# Effects of Diffusion on the Kinetic Study and TTT Cure Diagram for an Epoxy/Diamine System

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**ABSTRACT:** The curing reactions of an epoxy system consisting of a diglycidyl ether of bisphenol A (BADGE n = 0) and 1,2-diamine cyclohexane (DCH) were studied to determine a time-temperature-transformation (TTT) isothermal cure diagram for this system. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and a solubility test were used to obtain the different experimental data reported. Two models, one based solely on chemical kinetics and the other accounting for diffusion, were used and compared to the experimental data. The inclusion of a diffusion factor in the second model allowed for the cure kinetics to be predicted over the whole range of conversion covering both pre- and post-vitrification stages. The investigation was made in the temperature range  $60-100^{\circ}$ C, which is considered optimum for the isothermal curing of the epoxy system studied. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1931–1938, 1998

Key words: epoxy-amine reactions; TTT diagram; diffusion

# **INTRODUCTION**

Chemical reactions that take place during the cure reaction of thermosets determine the resin morphology, which is a key factor in determining the properties of the cured thermoset. Consequently, understanding of the mechanism and kinetics of cure is very important in the evaluation of processing-morphology-property relationships of the material. In this study, differential scanning calorimetry (DSC) was used to investigate the cure kinetics of the diglycidyl ether of bisphenol A (BADGE n = 0)/1,2-diamine cyclohexane (DCH) resin system. The heat evolution recorded by DSC is assumed to be proportional to the extent of consumption of the epoxide group in the epoxy resin or the amine group in the curing agent.

In a previous article,<sup>1</sup> the kinetics of cure of this same resin system was studied following the model proposed by Horie et al.<sup>2</sup> Reaction-rate experimental data were compared with those predicted by the kinetic model. An excellent agreement was found at 100°C, which worsened with decreasing temperature. The deviations are due to the onset of gelation, which is the transition from viscous liquid to elastic gel, and to the vitrification process, which is the transition from either a viscous liquid or elastic gel to a vitrous solid. At these stages, the mobility of the reacting groups is hindered and the reaction rate is controlled by diffusion rather than by chemical factors. Flory<sup>3</sup> predicted the critical conversion,  $\alpha_c$ , for the formation of a three-dimensional crosslinking network to be about 58% for the polycondensation of a bifunctional unit (e.g., BADGE) with an equivalent amount of a tetrafunctional unit (e.g., DCH). This value can be used to calculate the critical fractional free volume at which the curing reaction of thermosets become diffusion-controlled.

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**Figure 1** (a)  $f(\alpha)$  versus  $\alpha$  plot at  $T_c = 100^{\circ}$ C; (b)  $f(\alpha)$  versus  $\alpha$  plot at  $T_c = 90^{\circ}$ C; (c)  $f(\alpha)$  versus  $\alpha$  plot at  $T_c = 80^{\circ}$ C; (d)  $f(\alpha)$  versus  $\alpha$  plot at  $T_c = 70^{\circ}$ C; (e)  $f(\alpha)$  versus  $\alpha$  plot at  $T_c = 60^{\circ}$ C.

At higher values of conversion,  $\alpha$ , a deviation between the experimental values of the reaction rate and the values predicted by the model is observed. The deviations, as discussed previously, are due to gelation and vitrification phenomena. As the cure progresses and the resin crosslinks, the glass transition temperature,  $T_g$ , of the system increases. As  $T_g$  approaches the curing temperature, the resin passes from a rubbery to a glassy state, the mobility of the reacting groups is

$T_c~(^{\circ}\mathrm{C})$	$lpha_c$	$A_{I}$	$ T_c - T_g $ (°C)
100 90 80 70 60	$\begin{array}{c} 0.929 \\ 0.924 \\ 0.891 \\ 0.831 \\ 0.725 \end{array}$	$\begin{array}{c} 43.9 \\ 32.7 \\ 30.7 \\ 7.6 \\ 9.4 \end{array}$	$11.5 \\ 2.7 \\ 5.3 \\ 23.5 \\ 33.5$

Table I Values of Critical Conversion,  $\alpha_{c,}$ and Constant  $A_{I}$  at Various Isothermal Cure Temperatures

restricted, and the reaction becomes diffusion-controlled.

The mathematical treatment of this phenomenon can be followed using a semiempirical relationship based on the free-volume consideration proposed by Chern and Poehlein.<sup>4</sup> This model has been successfully used by Cole et al.<sup>5</sup> and Khanna and Chanda<sup>6</sup> to study the cure reactions of epoxy systems. At early stages of cure, before gelation and vitrification, the reaction takes place in the liquid phase and is controlled by the chemical reactivity of the functional groups. As the reaction progresses, the free volume of the material decreases, and when conversion reaches a critical value,  $\alpha_c$ , the mobility of the reacting species is reduced, leading to diffusional effects. Hence, the critical value,  $\alpha_c$ , would reflect the state of cure of the system rather than the temperature of the cure.

During the curing reactions of epoxy resins, the critical conversion for the onset of diffusion-controlled reactions is taken as the point at which a three-dimensional crosslink network is formed. This seems reasonable since at this point the molecular weight of the reacting system increases dramatically. In this article, the time-temperature-transformation (TTT) cure diagram reported recently<sup>7</sup> for this epoxy system was modified to account for diffusion. The introduction of the diffusion-controlled region modifies the vitrification and isoconversion contours.

#### **EXPERIMENTAL**

#### **Materials**

The epoxy resin was a commercial BADGE (n = 0) (resin 332, Sigma Chemical Co., St. Louis, Missouri, U.S.A.) with an equivalent molecular weight of 173.6 g/eq, as determined by wet analysis.<sup>8,9</sup> The amine was 1,2-diaminecyclohexane (DCH) (Fluka)

with an amine hydrogen equivalent weight of 28.5.<sup>1</sup> Both materials were used as received.

#### Techniques

Differential scanning analysis (DSC) and dynamic mechanical analysis (DMA) were used to study the kinetic mechanisms and to determine a TTT isothermal cure diagram for the epoxy system studied. A Perkin-Elmer DSC-7 unit, under control of a 1020 system controller, was used for the calorimetric measurements. The experiments were carried out in a temperature range from -30to 250°C, which required the use of a cooling device (Intercooler II supplied by Perkin-Elmer) at a heating rate of 10°C/min. The calorimeter was calibrated following the procedure given in the Perkin-Elmer DSC-7 Manual.<sup>10</sup> Two standards, indium and bidistilled water obtained by the Milipore method, were used. The calorimeter was used in both dynamic and isothermal modes to measure the reaction enthalpies and glass transition temperatures.

Dynamic mechanical properties were measured using a Perkin–Elmer DMA-7 using a parallel-plate loading geometry. The DMA was calibrated using indium as a standard. Samples were under a constant dynamic force of 60 mN. The loading frequency was 1 Hz and the experiments were carried out in the temperature range from 30 to 250°C at a heating rate of 10°C/min.

# **RESULTS AND DISCUSSION**

Changes in the free volume taking place during a cure process are related to changes in the reaction rate constants with conversion. Arai and Saito<sup>11</sup> and Marten and Hamielec<sup>12</sup> independently proposed a semiempirical equation for variation of the propagation rate constant for free-radical polymerization. That equation was modified by Chern and Poehlein<sup>4</sup> to take the following form:

$$\frac{K_d}{K_c} = \exp\left[-V^*\left(\frac{1}{V_f} - \frac{1}{V_{fc}}\right)\right]$$
(1)

where  $K_d$  is the constant rate of diffusion at a given conversion;  $K_c$ , the constant rate corresponding to the kinetic chemical-controlled model proposed by Horie et al.<sup>2</sup>;  $V_f$ , the fractional free volume of the reacting system at a given conversion;  $V_{fc}$ , the critical fractional free volume when the three-dimensional crosslinking network is



**Figure 2** (a) Conversion versus time at  $T_c = 100^{\circ}$ C; (b) conversion versus time at  $T_c = 90^{\circ}$ C; (c) conversion versus time at  $T_c = 80^{\circ}$ C; (d) conversion versus time at  $T_c = 70^{\circ}$ C; (e) conversion versus time at  $T_c = 60^{\circ}$ C.

just formed; and  $V^*$ , an adjustable constant which can be regarded as a measure of the degree of diffusion control of the reactions.

Curing reactions of epoxy resins belong to the category of condensation polymerization characterized by the disappearance of the original monomer early in the reaction. Because of that, fractional free volumes cannot be measured during the reaction. For this reason, we used a semiempirical equation to describe the change of fractional free volume,  $V_{f}$ , with the extent of conversion,  $\alpha$ :

$$\frac{V_f^*}{V_f} = A_0 + A_1^{\alpha} + A_2^{\alpha 2} + \dots$$
 (2)

where  $A_0$ ,  $A_1$ , and  $A_2$  are constants that depend on the kind of the epoxy resin used and the isothermical cure temperature. Chern and Poehlein<sup>4</sup> proposed a linear relationship between  $1/V_f$  and  $\alpha$  to study curing reactions of epoxy resins:

$$\frac{V^{*}}{V_{f}} = A_{0} + A_{1}^{\alpha}$$
(3)

Combination of eqs. (3) and (1) gives

$$\frac{K_d}{K_c} = e^{-A_1(\alpha - \alpha_c)} \tag{4}$$

According to Rabinowitch,<sup>13</sup> the overall effective (experimental) rate constants,  $K_e$ , can be expressed in terms of the diffusion rate constant



**Figure 2** (Continued from the previous page)

 $(K_d)$  and the chemical kinetics constant  $(K_c)$  as follows:

$$\frac{1}{K_e} = \frac{1}{K_d} + \frac{1}{K_c} \tag{5}$$

By combining eqs. (4) and (5), a diffusion factor  $f(\alpha)$  that is dependent on the degree of conversion and isothermal curing temperature can be defined as

$$f(\alpha) = \frac{K_e}{K_c} = \frac{1}{1 + \exp[A_1(\alpha - \alpha_c)]}$$
(6)

For  $\alpha \ll \alpha_c$ ,  $f(\alpha)$  tends to unity and the reaction is chemical kinetic-controlled. As  $\alpha$  approaches  $\alpha_c$ , the diffusion factor begins to decrease. When the conversion reaches its critical value,  $\alpha_c$ ,  $f(\alpha) = 0.5$ . For  $\alpha > \alpha_c$ ,  $f(\alpha)$  tends to zero and the reaction rate dramatically decreases and finally stops.

In this study,  $f(\alpha)$  was obtained as the ratio of the experimental reaction rate obtained in a previous article<sup>1</sup> to the reaction rate predicted by the Horie et al.<sup>2</sup> kinetic model which does not account for diffusion. Figure 1(a–e) shows the behavior of  $f(\alpha)$  versus conversion at different isothermal curing temperatures. The observed decrease in  $f(\alpha)$  and, hence, in the effective reaction rate is associated with the onset of diffusion at higher conversions. This decrease can be clearly seen at 100, 90, and 80°C isothermal curing temperatures but is difficult to see at lower temperatures (70 and 60°C). The values of the critical conver-



**Figure 2** (Continued from the previous page)

sion  $(\alpha_c)$  and  $A_1$  obtained by applying nonlinear regression to  $f(\alpha)$  versus  $\alpha$  data are listed in Table I. It can be observed that  $\alpha_c$  decreases by 20% for a 40°C increase in temperature, in good agreement with the data reported by Cole et al.<sup>5</sup> for epoxy-amine systems. On the other hand, for the coefficient  $A_1$ , there is considerable scatter with temperature.<sup>5,6</sup> In the temperature range 80–100°C, the reaction is chemical kinetics-controlled as diffusion begins at high conversions.

Vitrification is defined at the time at which  $T_g = T_c$ .<sup>14</sup> However, vitrification effects may be observed when  $|T_g - T_c| = 20-30$ °C. From the values of  $|T_g - T_c|$  shown in Table I, it could be concluded that in the temperature range 100-80°C in which maximal conversions are achieved the epoxy system has not vitrified. However, at lower curing temperatures (60–70°C), after reaching the critical conversion value, vitrification was achieved.

Using the diffusion factor, the reaction rate can be expressed in the following form to account for effects of diffusion:

$$\frac{d\alpha}{dt} = (K'_1 + K_1^{\alpha m})(1 - \alpha)^n f(\alpha)$$
(7)

This differential equation does not have an analytical solution, and to calculate the degree of conversion, numerical integration of eq. (7) was performed.

Figure 2(a-e) shows values of  $\alpha$  versus t at different temperatures. The experimental results reported in a previous article<sup>1</sup> are compared with those obtained using a chemical kinetics-controlled model and to the results predicted with the inclusion of a diffusion factor into this model. Figure 2(d,e) show that the inclusion of a diffusion factor improves the agreement between experimental and model results at 60 and 70°C, mainly for small times. This may be because at these temperatures most of the conversion is achieved at short times, thus originating a diffusion-controlled mechanism.

# TEMPERATURE-TIME-TRANSFORMATION (TTT) DIAGRAM

Knowledge of the different effects that time and temperature have on the cure reaction of the epoxy system permits the construction of a TTT diagram. In a previous article,<sup>7</sup> a TTT diagram for the BADGE n = 0/1,2-DCH was calculated from the kinetic model without accounting for diffusion. In this study, a new TTT diagram which accounts for diffusion is calculated. With this aim,

Table IIVitrification Time for the Diffusionand the Chemical Kinetics-controlled Modelsat Various Isothermal Cure Temperatures

<i>T</i> (°C)	t (min) (Kinetic Model with Diffusion)	t (min) n-Order Fit Ref. 7
100	35.60	35.51
90	44.70	36.04
80	54.59	48.87
70	99.00	80.28
60	186.00	109.61



Figure 3 TTT diagram.

corrections in the vitrification and isoconversion curves were made.

The empirical DiBenedetto equation<sup>14</sup> has been rewritten in a modified form:

$$\frac{T_g - T_{g_0}}{T_{g_x} - T_{g_0}} = \frac{\lambda \alpha}{1 - (1 - \lambda)\alpha}$$
(8)

where  $T_{g_0}$  is the  $T_g$  of the uncured monomer;  $T_{g_x}$ , the maximum experimental  $T_g$  for the "fully cured" material; and  $\lambda$ , an adjustable structuredependent parameter between 0 and 1. Pascault and Williams<sup>14</sup> showed that  $\lambda$  is theoretically equated to  $\Delta_{p_x}/\Delta C_{p_0}$ , where  $\Delta_{p_x}$  and  $\Delta C_{p_0}$  are the differences in heat capacity between the glassy and rubbery (or liquid, prior to gelation) states at  $T_g$  for the fully cured network and monomer, respectively. For our epoxy system,  $\lambda = 0.165$ ,<sup>7</sup>  $T_{g_0} = -30.1^{\circ}\text{C}$ ,<sup>1</sup> and  $T_{g_{\pi}} = 146^{\circ}\text{C}$ .<sup>1</sup> From the relationship existing between  $T_g$  and  $\alpha$  shown in eq. (8), values of  $T_g$  corresponding to a given  $\alpha$ , which are the values corresponding to points where vitrification and isoconversion curves intersect, were obtained. By numerical integration of eq. (7), the corresponding cure times could be calculated.

The TTT isothermal cure diagram was calculated by plotting gelation and vitrification times at each cure temperature. Isoconversion contours at given values of  $\alpha$  were also recorded. The gelation curve was calculated using the value  $\alpha = 0.58$ predicted by Flory's theory and taking into account that gelation and vitrification curves intersect at a cure time corresponding to the value of  $_{\rm gel}T_g$  calculated using the DiBenedetto equation. Table II shows values for vitrification times calculated by numerical integration of the diffusioncontrolled model and those obtained for the chemical kinetics-controlled model by fitting n-order functions to the  $T_g$  versus  $\ln t$  curves corresponding to different isothermal cure temperatures.<sup>7</sup> As can be seen, these values agree at higher temperatures (100-90°C) at which high conversion values were achieved. The concordance worsened at low-temperature values (70-90°C) due to diffusion effects, and a large deviation was observed at 60°C.

Gelation times for this epoxy system were measured in our laboratories using DMA and solubility testing.<sup>1</sup> Figure 3 shows isothermal contours parallel to the gelation and vitrification curves. This TTT diagram gives information about the values of  $T_g$ , and thus conversion, along the whole cure process. The different transformations exhibited by the epoxy system (liquid, elastomer sol/gel, elastomer gel, vitrous gel, and vitrous sol) can be followed by analysis of the TTT diagram.

### CONCLUSIONS

The cure of a BADGE (n = 0)/DCH system was studied. A kinetic model which accounts for diffu-

sional effects was used. Plots of the diffusion factor  $f(\alpha)$  versus conversion  $\alpha$  at different cure temperatures show a good agreement between experimental and predicted results at 100°C, which was found to be the optimum cure temperature. This agreement worsened with decreasing temperatures. However, the concordance between experimental and predicted results improves with respect to the chemical kinetics-controlled model which does not account for diffusion.

A TTT isothermal cure diagram for the epoxy system was calculated using a kinetic model which accounts for diffusion. The isoconversion contours slightly deviate from those calculated in a previous article<sup>7</sup> for a chemical-controlled model. However, at low temperatures and conversions, deviations from both models are significant.

# REFERENCES

- L. Núñez, F. Fraga, L. Fraga, and A. Castro, J. Appl. Polym. Sci., 63, 635 (1997).
- K. Horie, H. Hiura, M. Sawad, I. Mita, and H. Kambe, J. Polym. Sci., 8, 1357 (1970).
- P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, p. 348.
- C. S. Chern and G. W. Poehleim, *Polym. Eng. Sci.*, 27, 788 (1987).
- K. C. Cole, J. J. Hechler, and D. Noël, *Macromolecules*, 24, 3098 (1991).
- U. Khanna and M. Chandas, J. Appl. Polym. Sci., 49, 319 (1993).
- L. Núñez, J. Taboada, F. Fraga, and M. R. Núñez, J. Appl. Polym. Sci., 66, 1377 (1997).
- H. Lee and K. Neville, Handbook of Epoxy Resin, McGraw-Hill, New York, 1967.
- 9. C. A. May, *Epoxy Resins: Chemistry and Technology*, Marcel Dekker, New York, 1988.
- Users Manual 1020 Series DSC-7 Thermal Analysis System, Perkin–Elmer Corp., 1991.
- K. Arai and S. Saito, J. Chem. Eng. Jpn., 9, 302 (1976).
- F. L. Marten and A. E. Hamielec, Am. Chem. Soc. Symp. Ser., 104, 43 (1978).
- E. Rabinowitch, Trans. Faraday Soc., 33, 1225 (1937).
- J. P. Pascault and R. J. J. Williams, J. Polym. Sci. Polym. Phys., 28, 85 (1990).