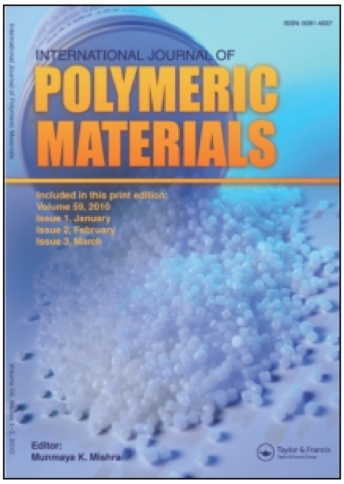


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

CURING KINETICS AND THERMAL PROPERTY CHARACTERIZATION OF BISPHENOL-F EPOXY RESIN AND DDS SYSTEM

Gao Jungang[a]; Shen Shigang[a]; Li Yangfang[a]; Li Deling[b]
[a] College of Chemical and Environmental Science, Department of Chemistry, Baoding, People's Republic of China [b] Department of Chemistry, Tangshan, People's Republic of China

To cite this Article Jungang, Gao , Shigang, Shen , Yangfang, Li and Deling, Li(2004) 'CURING KINETICS AND THERMAL PROPERTY CHARACTERIZATION OF BISPHENOL-F EPOXY RESIN AND DDS SYSTEM', International Journal of Polymeric Materials, 53: 4, 341 — 354

To link to this Article: DOI: 10.1080/00914030490429852

URL: http://dx.doi.org/10.1080/00914030490429852

International Journal of Polymeric Materials, 53:341–354, 2004
Copyright © Taylor & Francis Inc.
ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490429852

CURING KINETICS AND THERMAL PROPERTY CHARACTERIZATION OF BISPHENOL-F EPOXY RESIN AND DDS SYSTEM

Gao Jungang
Shen Shigang
Li Yangfang
College of Chemical and Environmental Science,
Department of Chemistry, Hebei University,
Baoding, People's Republic of China

Li Deling
Department of Chemistry,
Tangshan Teachers College,
Tangshan, People's Republic of China

The curing kinetics of bisphenol-F epoxy resin (BPFER)/4,4′-diaminodiphenyl sulfone (DDS) system were studied by isothermal experiments using a differential scanning calorimeter (DSC). Autocatalytic behavior was shown in the first stages of the cure for the system, which could be 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 due to the onset of gelation and vitrification. To consider the diffusion effect more precisely, diffusion factor, $f(\alpha)$, was introduced into Kamal's equation. Thus, the curing kinetics could be predicted well over the whole range of conversion covering both pre- and postvitrification stages. The glass transition temperatures (T_gs) of the BPFER/DDS system isothermally cured partially were determined by means of torsional braid analysis (TBA), and the results showed that T_gs increased with conversion up to a constant value. The highest T_g was 406.2 K. The thermal degradation kinetics of cured BPFER were investigated by thermogravimetric analysis (TGA), revealing two decomposition steps.

Keywords: Bisphenol-F epoxy resin, 4-4′-diaminodiphenyl sulfone, cure reaction kinetics, diffusion, glass transition temperature, thermal degradation kinetics

Received 26 June 2001; in final form 7 July 2001.

Address correspondence to Gao Jungang, College of Chemical and Environmental Science, Department of Chemistry, Hebei University, Baoding, P. R. China, 071002, E-mail: gaojg@mail.hbu.edu.cn.

INTRODUCTION

Bisphenol-A epoxy resin (BPAER) is the most important epoxy resin used widely in the polymer industry for coatings, adhesives, insulating materials and polymer matrices for composite materials, etc. Its widespread use, however, is limited in many applications because of its higher viscosity. Compared with BPAER, bisphenol-F has a lower viscosity and good processibility. So, it could well be applied in the liquid state at lower viscosity [1]. Because it is not necessary to add reactive diluent or solvent into BPFER reaction system, the thermal stability, chemical resistance and corrosion resistance, especially, do not decrease. Further-more, the overall properties of a BPAER system modified by BPFER will be improved greatly [2].

Studies of BPFER's applications [3, 4] and physical properties [5] of cured BPFER have been extensively reported in recent years. However, descriptions of cure kinetics and thermal characterization of the BPFER/amine system have been lacking until now. In order to provide a basis for curing process theory for the applications of BPFER, it is necessary to conduct research on the curing kinetics and thermal characterization of the BPFER/amine system. In this study, therefore, the curing kinetics, glass transition temperature and thermal degradation kinetics of DDS-cured BPFER were evaluated by isothermal DSC, torsional braid analysis (TBA) and thermogravimetric analysis, respectively. The structures of non-cured and cured BPFER were investigated by Fourier transform infrared spectrometer (FTIR).

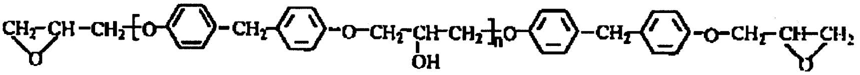
EXPERIMENTAL

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 sulfone were all analytically pure grade and were supplied by Beijing Chemical Reagent Co.

Synthesis of BPFER

Epoxy resin based on bisphenol-F used in this work was synthesized according to Rainer et al. [6] The molecular structure of this resin has the following approximate form (Scheme 1).



SCHEME 1 Epoxy resin based on bisphenol-F.

where $n = 0 \sim 1$. The epoxy value was determined according to Jay [7] to be 0.496 mol/100 g.

IR Measurements

The BPFER/DDS samples were prepared with a stoichiometric ratio of epoxy group and hydrogen group. The sample was dissolved in acetone, then coated as a thin film on a potassium bromide plate. During the isothermal curing, an FTS-40 IR spectrometer was used for investigation of the structure changes of the curing system.

DSC Method

Curing studies were carried out by a Shimadzu DT-41 differential scanning calorimeter. The DSC was calibrated with high-purity indium, α-Al_2O_3 was used as the reference material. Isothermal and dynamic-heating experiments were carried out according to Opalicki et al. [8] under a nitrogen flow of 40 ml/min.

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

Isothermal cure reaction was conducted at 160, 170, 180, 190 and 200°C, respectively. The reaction was considered complete when the isothermal DSC thermogram leveled off to a baseline. The total area under the exothermal curve, based on the extrapolated baseline at the end of reaction, was used to calculate the isothermal heat of cure, ΔH_i, at a given curing temperature. After each isothermal run, the sample was quenched to 10°C, and then scanned at 10°C/min from 10°C to 300°C in order to determine the residual heat of reaction. ΔH_r (ΔH_r is the heat evolved due to the residual isothermal reactivity of the sample at this curing temperature). The total heat evolved during the curing reaction is $\Delta H_0 = \Delta H_i + \Delta H_r$.

Torsional Braid Analysis (TBA)

Specimens, prepared by dipping heat-cleaned glass fiber braid in the solution of BPFER/DDS system (an equivalent ratio of 1:1), were completely evaporated in a vacuum. The curing temperatures were 160, 170, 180, 190 and 200°C. The air oven was first heated up to a desired curing temperature and kept for a certain period of time until the system reached the equilibrium state. Specimens were quickly set into the thermostatic baths of the air oven for 10, 20, 30, 60, 120, 180 and 240 minutes, then taken out and cooled to room temperature, and their T_gs determined using torsional braid analysis with the heating rate of 2 K/min.

TGA Measurement

A sample of BPFER/DDS, mixed homogeneously at a 1:1 equivalent ratio, was cured at 473 K for 4 h. 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, 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 BPFER/DDS 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): it is observed that the absorption peak of BPFER/DDS cured for 2 h at 200°C becomes much lower than that of non-cured BPFER.

The mechanism of the curing reaction of thermosetting resins has the two general kinetic models; that is, nth-order and an autocatalytic mechanism [9]. The reaction rate of nth-order kinetics can be expressed as:

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

The reaction rate of autocatalytic kinetics can be defined as:

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

where α is the extent of reaction, and α 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.

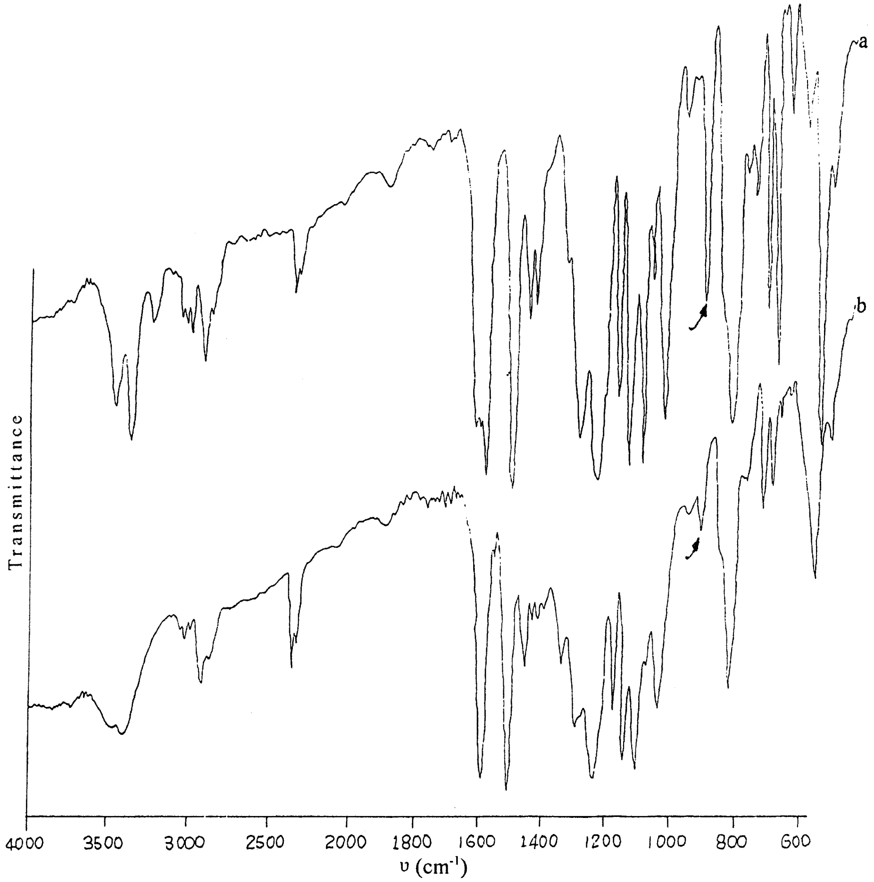


FIGURE 1 The FTIR spectra of BPFER/DDS after curing at 200°C. (a) non-cured BPFER, (b) BPFER/DDS cured for 600 min.

To take into account the autocatalytic reaction, where initial reaction rate of an autocatalytic reaction is not zero, Kamal [10] proposed the generalized expression:

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

where k_1 and k_2 are the specific rate constants that are functions of temperature. According to nth-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 [11, 12], namely, the released heat is 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 [9], dH/dt, that is:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \tag{4}$$

so, the curing kinetics were studied and the kinetics data were determined [13, 14].

Figure 2 shows plots of the curing reaction conversion α versus time t at a 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 is seen to increase with time at the

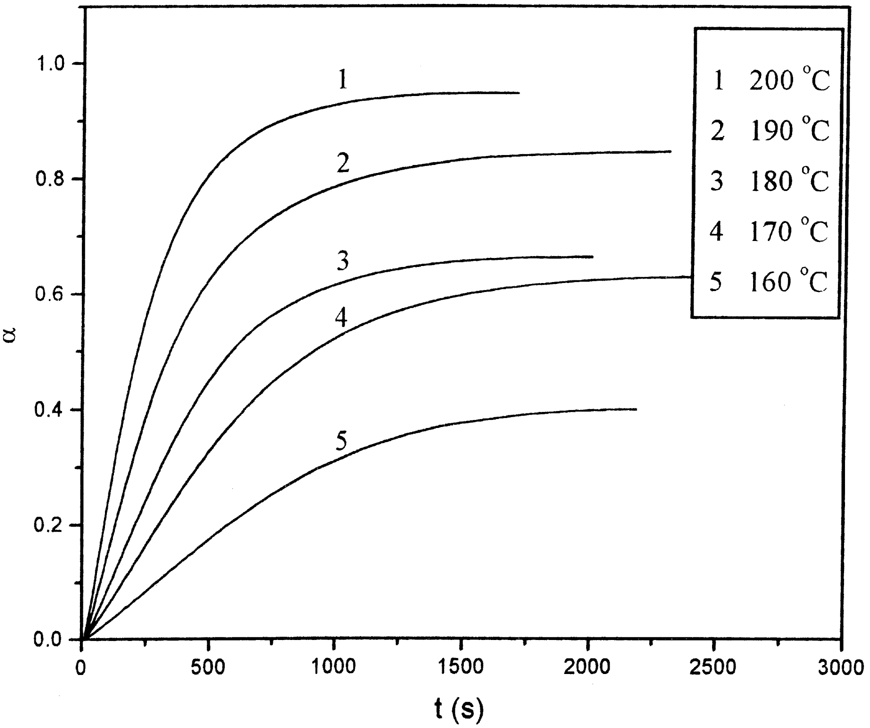


FIGURE 2 Conversion, α, versus time, t, curves at different curing temperatures.

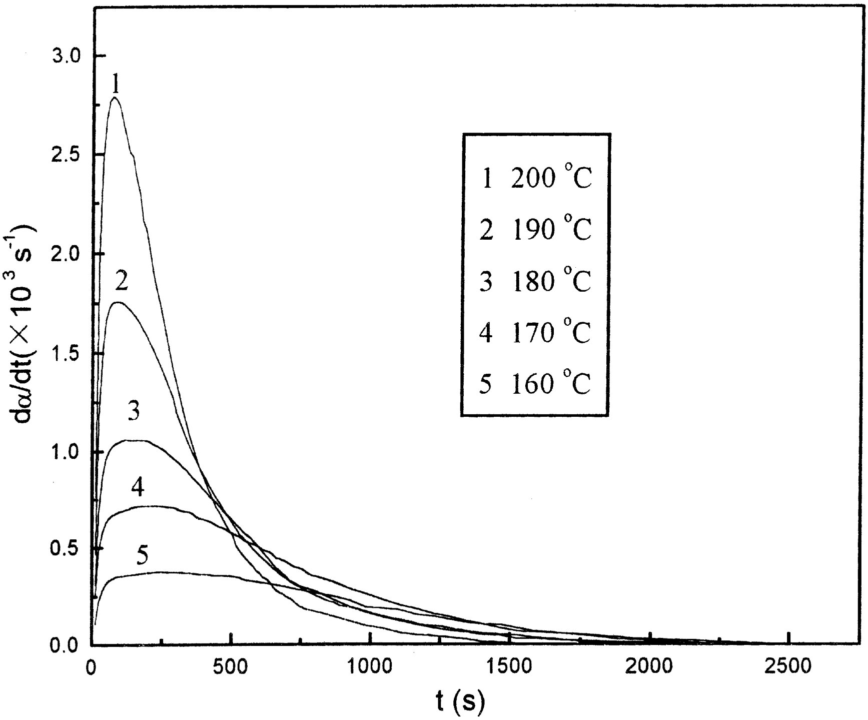


FIGURE 3 Reaction rate, $d\alpha/dt$, versus time, t, curves at different curing temperatures.

initial stage of cure and passes through a maximum. The peak of reaction rate becomes higher and shifts to a shorter time with increasing curing temperatures. The plots show a maximum reaction rate at time $t > 0$, thereby negating simple nth-order kinetics. To compute the kinetic parameters in equation (3), several methods have been proposed [15,16]. In this study, k_1 was graphically calculated as the initial reaction rate at time $t = 0$, given by the intercept of

TABLE 1 Kinetic Parameters for Isothermal Curing of BPFER/DDS

T(°C)	160	170	180	190	200
k_1 ($\times 10^{-1}$ s^{-1}	2.88	5.05	7.09	12.49	15.77
k_2 ($\times 10^{-3}$ s^{-1}	1.02	1.88	2.57	4.42	5.45
m	0.67	0.68	0.63	0.71	0.55
n	2.88	2.20	2.01	1.89	1.45
$m + n$	3.55	2.88	2.64	2.60	2.00

Figure 3. Then, k_2, m and n were calculated by fitting the experimental data to equation (3) in the first portion of cure. The resulting data obtained from this method for all isothermal experiments are shown in Table 1. As seen from Table 1, the kinetic rate constants, k_1 and k_2 increase with the curing temperatures, whereas the total reaction order, $m+n$, decreases with the curing temperatures.

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

$$k_i = A_i \exp(-E_i/RT) \qquad i = 1, 2 \tag{5}$$

where A_i is the pre-exponential constant, E_i the activation energy, R the gas constant, and T the absolute temperature. The activation energies E_1 and E_2, obtained from the plot of ln k_i versus $1/T$, are 73.36, 71.75 KJ/mol, respectively. The result shows that the curing reaction does not obey an nth-order mechanism.

Typical comparisons between the experimental DSC data and the autocatalytic model with previously determined parameters are shown in Figure 4. At early stages of cure, before gelation and vitrification, the reaction takes place in the liquid phase and is controlled by chemical kinetics. So, the kinetic behavior described by this model coincides with the experimental data. As the reaction progresses, a deviation appears 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 by kinetic factors [17]. Differences between model predictions and experimental data were observed to be greater when the curing temperature decreases under the same conversion. This can be interpreted by free volume consideration [18]. The free volume of materials decreased with temperature, then the rate of diffusion of reactive groups reduced, leading to 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 [18]. In this relationship, diffusion factor, $f(\alpha)$, was defined by two empirical parameters as follows:

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

where C is the diffusion coefficient and α_c is the critical conversion depending on the curing temperature. The plots of $f(\alpha)$ versus conversion α at different curing temperatures are shown in Figure 5. For $\alpha << \alpha_c, f(\alpha)$ approximately equals unity and the effect of diffusion

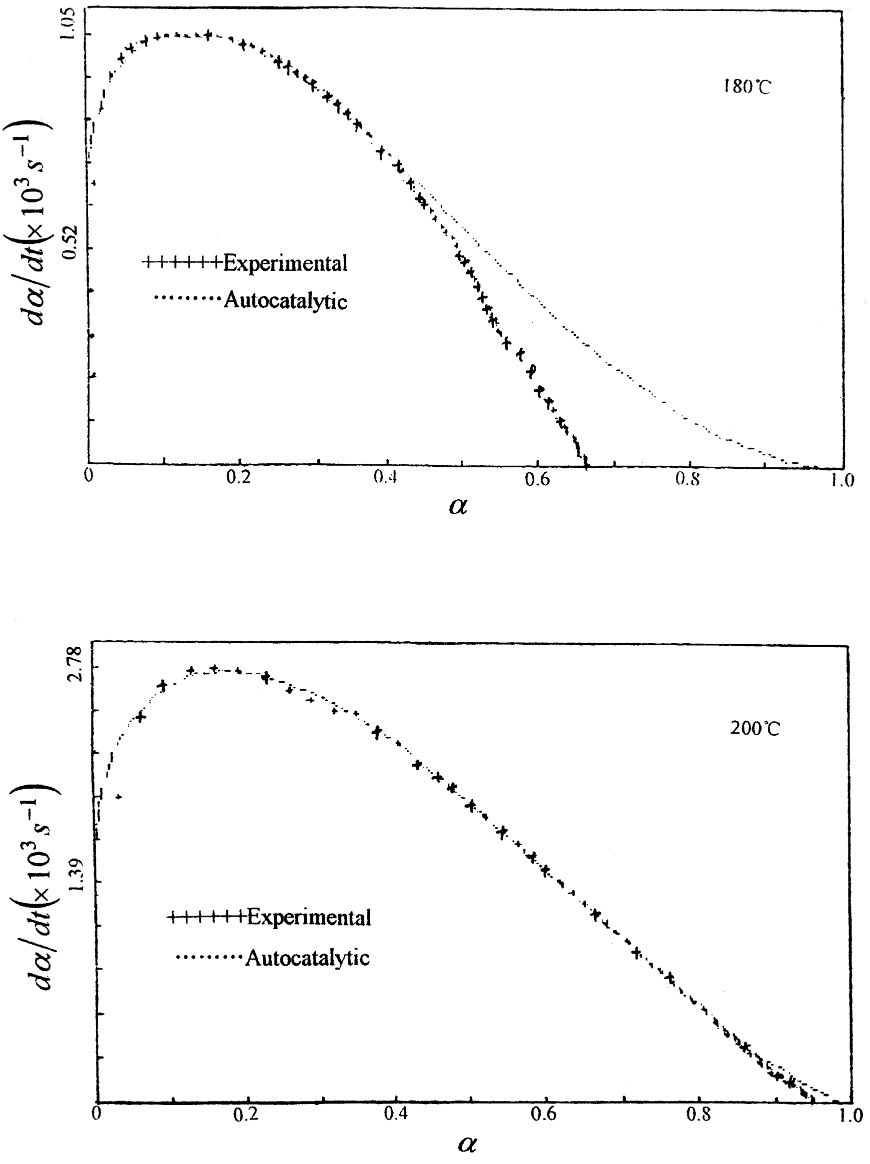


FIGURE 4 Comparison of experimental data with theoretical values calculated from equation (3). Reaction rate, $d\alpha/dt$, versus conversion, α, at 180 and 200°C.

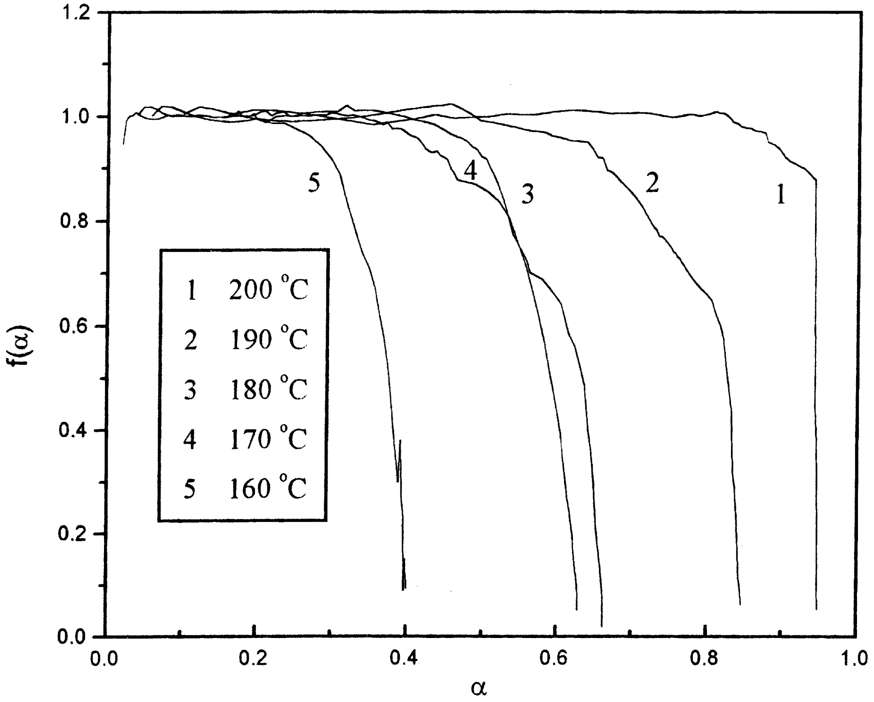


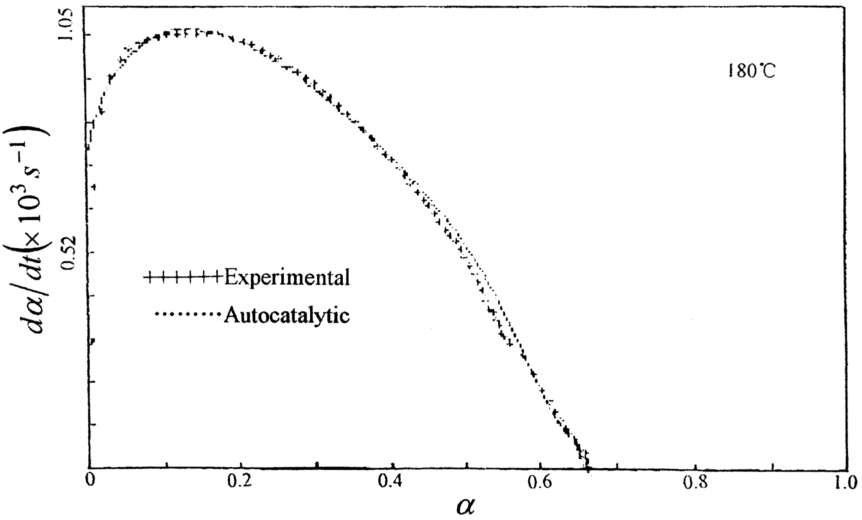
FIGURE 5 Plot of diffusion factor, $f(\alpha)$, versus conversion, α, at different curing temperatures.

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.

Considering the diffusion effect, the reaction rate of cure can be expressed in the following form to account for the effects of diffusion.

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

Figure 6 shows the comparison between experimental values and those obtained from equation (7). The calculated values agree very well with experimental data. Thus, we employ the proposed generalized kinetic model to predict and describe the advance of our epoxy resin systems as a function of the curing temperature.



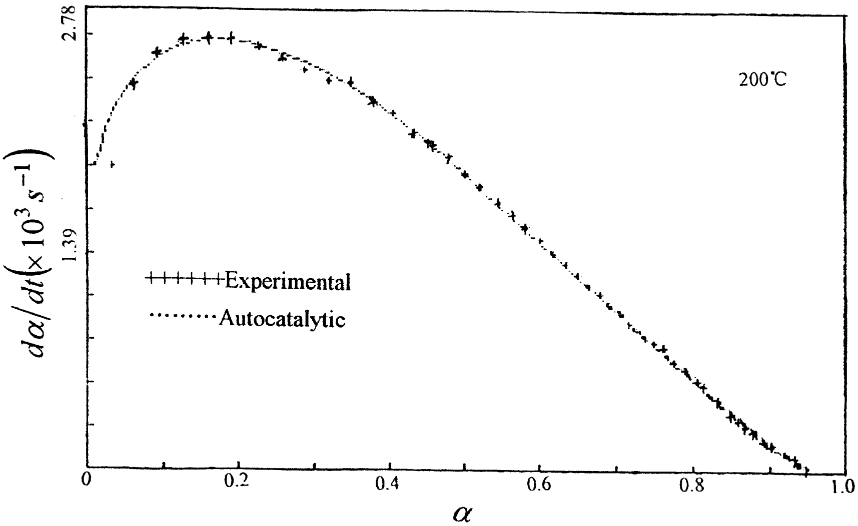


FIGURE 6 Comparison of experimental data with theoretical values calculated from equation (7). Reaction rate, $d\alpha/dt$, versus conversion α, at 180 and 200°C.

T_g Value and the Curing Process

T_g has been used directly as a parameter for conversion in analysis of reaction kinetic models [19], and there is a one-to-one relationship between the T_g and the degree of cure. It is a convenient parameter because of the ease of measurement of T_g by TBA, and is particularly useful at high conversion and after vitrification because of the non-linearity of T_g versus conversion reaction [20]. Figure 7 shows plot of T_g versus curing time. As seen from Figure 7, different glass transition behaviors occurred for the samples with different temperature of cure. The highest T_g is 406.2 K.

At low T_cs, as observed, T_g increases during the early stages of cure. Then levels off and remains at a lower temperature value compared with higher T_cs. Even if we prolong the curing time under low T_cS, it is difficult for the resin system to reach high conversion. Because the process of vitrification usually drastically lowers the reaction rate,

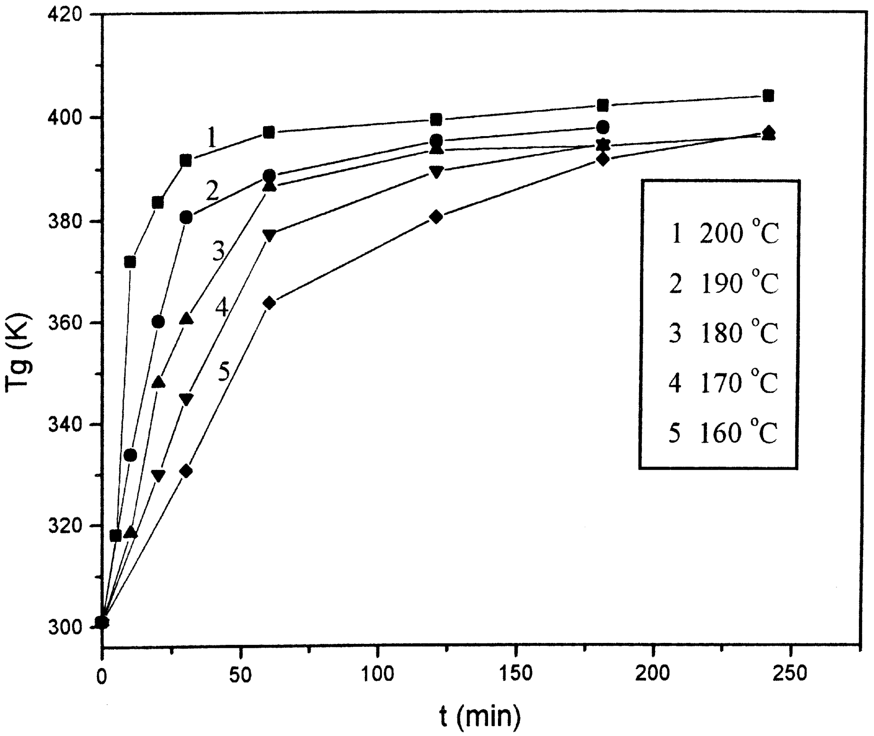


FIGURE 7 T_g values of the BPFER/DDS cured isothermally at different temperatures for various periods.

complete cure usually involves temperatures in the vicinity of the maximum of glass transition temperature. This is indicative of autocatalytic kinetics in the first stage and diffusion-controlled reaction as the T_g rises [21]. Similar results have been obtained based on our study of conversion or reaction rate versus time at different isothermal cure temperature.

At the beginning of the curing reaction process, the degree of cure is low, and the sample gives low T_g value. At this stage, the process is characterized by a gradual increase in molecular weight, and this transition behavior reflects the movement of linear molecular chain in the system. Since 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 as their mobility is very limited, the curing reaction becomes diffusion-controlled. The crosslinking density increases with the reaction time, 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 gets higher.

Thermal Degradation

The TGA trace of DDS-cured BPFER revealed two degradation steps in an air atmosphere. The following kinetic equation was assumed to hold for this reaction [21].

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

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 the plots of ln $(C/T^{1.92})$ verse $1/T$, and the value in first and second stage was 51.3, 136.3 $\mathrm{KJ{\cdot}mol^{-1}}$, respectively. The degradation activation energy in the second stage is much higher than that in the first stage, illustrating that the breaking of strong bonds takes place in the second stage, while weak bonds were broken in the first stage.

CONCLUSIONS

1. The cure reaction for the system of BPFER/DDS system is shown to have autocatalytic behavior in the kinetically controlled stage,

and can be well described by 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 whole cure reaction of this epoxy resin. The theoretical values agree very well with the experimental data.

2. T_gs were investigated for BPFER/DDS samples cured partially. The curing reaction process and the thermal property of BPFER/DDS are discussed. The results show that the T_gs increase with the conversion up to a constant value. The highest T_g is 406.2 K.
3. TGA trace of this system revealed two decomposition stages. The activation energy of thermal degradation in the first and second stage was 51.3, 136.3 KJ·mol^{-1}.

REFERENCES

[1] Louis, B., Bo, P., Sonva, J. and Jan-Anders, M. (1995). *Proc. Int. Conf. Compos. Mater.* **6**: 389.
[2] Hideo, H., Akihiro, I. *Jpn. Kokai Tokkyo Koho JP* **11**, 116, 662.
[3] Toshiaki, O. *Jpn. Kokai Tokkyo Koho JP* **07**, 292, 072.
[4] Ivo, W., Ludmila, W., Vaclav, B., Ludek, K., Vladimer, M., Pravoslav, M., Antonin, R. *Czech Rep CZ* **280**, 402.
[5] Kasen, M., Santoys, R. (1995). *Cryogenics* **35**: 731.
[6] Rainer, E., Udo, G., Heinrich, H. W. and Eruin, B. (1985). *Ger. Pat. DD228*, 279.
[7] Jay, R. R. (1964). *Anal. Chem.* **36**: 665.
[8] Opalicki, M., Kenny, J. M. and Nicolais, L. (1996). *J. Appl. Polym. Sci.* **61**: 1025.
[9] Liu, Z. H. (1991). *Thermoanalysis Introduction*, Beijing, Chemical Industry Publishing Co.
[10] Kamal, M. R. (1974). *Polym. Eng. Sci.* **14**: 23.
[11] Woo, E. M. and Seferis, J. C. (1990). *J. Appl. Polym. Sci.* **40**: 1237.
[12] Ghaemy, M. and Riahy, M. H. (1996). *Eur. Polym. J.* **32**: 1207.
[13] Keenan, M. R. (1987). *J. Appl. Polym. Sci.* **33**: 1725.
[14] Barton, J. M. (1985). *Adv. Polym. Sci.* **72**: 111.
[15] Ryan, M. E., Dutta, A. (1979). *Polymer* **20**: 203.
[16] Moroni, A., Mijiovic, J., Pearce, E. M. and Foun, C. C. (1986). *J. Appl. Polym. Sci.* **32**: 3761.
[17] Cole, K. C., Hechler, J. J. and Noel, D. (1991). *Macromolecules* **24**: 3098.
[18] Chern, C. S. and Poehlein, G. W. (1987). *Polym. Eng. Sci.* **27**: 782.
[19] Simon, S. L. and Gillham, J. K. (1993). *J. Appl. Polym. Sci.* **47**: 461.
[20] Venditti, R. A. and Gillham, J. K. (1997). *J. Appl. Polym. Sci.* **64**: 3.
[21] Madhusudanan, P. M., Krishnan, K., Ninan, K. N. (1986). *Thermochem Acta* **97**: 189.