

Effects of Diffusion on the Kinetic Study of the System BADGE $n=0$ / m -Xylylenediamine

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ABSTRACT: The curing reactions of an epoxy system composed of a diglycidyl ether of bisphenol A (BADGE $n=0$) and m -xylylenediamine (m-XDA) were studied. Two models, the first based solely on chemical kinetics and the second accounting for diffusion, were used and compared to the experimental data. The epoxy resin was used as received in a first series of experiments. In a second series of experiments, the resin was purified *in vacuo* (180°C and 1 mmHg). 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 postvitrification stages. The investigation was made in the temperature range 50–110°C, which is considered optimum for the isothermal curing of the epoxy system studied. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2997–3005, 1999

Key words: epoxy resin; DSC; diffusion; BADGE $n=0$; m-XDA

INTRODUCTION

Properties of a cured thermoset strongly depend on the chemical reactions that take place during the cure process. The understanding of the mechanism and kinetics of cure provides essential information in the process of evaluating processing–morphology–property relationships in thermosets.

The kinetics of cure of an epoxy system consisting of a diglycidyl ether of bisphenol A (BADGE $n=0$) and m -xylylenediamine (m-XDA) as a curing agent has been studied by DSC and FTIR. In a previous investigation,¹ the system was studied at stoichiometric ratio. In a first series of experiments the resin was used as received, whereas in a second series the resin was purified by distillation *in vacuo*. A second study² was done using the same epoxy system at nonstoichiometric proportion. The kinetics of cure was studied following

the model proposed by Horie et al.³ Reaction rate experimental data were compared with values determined from the kinetic model. Good agreement was found at 110°C, which worsened with decreasing temperatures. The deviations between theoretical and experimental results are due to the onset of gelation, which is the transition from either viscous liquid or elastic gel to vitreous solid, in which a gradual decrease in the reaction and a dramatic increase of the viscosity are observed. According to Flory,⁴ the critical conversion α_c for the formation of a three-dimensional crosslinking network is about 58% for the polycondensation of a difunctional monomer (e.g., epoxy) with an equivalent amount of a tetrafunctional unit (e.g., primary diamine). This value can be used to calculate the critical fractional free volume at which the curing reaction of thermosets becomes diffusion controlled. A semiempirical model proposed by Chern and Poehlein⁵ was used to study the diffusion-controlled reaction rate.

This model, based on free volume considerations, has been successfully used by Cole et al.⁶ and Khanna and Chanda⁷ to study cure reactions of epoxy materials. At early stages of cure, before

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Table I Values of Critical Conversion α_c and Constant A_1 at Various Isothermal Cure Temperatures

Temperature (°C)	Commercial Resin		Purified Resin	
	α_c	A_1	α_c	A_1
110	0.948	22.7	0.961	38.8
100	0.918	16.3	0.946	39.0
90	0.881	21.3	0.910	22.2
80	0.877	36.6	0.874	26.5
70	0.819	28.8	0.829	47.3
60	0.796	44.1	0.811	47.4
50	0.716	34.3	0.718	27.4

gelation and vitrification, the reaction takes place in the liquid phase and is controlled by chemical kinetics. As the reaction progresses, the free volume of the material dramatically reduces and when conversion reaches a critical value α_c , the mobilities of the reaction species are seriously restricted, such that the curing reactions become diffusion controlled. During the curing reaction of epoxy resins, the critical conversion is taken as the point at which a three-dimensional network is formed. This seems reasonable, since at this point the molecular weight of the reacting system drastically increases and the viscosity shows a significant increase.

EXPERIMENTAL

Materials

The epoxy resin used was a commercial diglycidyl ether of bisphenol A (BADGE $n=0$; Epikote 828 from S.P.E. Shell) and *m*-xylylenediamine (*m*-XDA; Aldrich Chemical Co. (Milwaukee, WI, USA), 99% pure) the curing agent.

Two series of experiments were carried out. In the first series, the materials were used as received. The molecular weight of the resin was 180 g/eq. In a second series, the resin was purified by distillation *in vacuo* (180°C and 1 mmHg) followed by repeated crystallization from methanol. The equivalent molecular weight of the purified resin was 172 g/eq, as determined by wet analysis.^{8,9}

Techniques

Differential scanning calorimetry (DSC) was used to study the kinetics mechanism and to determine

experimental data. The calorimeter was a Perkin-Elmer DSC-7 unit, under control of a 1020 system controller. The experiments were carried out in a temperature range from -30 to 250°C at a heating rate of $10^\circ\text{C}/\text{min}$. Because of the low temperature necessary for the performance of measurements, a cooling device (Intercooler II supplied by P.E.) was adapted to the DSC-7 equipment. The calorimeter was calibrated following the procedure given in the P.E. DSC7 Manual.¹⁰ Two standards, indium and bidistilled water obtained by the Millipore Method, were used. The calorimeter was used in both dynamic and isothermal modes to measure glass transition temperatures and reaction enthalpies.

RESULTS AND DISCUSSION

Changes in the volume taking place in the cure reaction of an epoxy system are related to changes in the reaction rate constants with conversion. Arai and Saito¹¹ and Marten and Hamielec¹² proposed a semiempirical equation for variations of the propagation rate constant for free radical polymerization. That equation was modified by Chern and Poehlein⁵ to take the following form

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

where K_d is the diffusion constant rate at a given conversion; K_c is the chemical reaction controlled rate constant according to the model proposed by Horie et al.³; V_f is the fractional free volume of the reaction system at a given conversion; V_{fc} is the fractional free volume at a critical conversion; and V^* is an adjustable constant, which depends on the degree of diffusion control of the reactions.

The curing reactions of epoxy resins belong to the category of condensation polymerization, characterized by the disappearance of the original monomer early in the reaction. For this reason, fractional free volumes cannot be measured during the curing reaction. Because of that, changes of free volume were determined using a semiempirical equation that relates fractional free volume with the extent of conversion α :

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

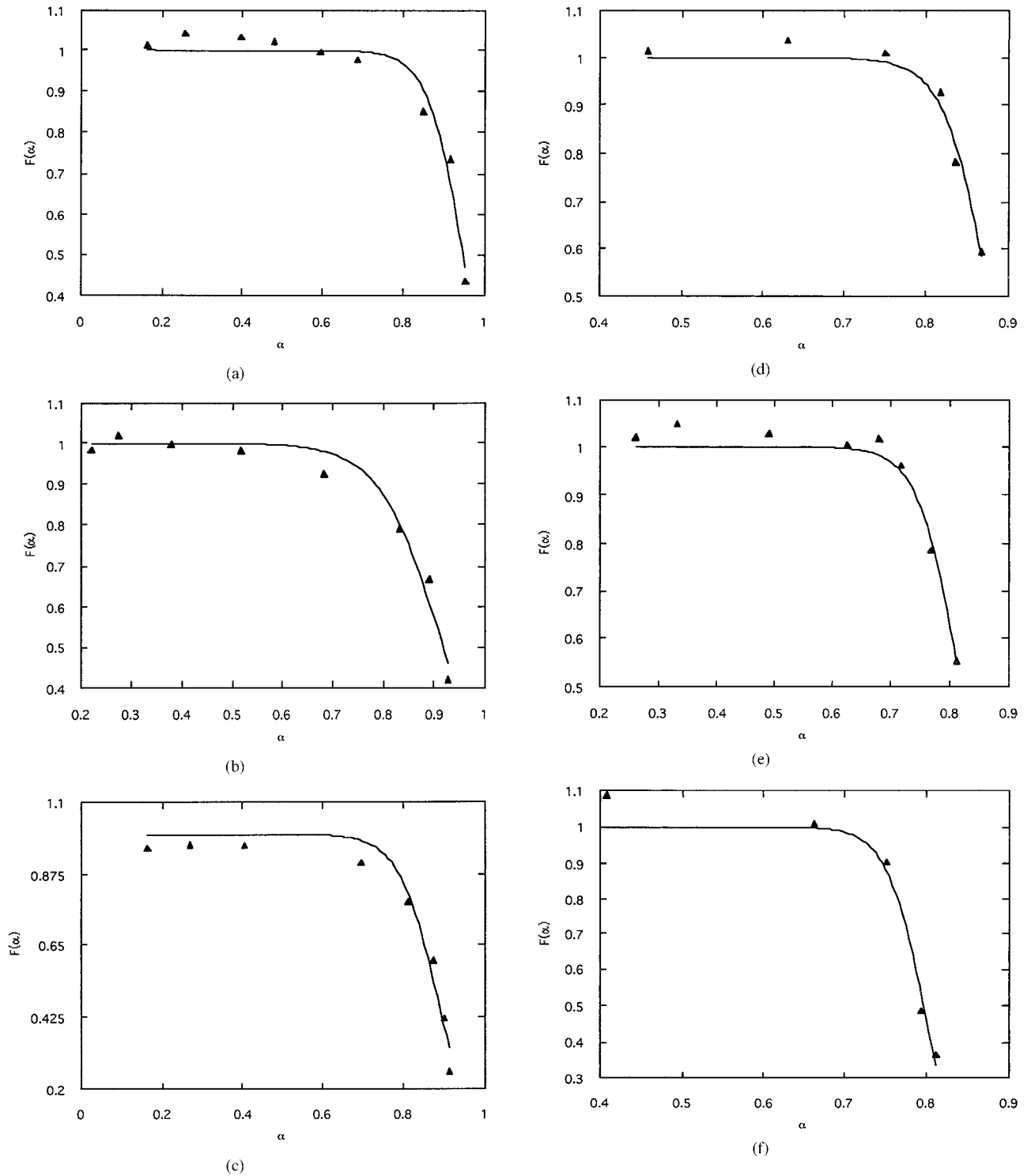


Figure 1 (a) $f(\alpha)$ versus α plot at $T_c = 110^\circ\text{C}$ for commercial resin. (b) $f(\alpha)$ versus α plot at $T_c = 100^\circ\text{C}$ for commercial resin. (c) $f(\alpha)$ versus α plot at $T_c = 80^\circ\text{C}$ for commercial resin. (d) $f(\alpha)$ versus α plot at $T_c = 90^\circ\text{C}$ for commercial resin. (e) $f(\alpha)$ versus α plot at $T_c = 70^\circ\text{C}$ for commercial resin. (f) $f(\alpha)$ versus α plot at $T_c = 60^\circ\text{C}$ for commercial resin.

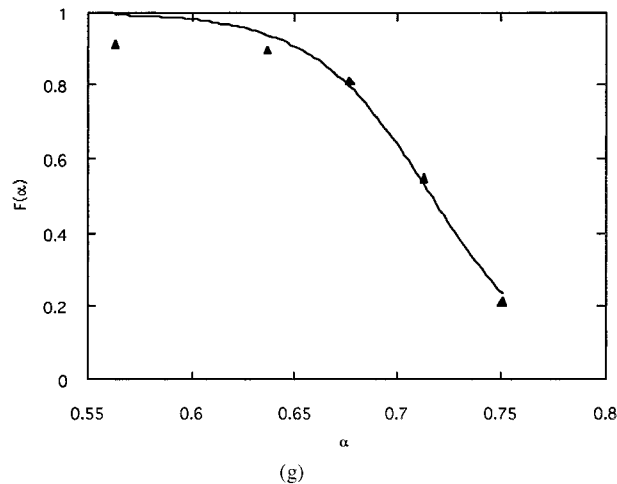


Figure 1(cont.) (g) $f(\alpha)$ versus α plot at $T_c = 50^\circ\text{C}$ for commercial resin.

where the constants A_0 , A_1 , and A_2 depend on the kind of epoxy resin used and the isothermal cure temperature. A linear relationship between $1/V_f$ and α was proposed by Chern and Poehlein⁵:

$$\frac{V^*}{V_f} = A_0 + A_1\alpha \quad (3)$$

A combination of eqs. (1) and (3) yields

$$\frac{K_d}{K_c} = \exp[-A_1(\alpha - \alpha_c)] \quad (4)$$

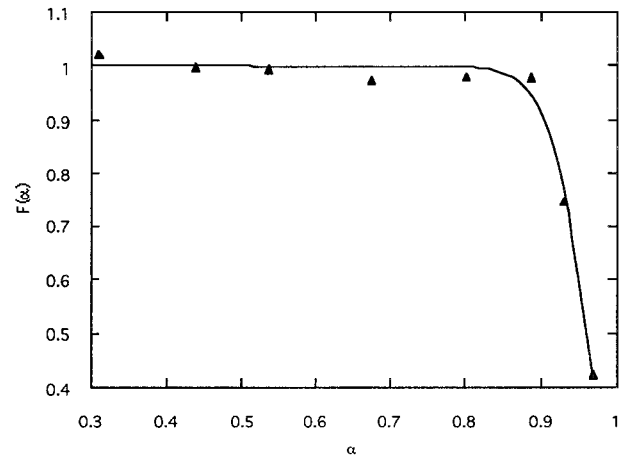
Following the work of Rabinowitch,¹³ the overall effective (experimental) rate constant K_e can be expressed in terms of the chemical kinetics rate constant K_c and the diffusion rate constant K_d , as follows:

$$\frac{1}{K_e} = \frac{1}{K_d} + \frac{1}{K_c} \quad (5)$$

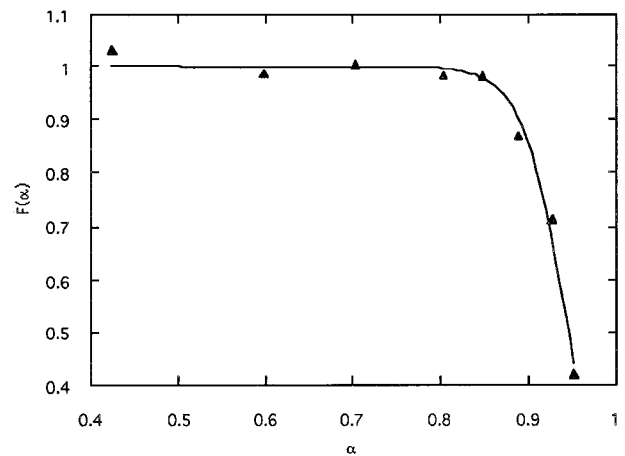
By combining eqs. (4) and (5), a diffusion factor that is dependent on the degree of conversion and the isothermal curing temperature can be defined as

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

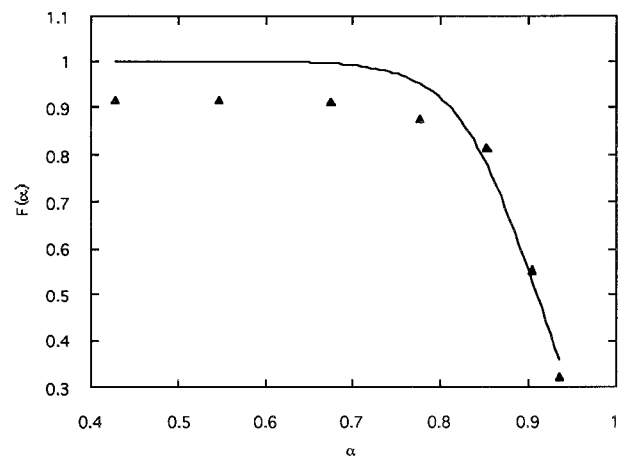
Analysis of eq. (6) shows that when $\alpha \ll \alpha_c$, $f(\alpha)$ tends to unity and the reaction is chemical kinetics controlled. As α approaches α_c , the diffu-



(a)



(b)

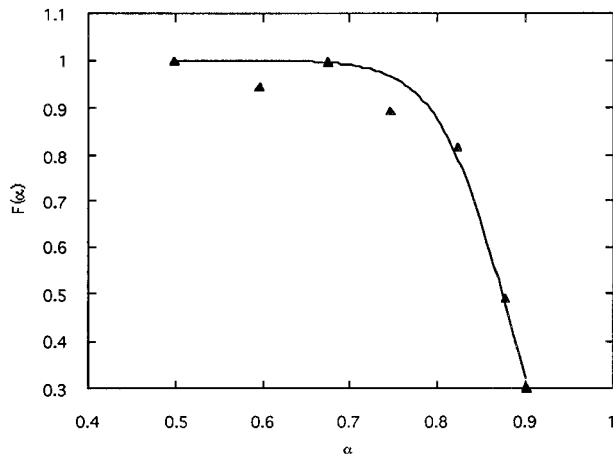


(c)

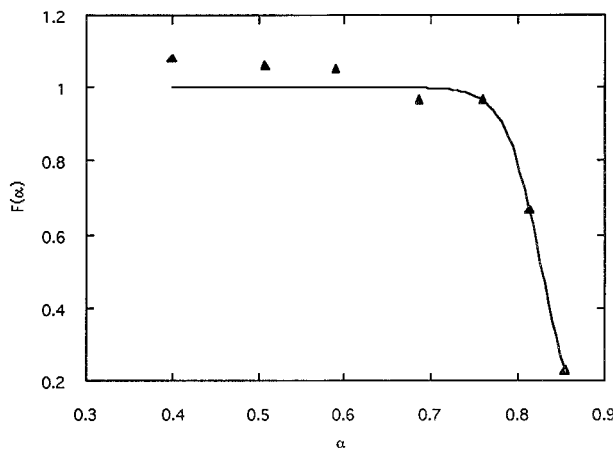
Figure 2 (a) $f(\alpha)$ versus α plot at $T_c = 110^\circ\text{C}$ for purified resin. (b) $f(\alpha)$ versus α plot at $T_c = 100^\circ\text{C}$ for purified resin. (c) $f(\alpha)$ versus α plot at $T_c = 90^\circ\text{C}$ for purified resin.

sion factor gradually decreases and for $\alpha = \alpha_c$, $f(\alpha) = 0.5$. As the reaction progresses, α becomes greater than α_c , $f(\alpha)$ tends to zero, and the reaction dramatically decreases and finally stops.

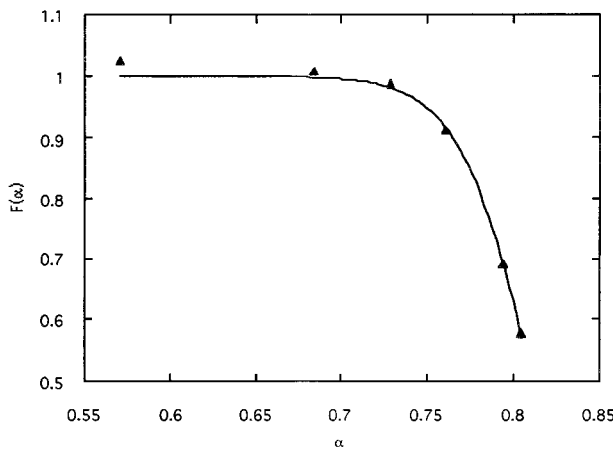
In this study, $f(\alpha)$ was obtained as the ratio of experimental reaction rate obtained for the epoxy



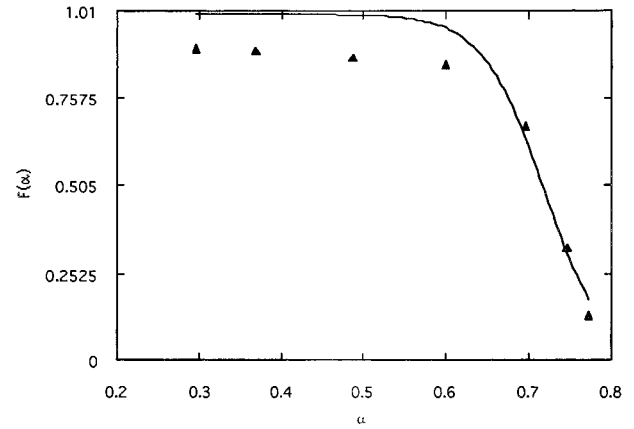
(d)



(e)



(f)



(g)

Figure 2(cont.) (g) $f(\alpha)$ versus α plot at $T_c = 50^\circ\text{C}$ for purified resin.

system in a previous investigation¹ to the reaction rate predicted by the kinetic model proposed by Horie et al.,³ which does not account for diffusion. Calculations were made for as-received and purified resin samples.

Values of critical conversion α_c and constant A_1 obtained by applying nonlinear regression to $f(\alpha)$ versus α data are shown in Table I.

The behavior of $f(\alpha)$ versus conversion at different curing temperatures for the commercial and the purified resins is shown in Figures 1a–1g and 2a–2g, respectively. The observed decrease in $f(\alpha)$ and, hence, in the effective reaction rate is associated with the onset of diffusion, which increases at higher conversions. Table I shows values of α_c and A_1 at various temperatures for the commercial and purified resins. In a previous investigation,¹ it was found that the optimum cure temperature for the two epoxy systems studied in this present investigation corresponds to 110°C , at which highest conversions of 95.37%, for the as-received samples, and 96.94%, for the purified resin, were achieved. As can be seen from Table I, critical conversions for the two systems were measured as 0.948 and 0.961, respectively. These values are very close to maximum conversions and because of that, $f(\alpha)$ shows a very well defined decrease for both resins, as can be seen in Figure

Figure 2(cont.) (d) $f(\alpha)$ versus α plot at $T_c = 80^\circ\text{C}$ for purified resin. (e) $f(\alpha)$ versus α plot at $T_c = 70^\circ\text{C}$ for purified resin. (f) $f(\alpha)$ versus α plot at $T_c = 60^\circ\text{C}$ for purified resin.

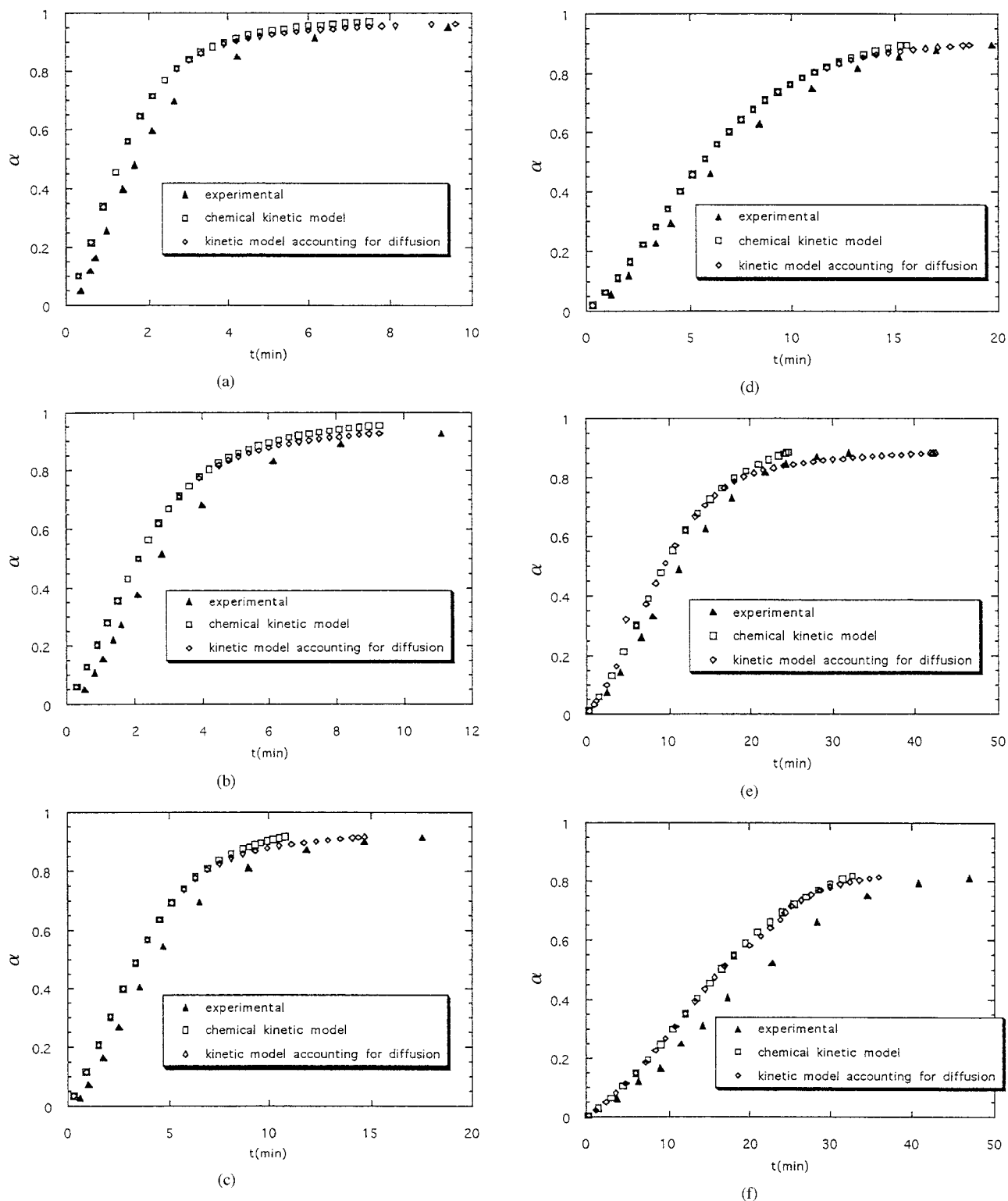


Figure 3 (a) Conversion versus time at $T_c = 110^\circ\text{C}$ for commercial resin. (b) Conversion versus time at $T_c = 100^\circ\text{C}$ for commercial resin. (c) Conversion versus time at $T_c = 90^\circ\text{C}$ for commercial resin. (d) Conversion versus time at $T_c = 80^\circ\text{C}$ for commercial resin. (e) Conversion versus time at $T_c = 70^\circ\text{C}$ for commercial resin. (f) Conversion versus time at $T_c = 60^\circ\text{C}$ for commercial resin.

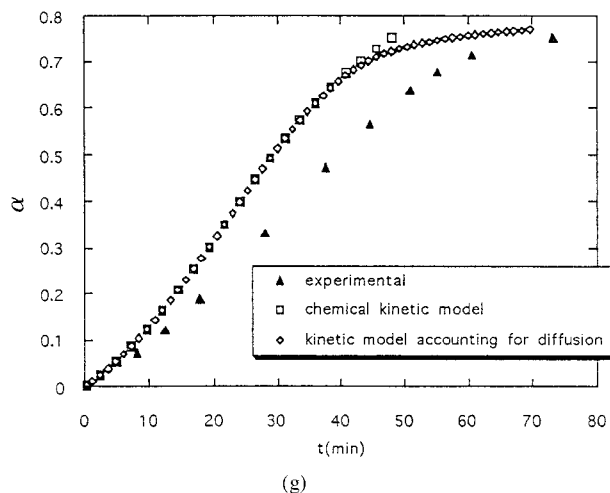


Figure 3g Conversion versus time at $T_c = 50^\circ\text{C}$ for commercial resin.

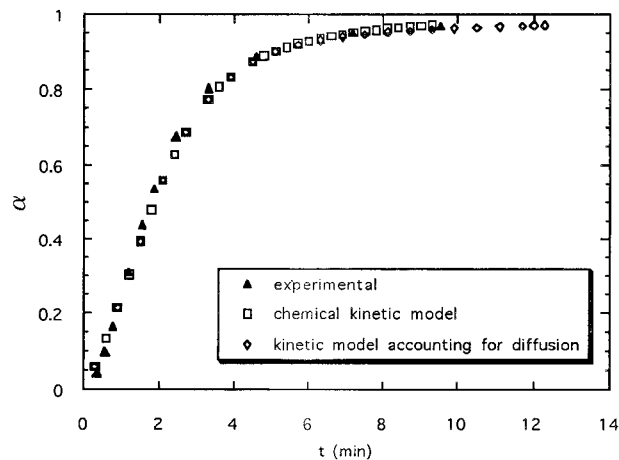
1a (as-received resin) and Figure 2a (purified resin).

For the purified resin, this decrease can be clearly seen for all the temperatures studied in the range $100\text{--}50^\circ\text{C}$ (Figs. 2b–2g); however, it is difficult to see at 50°C for the commercial resin (Fig. 1g). At low temperatures, the decrease in $f(\alpha)$ for the purified resin is better defined than for similar epoxy systems studied by Chern and Poehlein⁵ and Cole et al.⁶ This might be due to the fact that for the purified resin, OH^- content decreased by 5.2% and the hydrolyzable chlorine changed from 631 ppm in the commercial resin to be negligible in the purified resin.¹

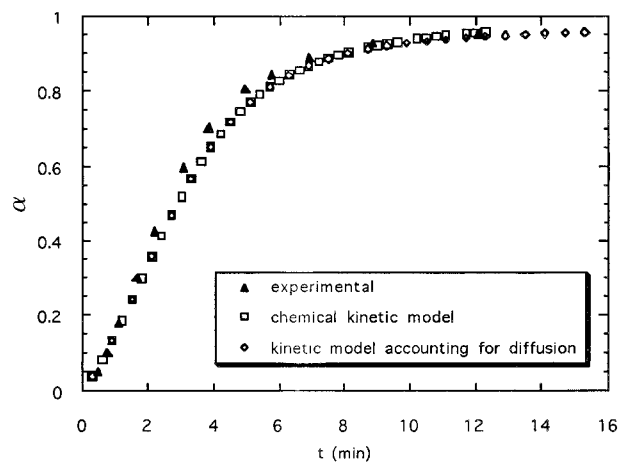
Table I also shows that α_c increased by 13.6 and 13.7% for the commercial and purified resins, respectively, for a 40°C increase in temperature. These increases in α_c are significantly lower than those reported by Kanna and Chanda⁷ for epoxy-amine systems. These low percentages show, once more, that at all the isothermal cure temperatures, chemical kinetics controlled at least 95% of the cure reactions. No trends were observed for the variation of A_1 with temperature. It may also be noted that in their studies on epoxy-amine curing, Cole et al.⁶ and Chern and Poehlein⁵ did not observe any trend for variations of A_1 with temperature.

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

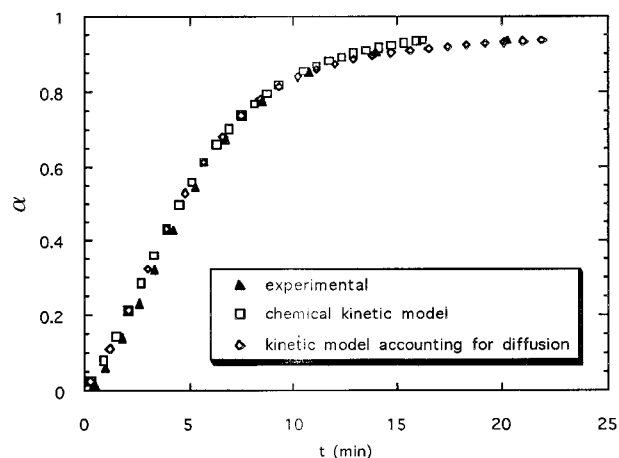
$$\frac{d\alpha}{dt} = (K_1' + K_1\alpha^m)(1 - \alpha)^n f(\alpha) \quad (7)$$



(a)

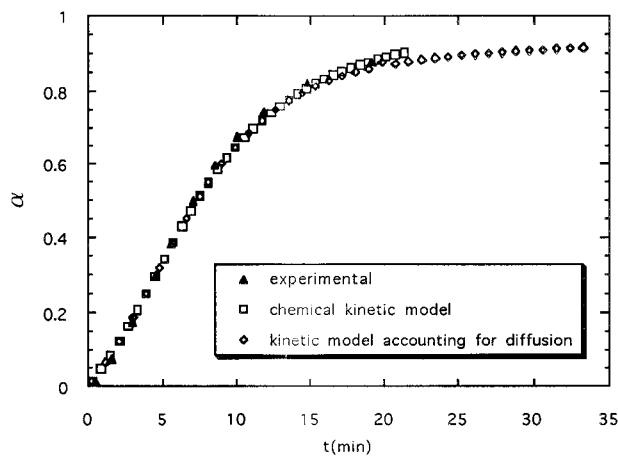


(b)

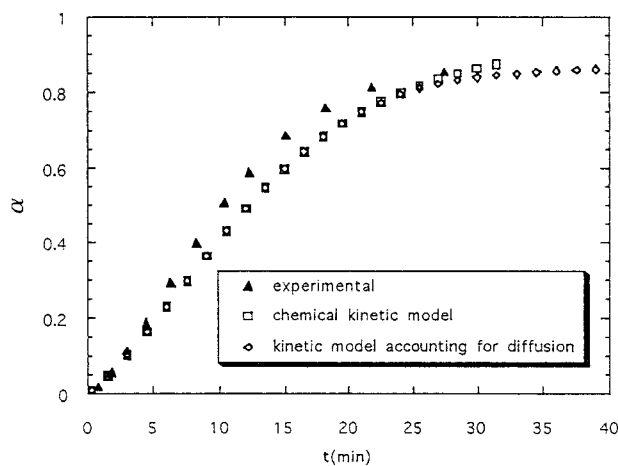


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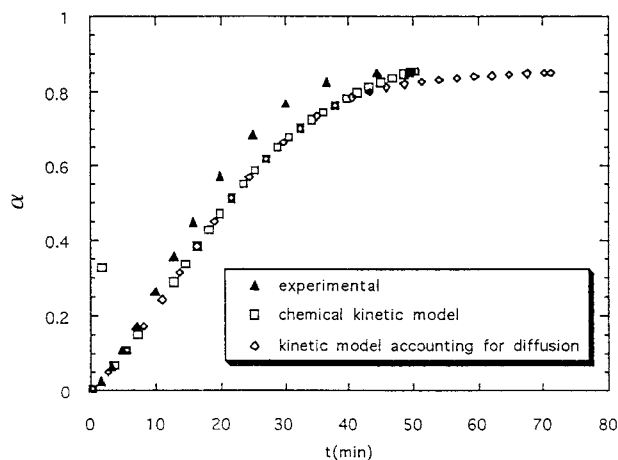
Figure 4 (a) Conversion versus time at $T_c = 110^\circ\text{C}$ for purified resin. (b) Conversion versus time at $T_c = 100^\circ\text{C}$ for purified resin. (c) Conversion versus time at $T_c = 90^\circ\text{C}$ for purified resin.



(d)



(e)



(f)

Figure 4 (d) Conversion versus time at $T_c = 80^\circ\text{C}$ for purified resin. (e) Conversion versus time at $T_c = 70^\circ\text{C}$ for purified resin. (f) Conversion versus time at $T_c = 60^\circ\text{C}$ for purified resin.

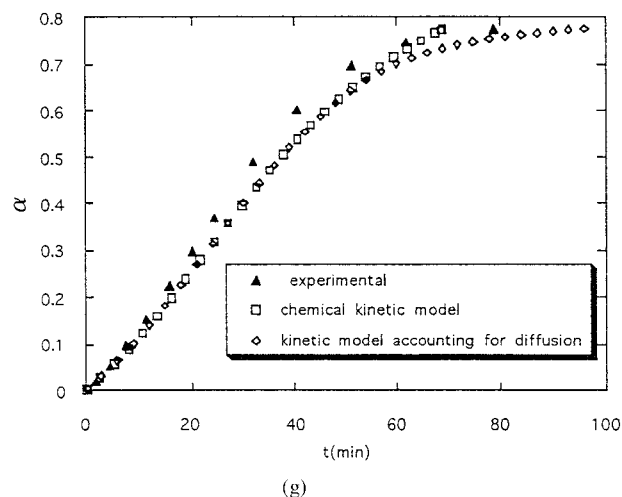


Figure 4g Conversion versus time at $T_c = 50^\circ\text{C}$ for purified resin.

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

Figures 3a–3g and 4a–4g show plots of conversion versus time at different temperatures, where experimental results^{1,2} are compared with those obtained using the chemical kinetics model and the kinetic model accounting for diffusion for both the commercial and the purified resin, respectively. In Figures 3a–3g, it can be seen that the agreement is not extremely good and worsened for small times and conversions, mainly at low temperatures. However, as can be observed in Figures 4a–4g, a good agreement was found for the purified resin, which improves at high temperatures and high conversions. There is not a significant difference between both models, which might be due to the fact that diffusion mechanisms controlled only 2% of the overall conversion.

CONCLUSIONS

The curing reactions of two epoxy systems (BADGE $n=0/m$ -xylylenediamine), one commercial and one purified, were studied by considering two kinetic models, one chemical kinetics controlled and the other accounting for diffusion. It was found that, since chemical kinetics controls more than 95% of the overall reactions, there is not a significant difference between the two models.

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