Isothermal Cure Kinetics of a Diglycidyl Ether of Bisphenol A/1,3-Bisaminomethylcyclohexane (DGEBA/1,3-BAC) Epoxy Resin System

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SYNOPSIS

By employing differential scanning calorimetry, DSC, we have studied, under isothermal conditions, the kinetics of the cure reaction for a system containing a diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as a curing agent, over the temperature range of 60–110°C. We have determined the conversions reached at several cure temperatures and the reaction rates. The experimental data, showing an autocatalytic behavior, were compared with the model proposed by Kamal, which includes two rate constants, k_1 and k_2, and two reaction orders, m and n. This model gives a good description of cure kinetics up to the onset of vitrification. The activation energies for these rate constants were 44–57 kJ/mol. The reaction orders present a moderate change but their sum is in the range 2.5–3. Diffusion control is incorporated to describe the cure in the latter stages (postvitrification region). By combining the autocatalytic model and a diffusion factor, it was possible to predict the cure kinetics over the whole range of conversion. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The properties of a thermosetting polymer depend on the extent of reaction. The understanding of the mechanism and kinetics of cure is essential for a better knowledge of structure–property relationships and for the usage of these materials as structural adhesives, coatings, and as matrices in fiber-reinforced composites.

Curing kinetic models are generally developed by analyzing experimental results obtained by different thermal analysis techniques. Differential scanning calorimetry, DSC, both in the isothermal and dynamic mode, has been used extensively, assuming a proportionality between the heat evolved during the cure and the extent of reaction.

In general, the curing reactions show complex kinetics characterized by an initial acceleration due to autocatalysis, while the later stages may exhibit retardation due to the onset of gelation. As cure proceeds and the resin crosslinks, the glass transition temperature, T_g, of the curing resin increases. For cure temperatures well above T_g, the rate of reaction between the epoxy and hardener reactive groups is chemically kinetically controlled. When T_g approaches the curing temperature, the resin passes from a rubbery state to a glassy state and the curing reactions become diffusion controlled, and will eventually become very slow and finally stop.[1]

In this study, the cure kinetics of an epoxy system containing diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as curing agent were investigated by differential scanning calorimetry under the isothermal mode. This work was part of a larger study of the curing characteristics and structure–property relationships of the DGEBA/1,3-BAC epoxy system.[2] The objective of this part is concerned with an accurate description of the kinetics of cure
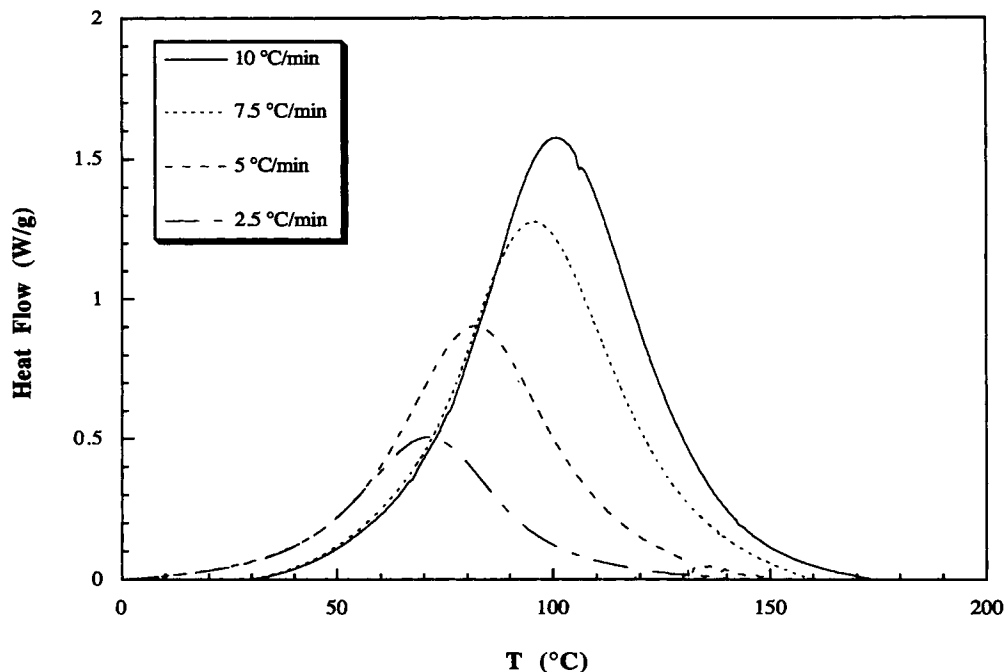
Figure 1   DSC thermograms in the dynamic mode at different heating rates.

not only in the first stages of cure reaction but also in the later stages where the vitrification effect is dominant and the reaction is controlled by diffusion instead of chemical kinetics.

EXPERIMENTAL

The epoxy resin used was a diglycidyl ether of bisphenol A (DGEBA), Shell Epikote 828, and the cur-
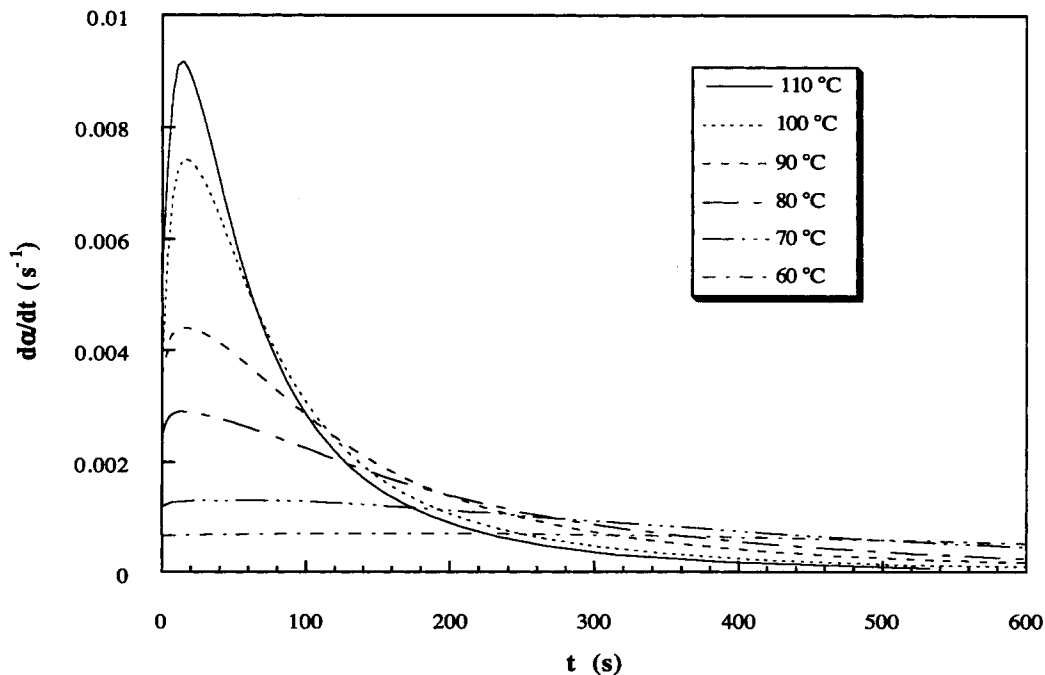

Figure 2   Reaction rate, $d\alpha/dt$, vs. time curves for different curing temperatures.
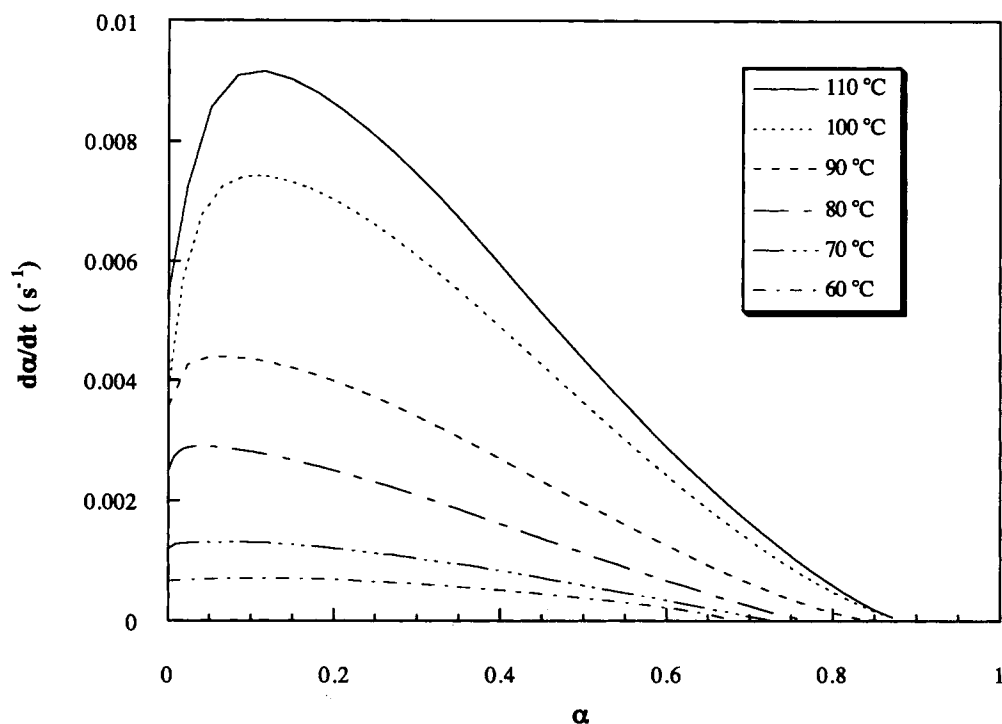
Figure 3 Reaction rate, $d\alpha/dt$, vs. conversion, α, curves at different temperatures.

ing agent was 1,3-bisaminomethylcyclohexane (1,3-BAC), manufactured by Mitsubishi Gas Chemical Co. Both components were commercial products, and were used as received without purification. The stoichiometric ratio amine/epoxy is 1. Formulation is 100 g DGEBA for 18.5 g 1,3-BAC. The mixture

was stirred at room temperature, and samples of about 5–6 mg weight were enclosed in aluminum capsules. DSC measurements were performed with a Perkin Elmer DSC-7 supported by a Perkin Elmer Computer for data acquisition. The DSC was calibrated with high-purity indium.
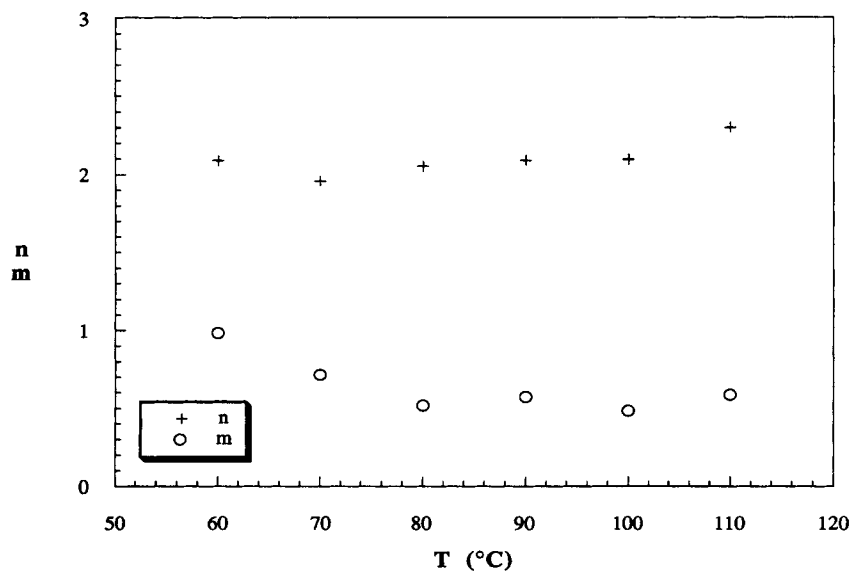

Figure 4 Estimated values of m and n at different curing temperatures.
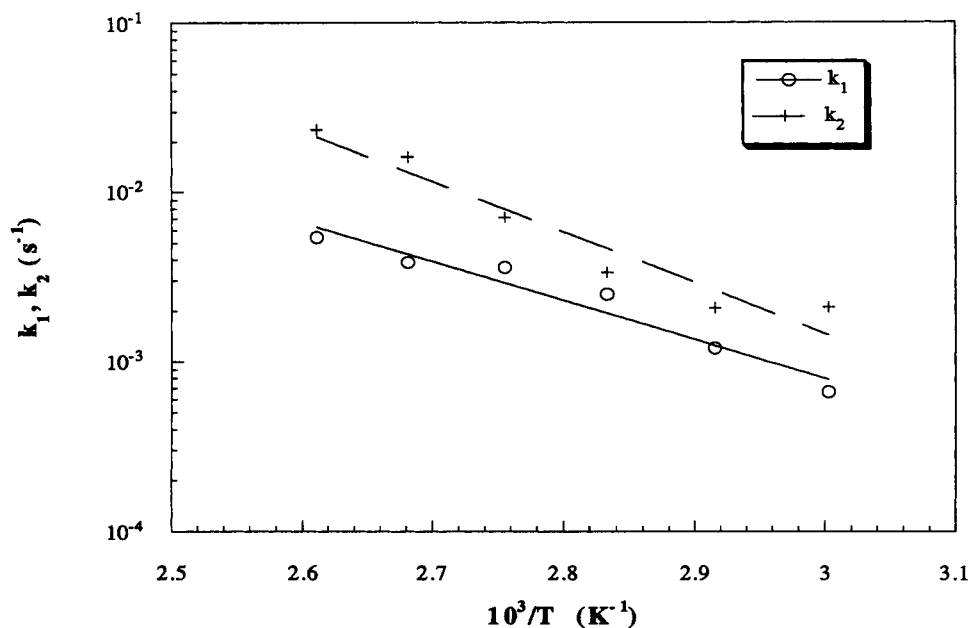
Figure 5 Arrhenius plot of rate constants, k_1 and k_2.

Isothermal and dynamic-heating experiments were conducted under a nitrogen flow of 40 mL/min. For dynamic heating experiments, four different heating rates were investigated: 2.5, 5, 7.5, and 10°C/min from −10°C to 200°C. In isothermal experiments, the DSC was stabilized to −10°C, then the sample pan was placed in the DSC cell and heated at high rate to the experimental temperature, ranging from 60 to 110°C with a 10°C temperature increment.

RESULTS AND DISCUSSION

If the cure reaction is the only thermal event, then the reaction rate $d\alpha/dt$ is equal to the heat flow, dH/dt, divided by the overall heat of reaction ΔH_0

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \qquad (1)$$
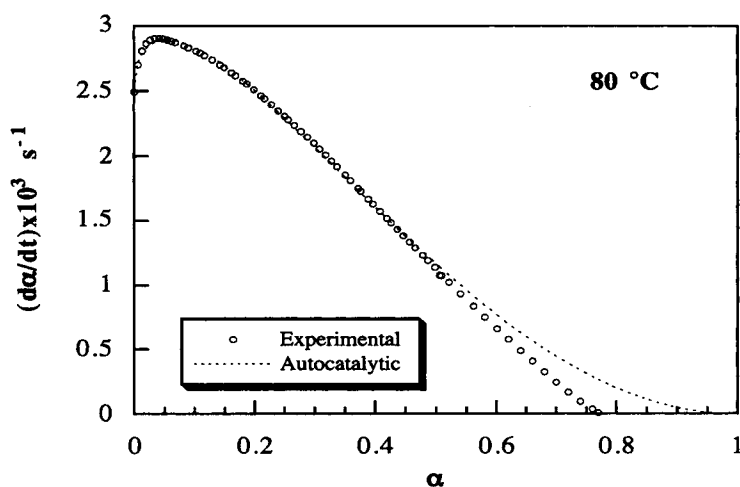
Figure 1 shows the DSC dynamic scans at differ-

Figure 6 Comparisons of experimental data with autocatalytic model: reaction rate, $d\alpha/dt$, vs. conversion, α.
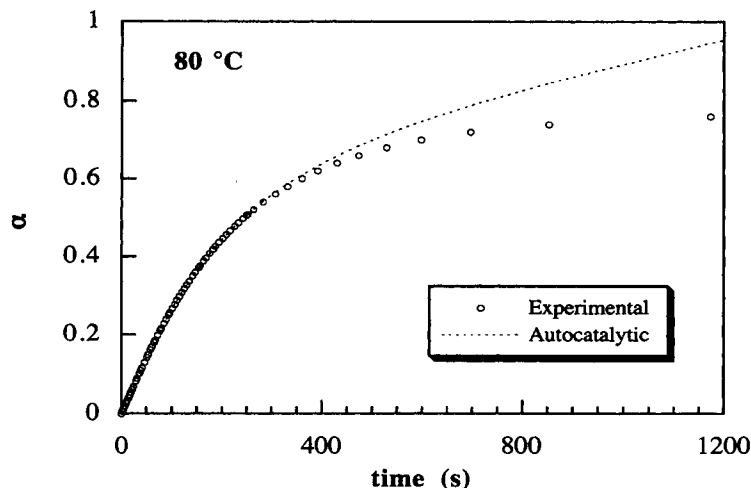
Figure 7 Comparisons of experimental data with autocatalytic model: conversion, a, vs. time.

ent heating rates. The overall heat evolved in the reaction has been determined as the average value of reaction heats calculated in each thermogram. The corresponding value found for the DGEBA/1,3-BAC system was $\Delta H_0 = 495.5$ J/g.

Isothermal DSC curves are shown in Figure 2, plotted as da/dt vs. time.

If one assumes that the extent of reaction, a, is proportional to the heat generated during reaction, the reaction rate can be expressed as a function of conversion and temperature:

$$\frac{da}{dt} = k(T)f(a) \qquad (2)$$

where $k(T)$ is the Arrhenius rate constant and $f(a)$ is a function that depends on the reaction mechanism.

Different models have been developed to describe the cure reactions of thermosets.[3] The so-called autocatalytic model proposed by Kamal[4]

$$\frac{da}{dt} = (k_1 + k_2 a^m)(1 - a)^n \qquad (3)$$

has been applied in this work, where k_1 and k_2 are reaction rate constants with two different activation energies and preexponential factors; m and n, reaction orders, and, $m + n$, the overall reaction order. Equation (3) embodies the experimental observations (Fig. 2) that the peak in the exotherms occurs at some $t > 0$, and that the rate of reaction at $t = 0$ is not zero and has found successful application for similar epoxy systems.[3]

To compute Eq. (3) parameters from experimental data, several methods have been proposed in the literature;[5-8] in many of them it was assumed that the total reaction order was 2, $m + n = 2$, restraining the range of application of the proposed model.

In the present study, the parameters m, n, k_1, and k_2, were estimated without any constraints on them by fitting the experimental data shown in Figure 3 to Eq. (3) in the first portion of cure (up to 30–50% of conversion, depending on the curing temperature) using a least squares method. The values of m and n obtained for each curing temperature are shown in Figure 4. The overall reaction order, $m + n$, is in the range 2.5–3 with $n \approx 2$ and m varying from 0.5 to 1. Rate constants k_1 and k_2 are shown as an Arrhenius plot in Figure 5, which yields the values of 44 kJ/mol and 57 kJ/mol for the associated activation energies in agreement with values reported for similar epoxy systems.[9-11] It is observed, however, that correlation for k_1 values (0.9657) is poor compared with that obtained for k_2 (0.9899). This may be attributed to the fact that k_1 is computed only with the two or three first experimental data, which may lead to imprecise calculated values.

Comparisons between typical experimental DSC data and predictions of the autocatalytic model, with values of model parameters determined above, are shown in Figures 6 and 7. Good fits are obtained for the initial stage of reaction. The model, however, predicts higher conversions and reaction rates for the latter stages of the cure reaction. Deviations observed are attributed to the reaction, becoming diffusion controlled at the onset of gelation. Differences between model predictions and experimental data
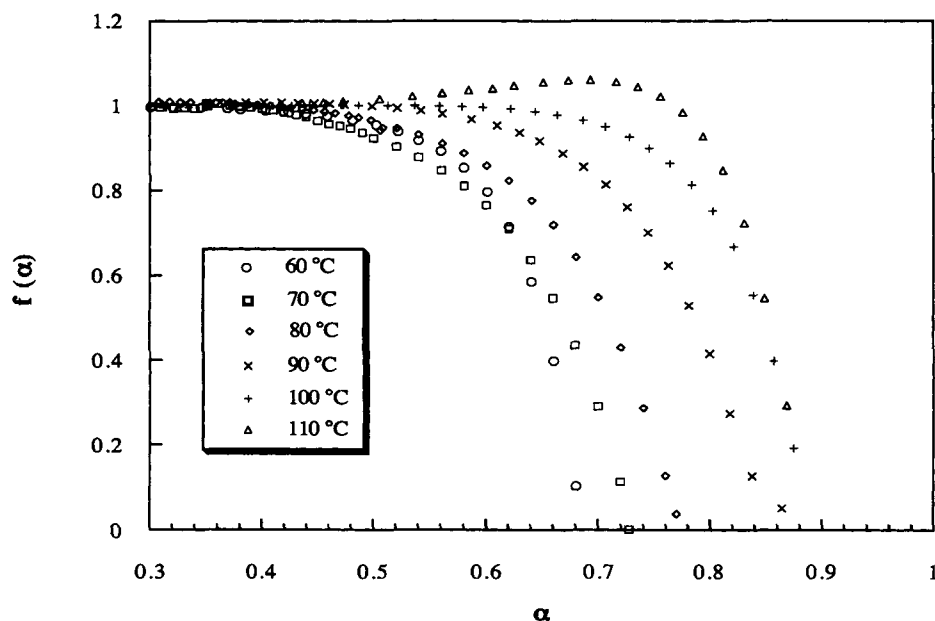
Figure 8 Plot of diffusion factor, $f(a)$, vs. conversion at different curing temperatures.

are observed to be greater when curing temperature decreases.

To consider diffusion effect we have used a semiempirical relationship, based on free volume considerations, proposed by Chern and Poehlein[12] and applied successfully by Khana et al., for a catalyzed epoxy-anhydride system.[13] In this relationship, a diffusion factor, $f(a)$, has been introduced and defined as the ratio, k_e/k_c, k_c being the rate

constant for chemical kinetics and k_e the overall effective rate constant which, according to Rabinowich,[14] includes the effect of both chemical kinetics and diffusion. This diffusion factor is given by

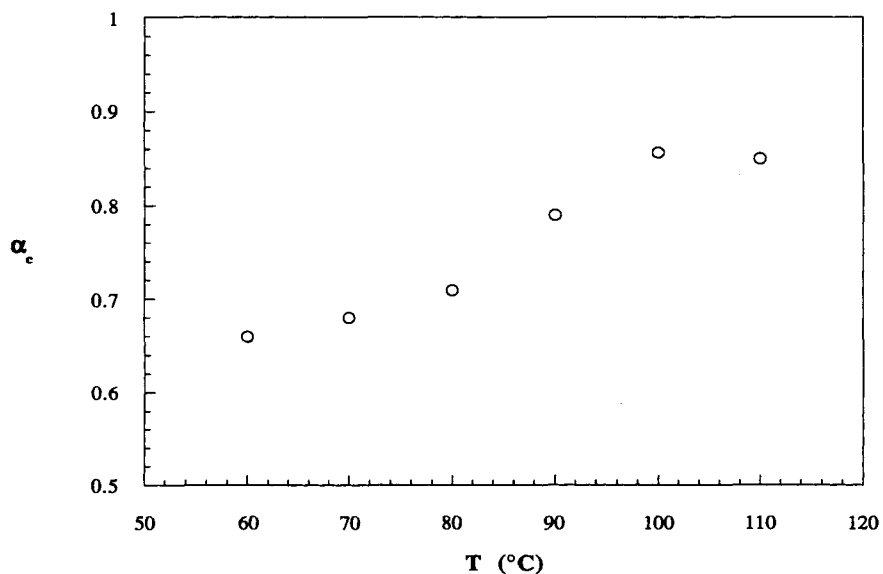$$f(a) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(a - a_c)]} \qquad (4)$$

Figure 9 Values of critical conversion, a_c, vs. curing temperatures.
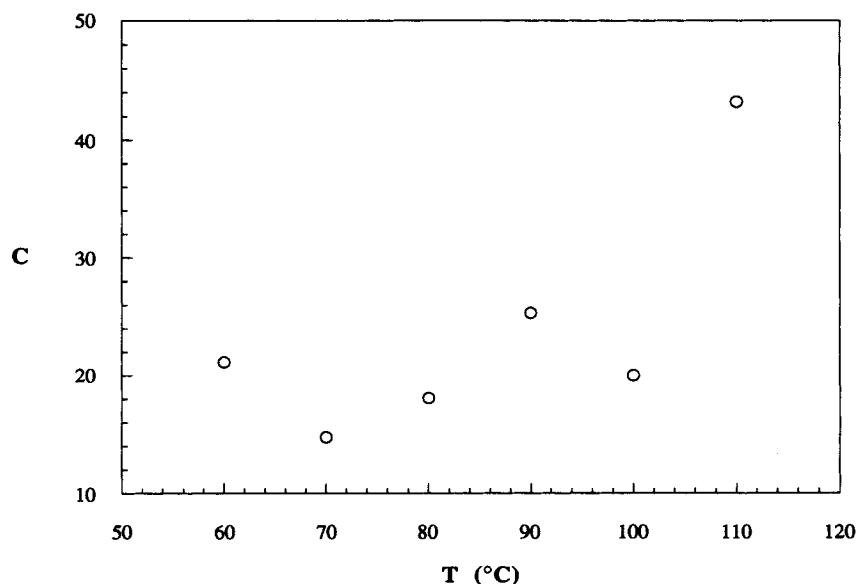
Figure 10   Values of C parameter vs. curing temperatures.

with C and a_c, *the critical conversion*, being two empirical parameters. When a is much smaller than the critical value, $a \ll a_c$, then $f(a)$ approximates unity, the reaction is kinetically controlled, and the effect of diffusion is negligible. As a approaches a_c,

$f(a)$ begins to decrease and approaches zero as the reaction effectively stops. Equation (4) corresponds to a rather abrupt onset of diffusion control at $a = a_c$; however, the onset is more gradual, and there is a region where both chemical and diffusion factors
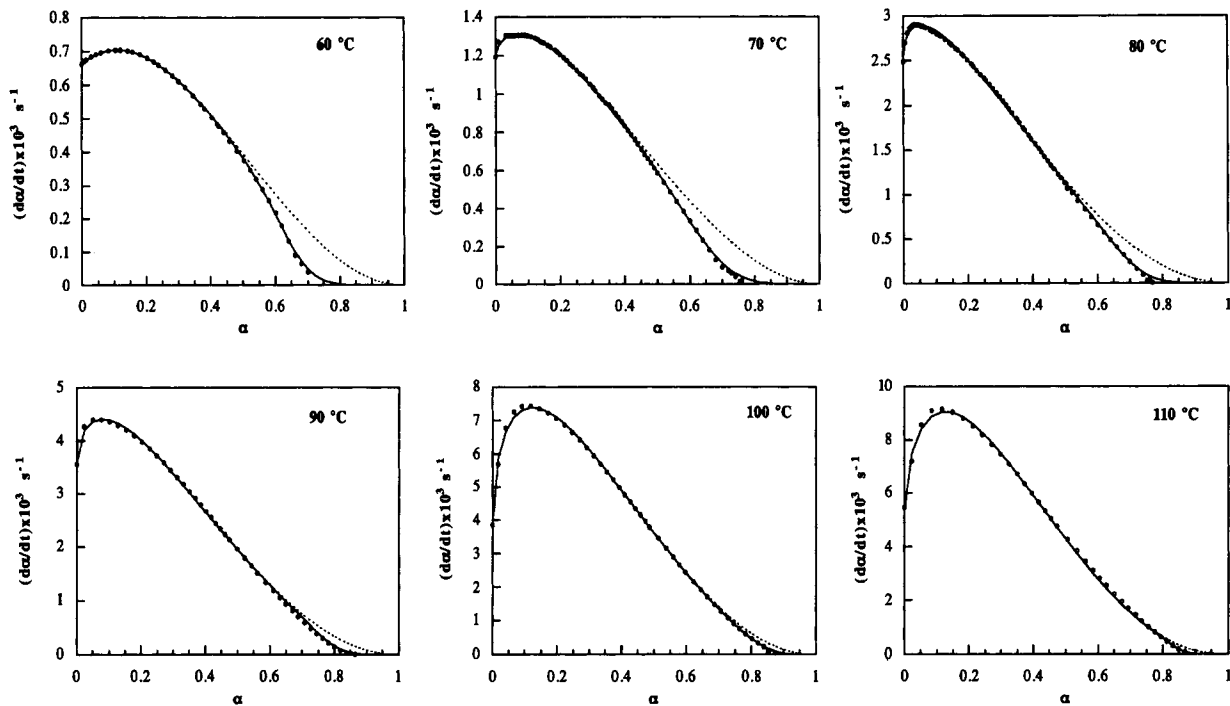

Figure 11   Comparisons of experimental data with model predictions: reaction rate, da/dt, vs. conversion, a, at different temperatures. ($\bigcirc\bigcirc\bigcirc$) experimental, (- - -) autocatalytic model, (—) autocatalytic model with diffusion.
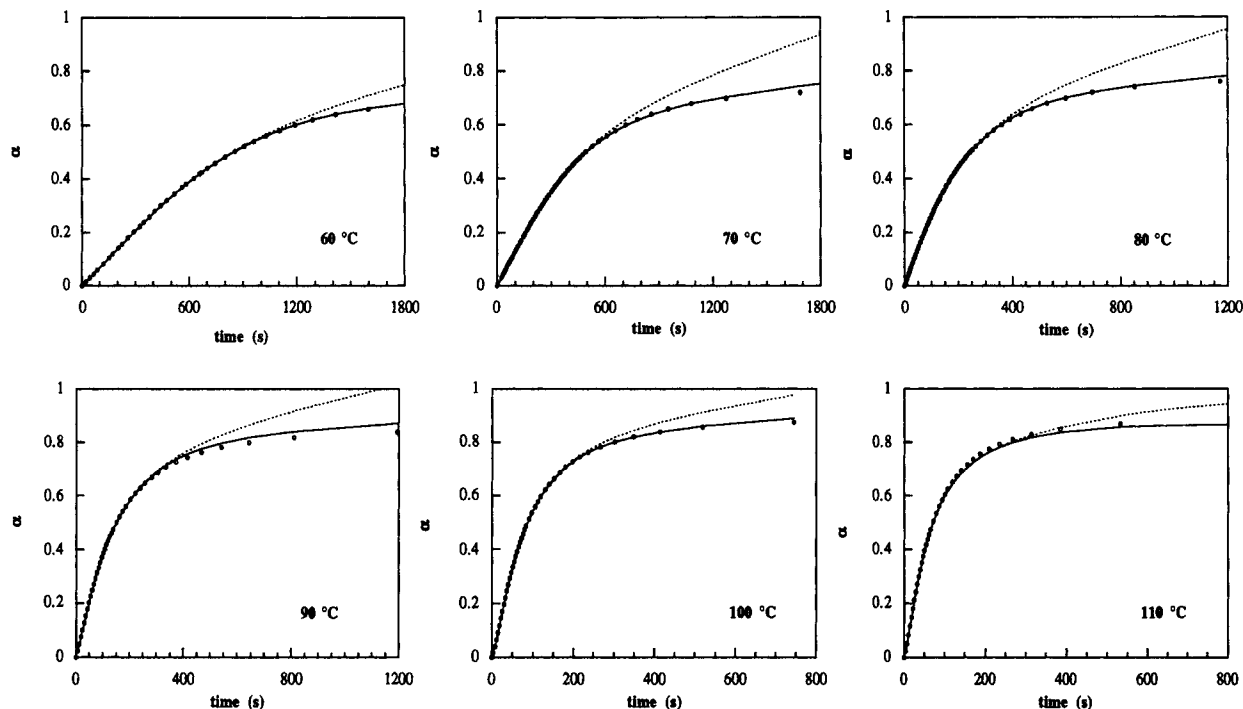
Figure 12   Comparisons of experimental data with model predictions: conversion, a, vs. time, at different temperatures. ($\infty\infty$) experimental, (- - -) autocatalytic model, (—) autocatalytic model with diffusion.

are controlling. The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(a)$.

As in other studies,[13] $f(a)$ was obtained as the ratio of experimental reaction rate to the reaction rate predicted by the autocatalytic model in Eq. (3). Figure 8 shows $f(a)$ vs. conversion at different curing temperatures for DGEBA/1,3-BAC epoxy system, illustrating the behavior commented above.

Values of a_c and C obtained by fitting $f(a)$ vs. a data to Eq. (4) are shown in Figures 9 and 10. An increase in a_c of 29% when increasing temperature from 60 to 110°C is observed, but for the coefficient C, no discernible trend is found, in agreement with the studies of Cole et al. on epoxy-amine systems.[15]

Figures 11 and 12 show the results for each curing temperature where the experimental values of da/dt are compared with those calculated by the autocatalytic model, coupled with the diffusion factor, according to Eq. (4). Excellent agreement was found over the whole curing temperature range.

CONCLUSIONS

A phenomenological kinetic model, successfully applied by other authors,[13] has been used in this work

to describe the cure kinetics of DGEBA/1,3-BAC epoxy system over the whole range of cure.

In the first stages of the cure, where the experimental data show an autocatalytic behavior, the model proposed by Kamal, which includes two reaction orders, m and n, and two rate constants k_1 and k_2, fits the experimental data well up to the vitrification point. k_1 and k_2 show a good Arrhenius fit to temperature yielding values of 44–57 kJ/mol for activation energies. The orders m and n calculated without imposing any constraint, present a moderate change, but the overall reaction order, $m + n$, is in the range 2.5–3, in agreement with values reported.

In order to describe the cure in the latter stages of reaction (postvitrification region) a diffusion factor has been introduced. With the introduction of this factor is possible to fit the experimental data well to the model and calculate with excellent precision the degree of conversion over the whole range of cure temperature.

REFERENCES

1. B. Ellis, *Chemistry and Technology of Epoxy Resins*, Blackie Academic and Professional, UK, 1993.

2. L. Barral, J. Cano, A. J. López, P. Nogueira, and C. Ramírez, *J. Thermal Anal.*, **41**, 1463 (1994).

3. J. M. Barton, in *Advances in Polymer Science, Vol. 72: Epoxy Resins and Composites I*, K. Dusek, Ed., Springer Verlag, Berlin, 1985.

4. M. R. Kamal, *Polym. Eng. Sci.*, **14**, 23, (1974).

5. M. E. Ryan and A. Dutta, *Polymer*, **20**, 203 (1979).

6. A. Moroni, J. Mijovic, E. Pearce, and C. Foun, *J. Appl. Polym. Sci.*, **32**, 3761 (1986).

7. J. M. Kenny, *J. Appl. Polym. Sci.*, **51**, 761 (1994).

8. E. P. Scott and Z. Saad, *Polym. Eng. Sci.*, **33**, 1157 (1993).

9. C. C. Riccardi, H. E. Adabbo, and R. J. J. Williams, *J. Appl. Polym. Sci.*, **29**, 2481 (1984).

10. C. C Riccardi and R. J. J. Williams, *J. Appl. Polym. Sci.*, **32**, 3445 (1986).

11. A. C. Grillet, J. Galy, J. P. Pascault, and I. Bardin, *Polymer*, **30**, 2094 (1989).

12. C. S. Chern and G. W. Poehlein, *Polym. Eng. Sci.*, **27**, 782 (1987).

13. U. Khanna and M. Chanda, *J. Appl. Polym. Sci.*, **49**, 319 (1993).

14. E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

15. K. C. Cole, J. J. Hechler, and D. Noel, *Macromolecules*, **24**, 3098 (1991).