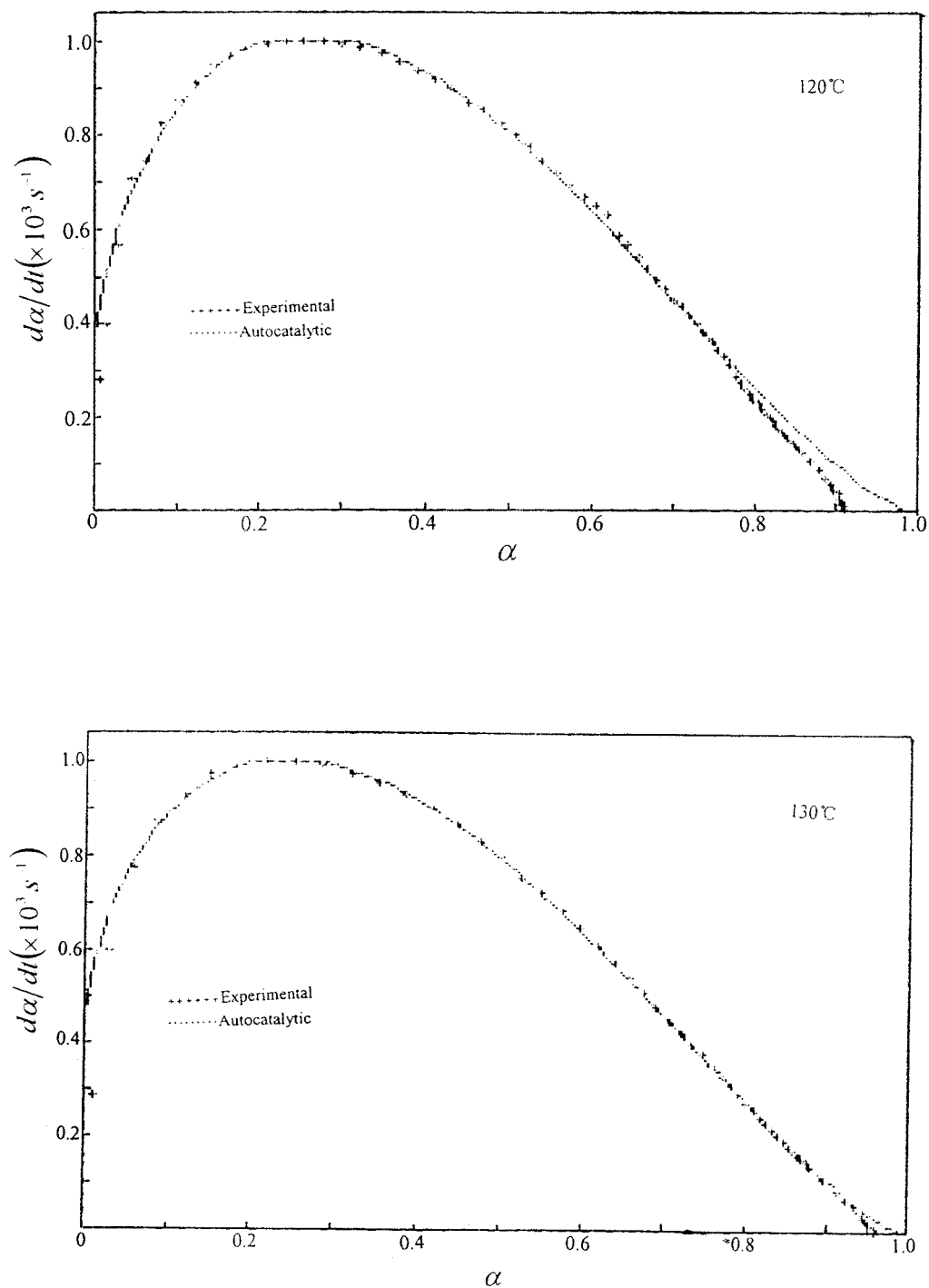


Figure 7 Comparisons of experimental data with theoretical values calculated from eq. (7): $d\alpha/dt$ versus α at 120 and 130°C.

calculated values agree very well with the experimental data. Therefore, we employ the proposed generalized kinetic model to predict and describe the advance of our epoxy resin systems as a function of T_c .

T_g Value and Curing Process

T_g has been used directly as a parameter for conversion in the analysis of reaction kinetic models,²² and there is a one-to-one relationship be-

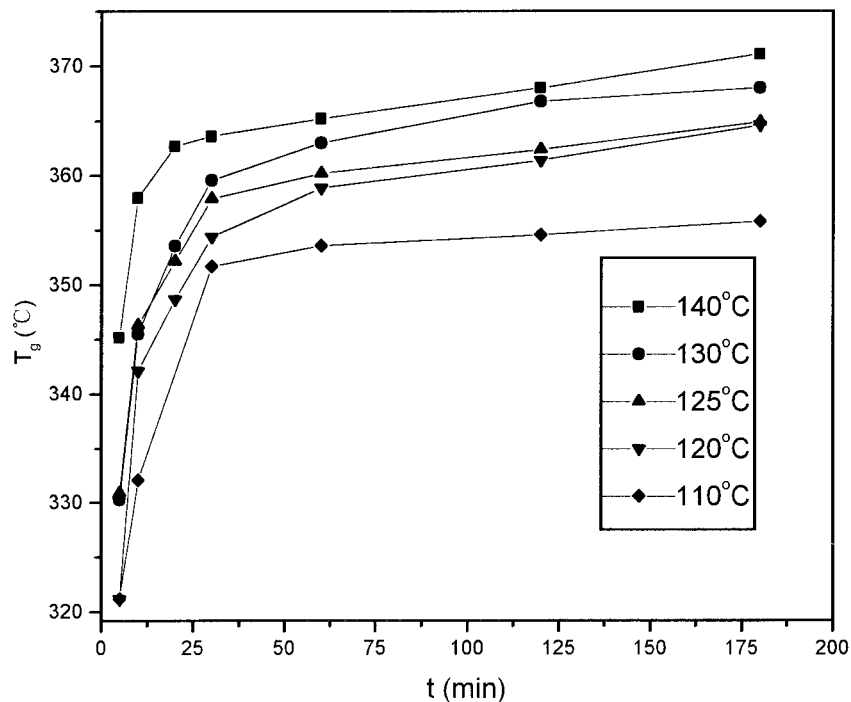


Figure 8 T_g values of BPFER/DDO cured isothermally at different temperatures for various periods.

tween T_g and the degree of cure. It is a convenient parameter because of the ease of measuring T_g by TBA and is particularly useful at high conversions and after vitrification because of the nonlinearity of T_g versus the conversion reaction.²³ Figure 8 shows plots of T_g versus the curing time. As seen from Figure 8, different glass-transition behaviors occurred for the samples with different T_c 's. The highest T_g was 376.3 K.

At low T_c 's, as observed, T_g increases during the early stages of cure. It then levels off and remains at a lower temperature value compared with its values at higher T_c 's. Even if we prolong the curing time under low T_c 's, it is difficult for the resin system to reach a high conversion. Because the process of vitrification usually drastically lowers the reaction rate, a complete cure usually involves temperatures in the vicinity of the maximum of T_g . This is indicative of autocatalytic kinetics in the first stage and a diffusion-controlled reaction as T_g rises.²¹ Similar results have been obtained based on our study of the conversion or reaction rate versus time at different isothermal T_c 's.

At the beginning of the curing reaction process, the degree of cure is low, and the sample gives a low T_g value. At this stage, the process is charac-

terized by a gradual increase in molecular weight, and this transition behavior reflects the movement of linear molecular chains in the system. Because only linear molecular chains exist at this stage, there are many chances for the molecules to collide, resulting in a high reaction rate. With the weight-average molecular weight increasing, most of the reactive functional groups are attached to the gel, and their mobilities are very limited; the curing reaction becomes diffusion-controlled. The crosslinking density further increases with the reaction time rising, and the T_g of the network is enhanced with a decrease in the distance between crosslink points. At this time, the sample is highly cured, and the T_g value becomes greater.

Thermal Degradation

The TGA trace of DDO-cured BPFER revealed two degradation steps under an air atmosphere. In the first stage, weight loss started at 240°C and continued to 474°C with a 49.5% weight loss. In the second stage, from 474 to 624°C, the weight loss was 48.5%. The following kinetic equation was assumed to hold for this reaction:^{7,8}

$$\ln(C/T^{1.92}) = \ln \frac{AE}{\phi R} + 3.77 - 1.92 \ln E - \frac{E}{RT} \quad (8)$$

where $C = W/W_0$, W is the remaining weight, W_0 is the total weight loss, E is the degradation activation energy, A is the frequency factor, ϕ is the heating rate, and R is the gas constant. The degradation activation energy can be calculated from plots of $\ln(C/T^{1.92})$ versus $1/T$, and the values in the first and second stages were 30.0 and 163.9 kJ mol⁻¹, respectively. The degradation activation energy in the second stage was much higher than that in the first stage, illustrating that the breaking of strong bonds took place in the second stage, whereas weak bonds were broken in the first stage.

CONCLUSIONS

1. The cure reaction for the BPFER/DDO system was shown to have autocatalytic behavior in the kinetically controlled stage and was well described with the model proposed by Kamal, which includes two rate constants, k_1 and k_2 , and two reaction orders, m and n . By combination of this proposed kinetic model with a diffusion term, it is possible to describe and predict the cure reaction of this epoxy resin. The theoretical values agree very well with the experimental data.
2. T_g 's were investigated for BPFER/DDO samples cured partially. The curing reaction process and the thermal property of BPFER/DDO were discussed. The results show that the T_g 's increased with the conversion up to a constant value. The highest T_g was 376.3 K.
3. The TGA trace of this system revealed two decomposition stages. The activation energies of thermal degradation in the first and

second stages were 30.0 and 163.9 kJ mol⁻¹.

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