

Effects of Diffusion on the Kinetic Study of an Epoxy System Diglycidyl Ether of Bisphenol A/1,2-Diamine Cyclohexane/ Calcium Carbonate Filler

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ABSTRACT: The curing reactions of an epoxy system consisting of a diglycidyl ether of bisphenol A (BADGE $n = 0$), 1,2-diamine cyclohexane (DCH) with calcium carbonate filler, were studied to determine different kinetic parameters. Two models—one based solely on chemical kinetics and the other accounting for diffusion—were used and compared to experimental data both for systems with and without filler. It was found that 100°C is the optimum service temperature, and also that the presence of the filler has no influence on the optimal service temperature range (60–100°C) of the epoxy system. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2285–2295, 2000

Key words: epoxy-amine reactions; diffusion; BADGE ($n = 0$); filler; DSC; DMA

INTRODUCTION

Differential scanning calorimetry (DSC) has been used in our laboratories to study the curing kinetics of an epoxy system consisting of a diglycidyl ether of bisphenol A (BADGE $n = 0$)/1, 2-diaminocyclohexane with calcium carbonate filler¹ following the models proposed by Kamal² and Horie et al.³ Experimental reaction rate and reaction orders were compared to the values predicted by both models. It was found that experimental data fit better to the Kamal³ model in the whole range of isothermal temperatures studied. An optimum fitting along the time, which worsened with decreasing isothermal temperatures, was found at 100°C. Owing to the sharp deviations between experimental data and values calculated from the model, an isothermal curing at 55°C was discarded. For a nonfilled system, these deviations observed at every curing temperature, 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 vitreous 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. In this article, the conversion at which diffusion begins, critical conversion, is calculated to find the critical fractional free volume at which the reaction becomes diffusion controlled. As the cure progresses, the crosslinking density of the material and thus the glass transition temperature, T_g , increase. As T_g approaches the curing temperature, the resin passes from a rubbery to a glassy state, the free volume reduces, and the mobility of the reacting groups is restricted. At this moment, the reaction rate decreases dramatically, and the reaction becomes diffusion controlled.⁴ The mathematical treatment of this phenomenon can be followed using a semiempirical relationship based on the free-volume considerations proposed by Chern and Poehlein.⁵ This model has been successfully used by Cole et al.,⁶ Khanna and Chanda,⁷ and Núñez et al.⁸ to study the cure reactions of epoxy systems. In this last

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article,⁸ the effects of diffusion on the kinetics of the nonfilled BADGE $n = 0/1,2$ DCH system is studied. 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, α_c , the mobility of the reacting species is reduced, leading to diffusional effects. Hence, the critical value, α_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, because at this point the

molecular weight of the reacting system increases dramatically.

EXPERIMENTAL

Materials

The epoxy resin was a commercial BADGE ($n = 0$) (Resin 332, Sigma Chemical Co., St Louis, MO) with an equivalent molecular weight of 173.6 g/Eq, as determined by wet analysis.^{9,10} The curing agent was 1,2 diaminecyclohexane (DCH) (Fluka, Switzerland) with an amine hydrogen weight of 28.5. The inert filler was calcium carbonate (Analema, Spain).

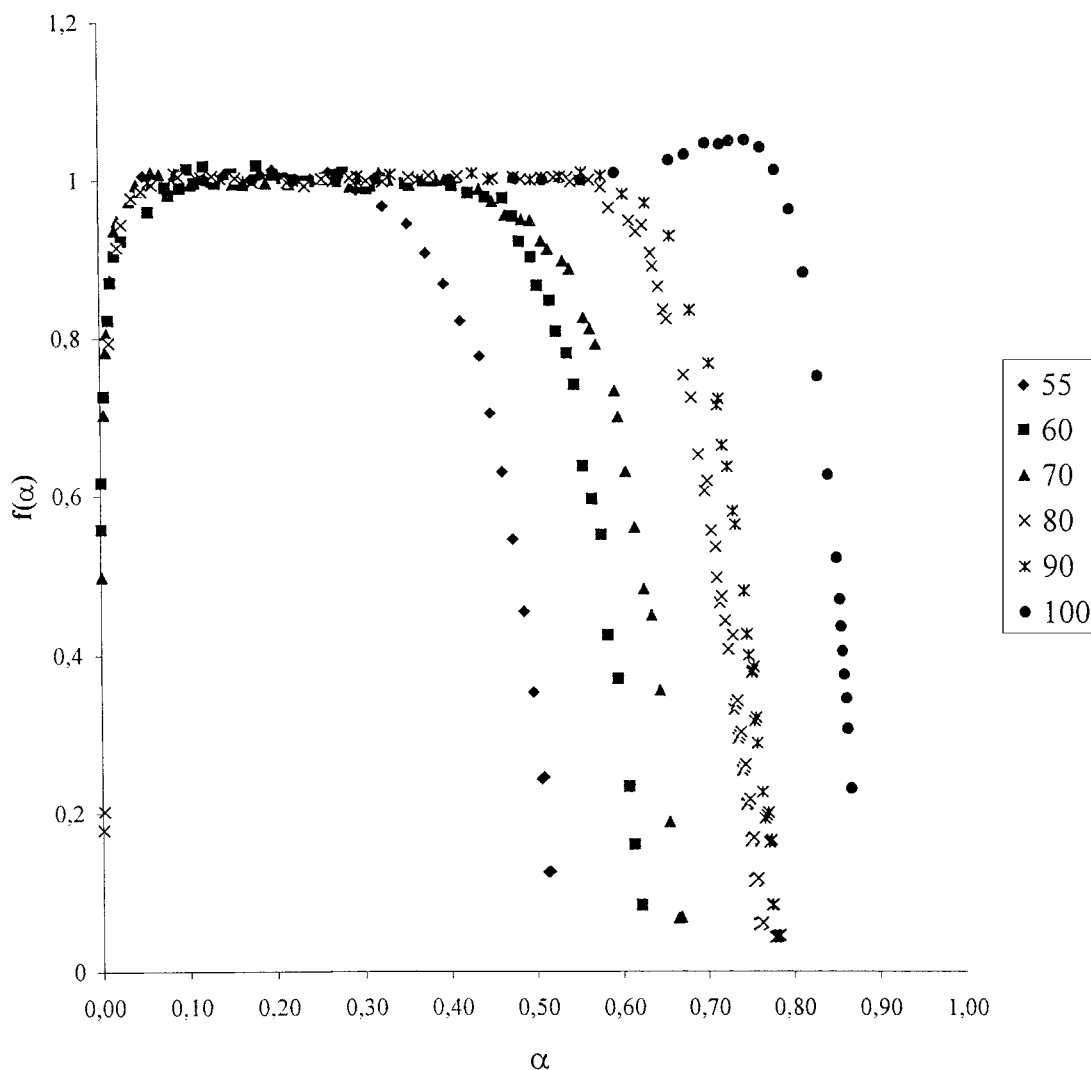


Figure 1 $f(\alpha)$ vs. α for various cure temperatures.

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC-7 unit, under control of a 1020 system controller, was used for calorimetric measurements. Owing to the wide range of temperature (-30 – 250°C) necessary for this study, the calorimeter was calibrated using two standards (indium and bidistilled water, obtained by the millipore method). For determination of the different kinetic parameters, the calorimeter was operated in isothermal and dynamic modes.

Dynamic Mechanical Analysis (DMA)

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 $10^\circ\text{C}/\text{min}$. The dynamic mechanical analyzer was used to measure the gel times.

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 Saito¹¹ and Marten and Hamielec¹² independently proposed a semiempirical equation for variation of the propagation rate constant for free radical polymerization. That equation was modified by Chern and Poehlein⁵ to take the following form:

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

where K_d is the diffusion rate constant at a given conversion; K_c , the rate constant corresponding to the chemical reaction-controlled model proposed by Kamal;² 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 just formed; and V^* , an adjustable constant that 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, α :

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

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

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

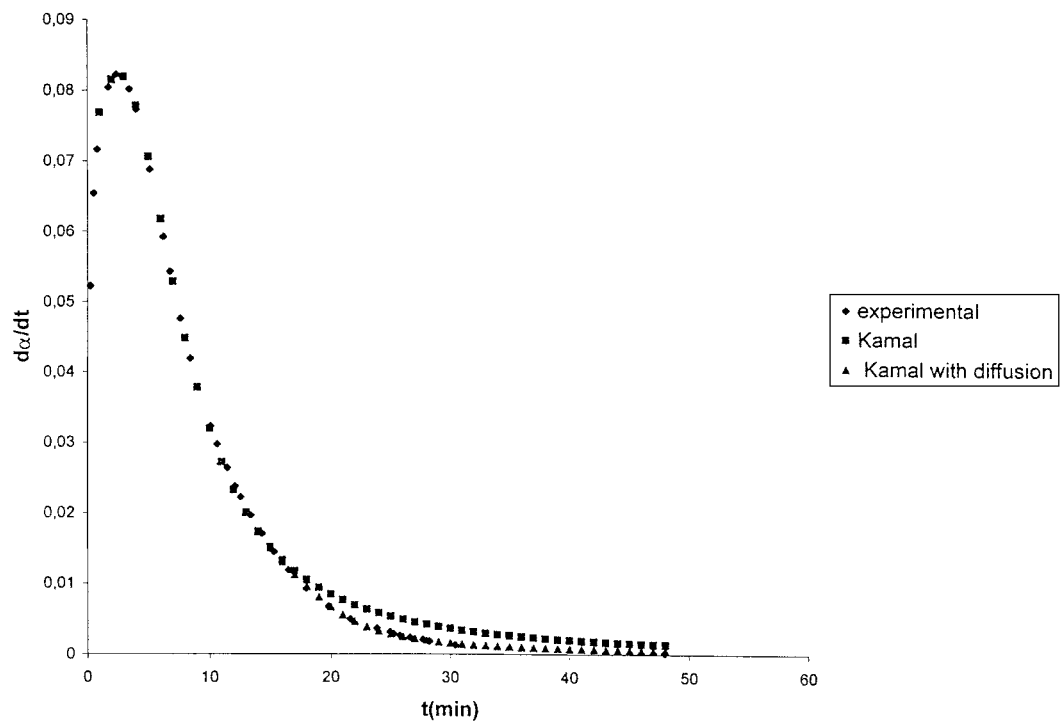
Combination of eqs. (3) and (1) gives

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

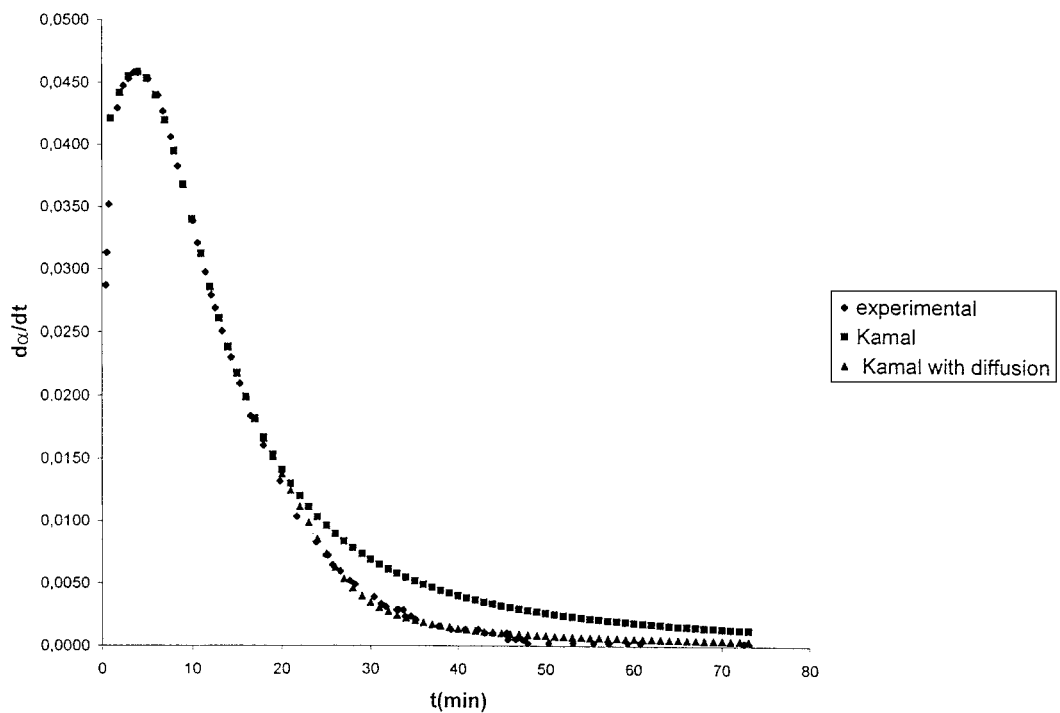
According to Rabinowitch,¹³ the overall effective (experimental) rate constants, K_e , can be ex-

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

T ($^\circ\text{C}$)	With Filler			Without Filler (ref. 8)		
	α_c	A_1	$ T_c - T_g $ ($^\circ\text{C}$)	α_c	A_1	$ T_c - T_g $ ($^\circ\text{C}$)
100	0.852	60.6	10.4	0.929	43.9	11.5
90	0.725	35.5	26.0	0.924	32.7	2.7
80	0.711	37.3	18.5	0.891	30.7	5.3
70	0.622	33.8	23.2	0.831	7.6	23.5
60	0.574	33.7	20.5	0.725	9.4	33.5
55	0.474	32.9	29.1	—	—	—

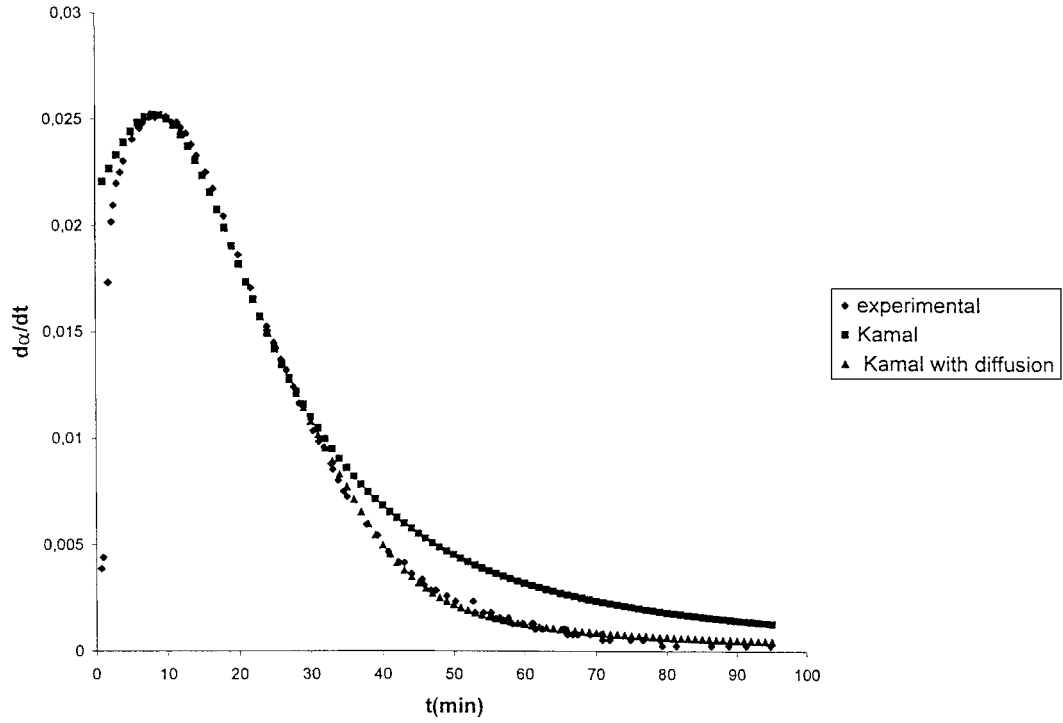


(a)

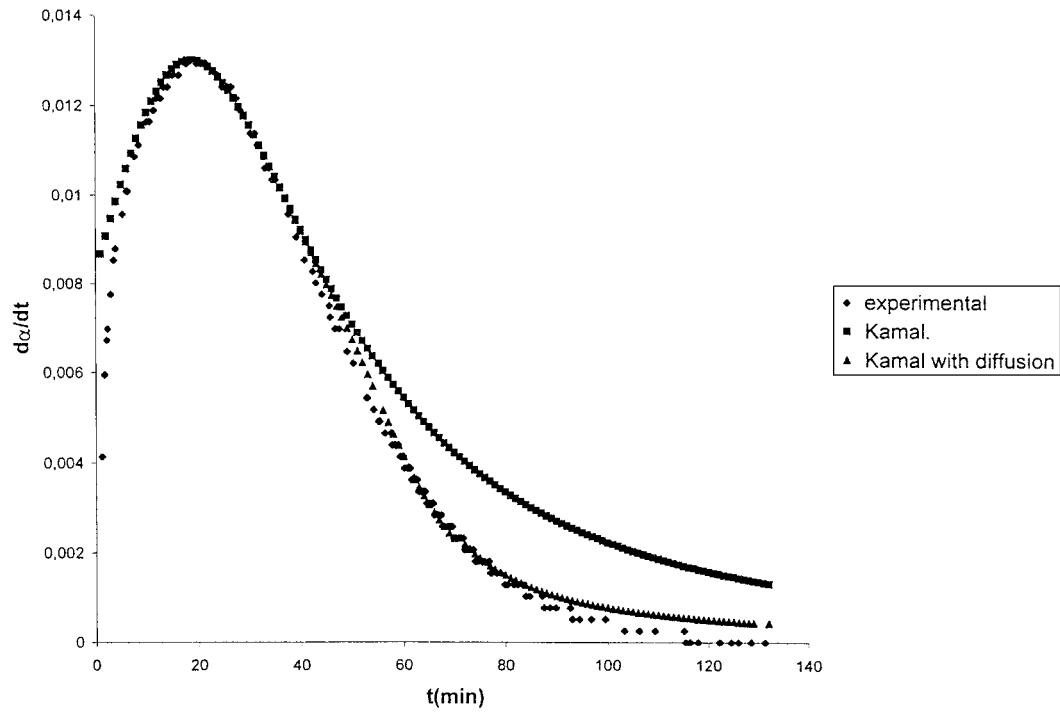


(b)

Figure 2 Reaction rate vs. time for various cure temperatures: (a) 100°C; (b) 90°C; (c) 80°C; (d) 70°C; (e) 60°C; (f) 55°C.



(c)



(d)

Figure 2 (Continued from previous page)

pressed in terms of the diffusion rate constant (K_d) and the reaction rate constant (K_c) as follows:

$$\frac{1}{\bar{K}_e} = \frac{1}{\bar{K}_d} + \frac{1}{\bar{K}_c} \tag{5}$$

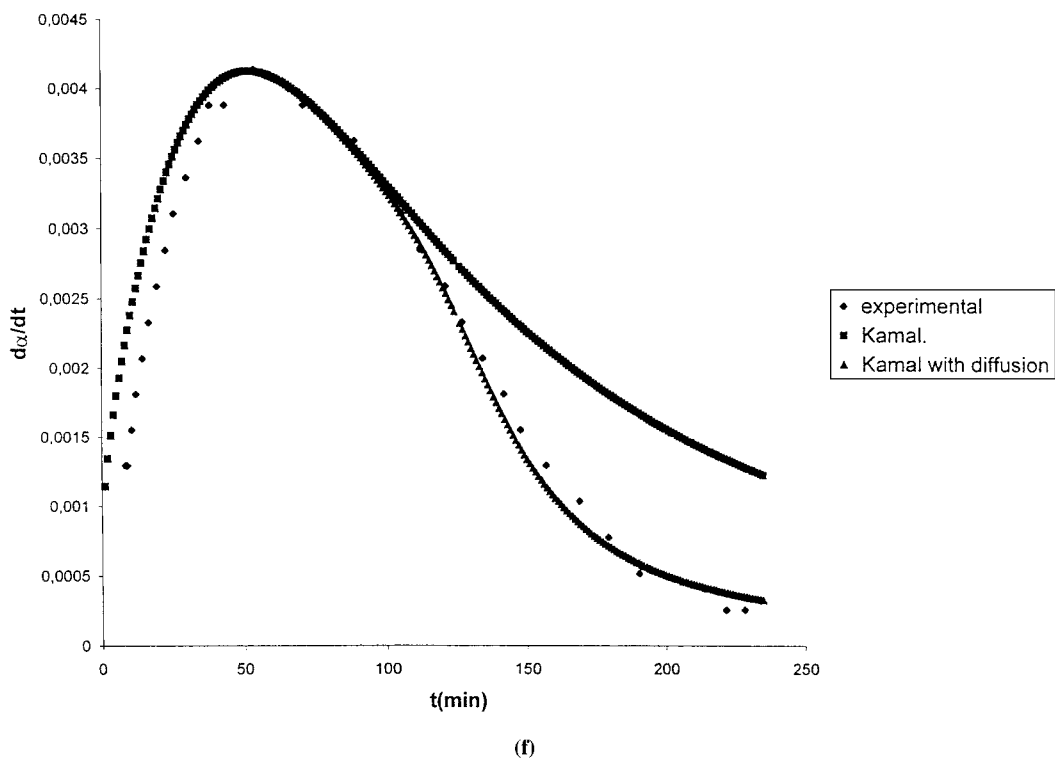
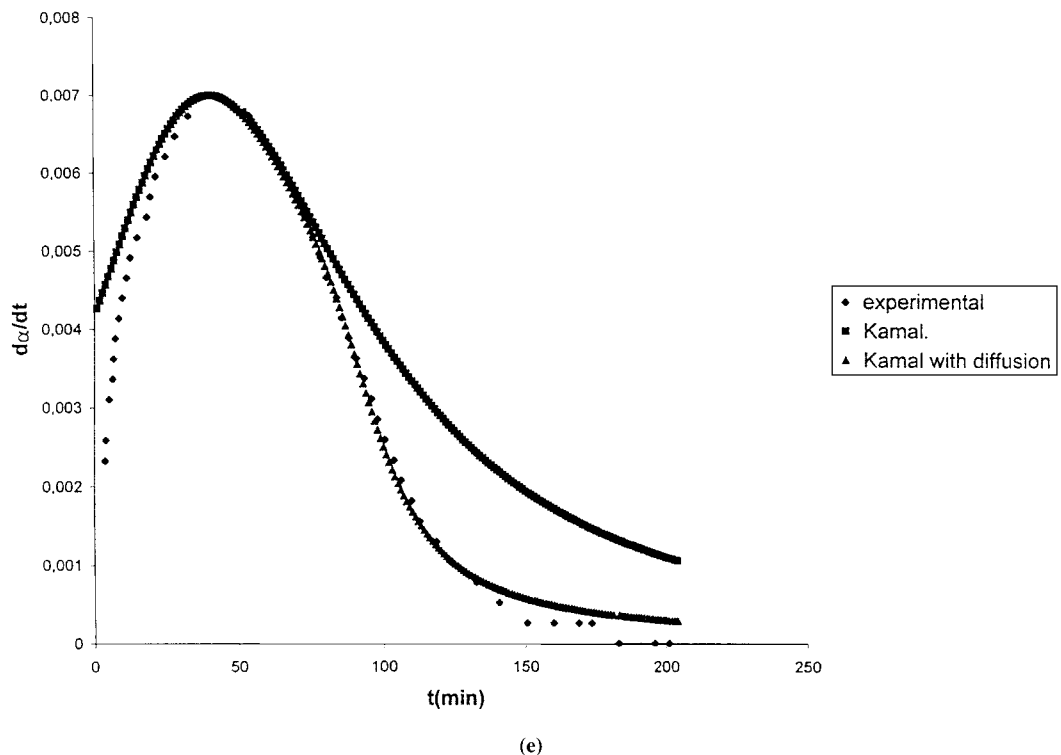


Figure 2 (Continued from previous page)

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

$$f(\alpha) = \frac{K_e}{K_c} = \frac{1}{1 + e^{A_1(\alpha - \alpha_c)}} \quad (6)$$

For $\alpha \ll \alpha_c$, $f(\alpha)$ tends to unity, and the reaction is chemical kinetic controlled. As α approaches α_c , the diffusion factor begins to decrease. When the conversion reaches its critical value, α_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 to the reaction rate predicted by the Kamal kinetic model.² Figure 1 shows the behavior of $f(\alpha)$ vs. conversion, α , at different isothermal curing temperatures. The decrease in $f(\alpha)$ observed at every temperature is associated with the onset of diffusion at higher conversions. Comparison of this plot with that obtained for the system without filler⁸ shows that for the filled system the decrease in $f(\alpha)$ is observed at every isothermal cure temperature, while for the nonfilled system this decrease is well defined only in the higher isothermal temperature range (80–100°C). For the filled system, an interesting phenomenon is observed at 100°C. At this temperature, when α reaches high values (>0.80) the reaction rate increases slightly above that predicted by the model, before it drops off because of diffusion control. Cole et al.⁶ have observed this same phenomenon at temperatures of 200°C and above. This behavior is believed to be due to another reaction, not included in the model, which becomes important only at higher temperatures. This reaction could be the formation of an ether group. In our kinetic study, we have not considered this type of reactions due to the fact that this anomalous behavior was observed only at one of the isothermal temperatures (100°C), and at high conversions the system achieved practically the maximum crosslinking.

The values of the critical conversion (α_c) and A_1 obtained by applying nonlinear regression to $f(\alpha)$ vs. α data, for the filled and nonfilled systems, are listed in Table I. It can be seen that α_c decreases by 20% (nonfilled system) and by 28% (system with filler) for a 40°C increase in temperature. Results for the system without filler are in good agreement with data reported by Cole et al.⁶ and Núñez et al.⁸ It can be observed also, that A_1 corresponding to the filled system keeps practically constant at every temperature except for 100°C. For the system without filler, A_1 values show a considerable scatter with temperature. For the filled system, the curing reaction becomes diffusion controlled at higher conversions in the range of experimental temperatures, while for the nonfilled system the reaction becomes diffusion controlled at conversions close to the maximum

value and high temperatures (80–100°C). Table I shows also values of $|T_g - T_c|$, useful for observing if vitrification starts before or after the reaction becomes controlled by diffusion.^{8,14} Values of $|T_g - T_c|$ were calculated according to a method previously reported.⁸ For this epoxy system $\lambda = 0$, 501, $T_{g\infty} = 127$, 64°C, and $T_{g0} = -20$ °C. Vitrification is defined at the time at which $T_g = T_c$.^{14,16} 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 for the system with filler, except for 100°C, vitrification has started at every isothermal temperature before the curing process becomes diffusion controlled. For the system without filler, vitrification was only achieved at lower curing temperatures (60–70°C).

Inclusion of the diffusion factor into the semiempirical equation proposed by Kamal, gives:

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

or

$$\frac{d\alpha}{dt} = (K_1' + K_1\alpha^m)(1 - \alpha)^n \frac{1}{1 + e^{[A_1(\alpha - \alpha_c)]}} \quad (8)$$

This differential equation does not have an analytical solution, and to calculate the degree of conversion, numerical integration must be performed.

Figure 2(a)–(f) shows values of $d\alpha/dt$ vs. t at different isothermal curing temperatures. The experimental results are compared with those obtained using the chemical kinetics-controlled Kamal model and with the results predicted with the inclusion of a diffusion factor into this model. The plots show that the inclusion of a diffusion factor improves the agreement between experimental and model results in the whole range of time. However, at lower cure temperatures (55–70°C), results obtained from the Kamal model accounting for diffusion show important deviation at high times, that is, after maximal conversions at those temperatures were achieved. It can be observed also, that reaction rate drops off faster at high temperatures.

To corroborate this behavior, eq. (7) was integrated using the Euler approximate numerical method to obtain the degree of conversion. Figure 3(a)–(f) shows values of α vs. t at different tem-

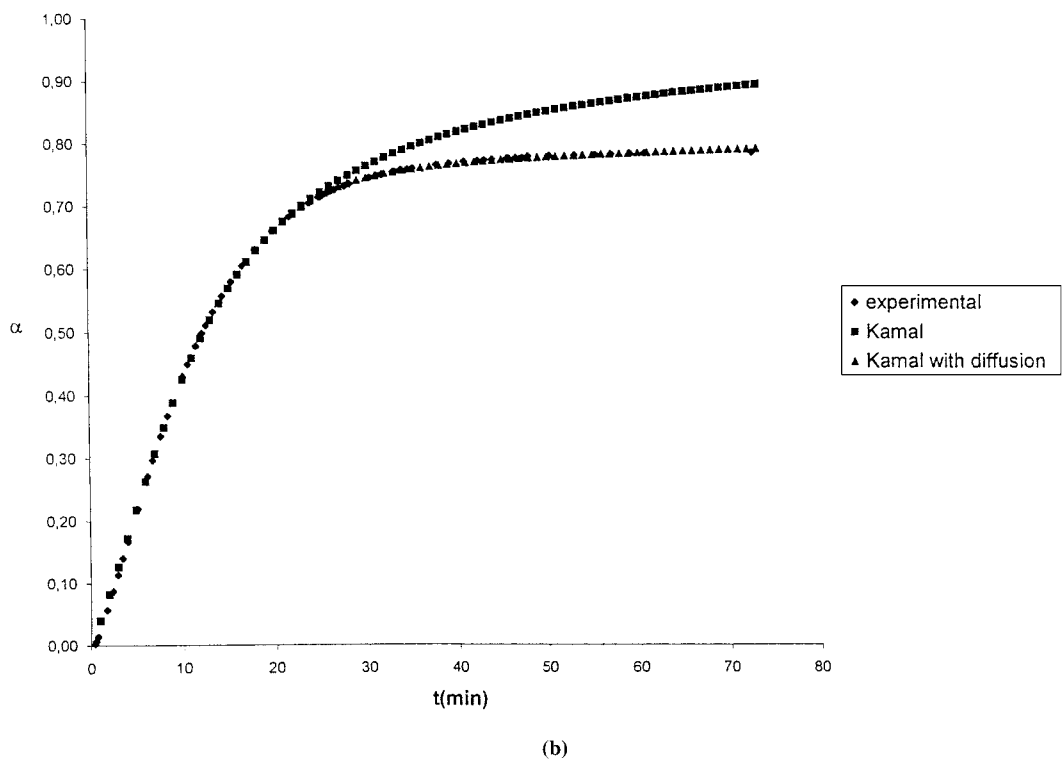
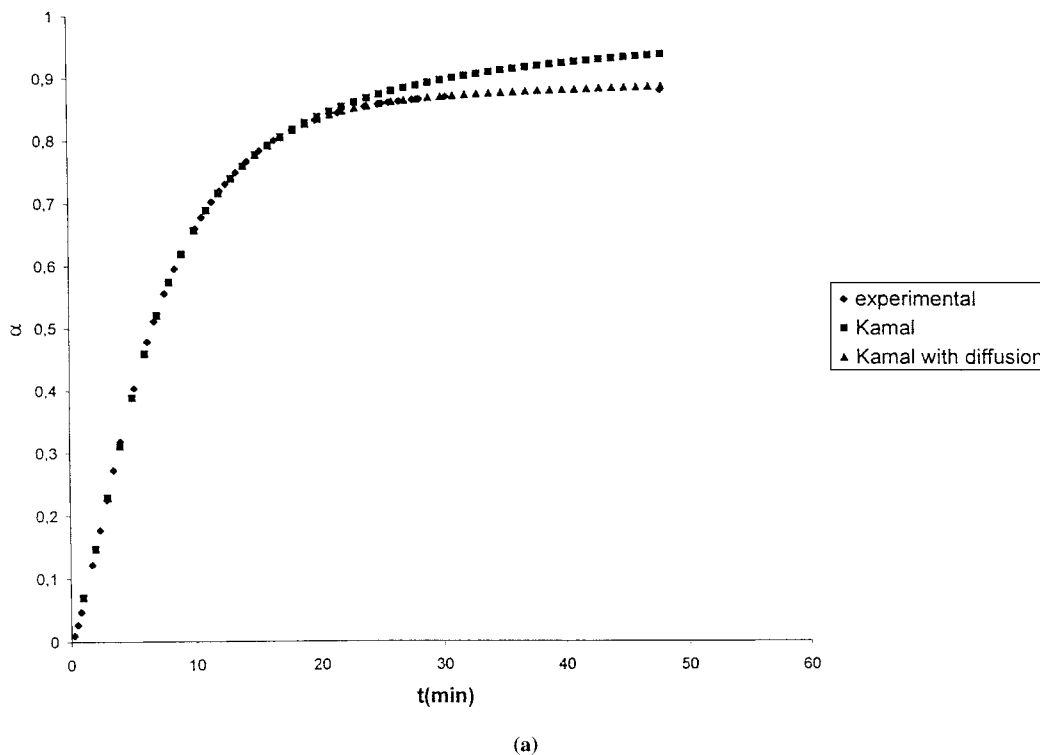
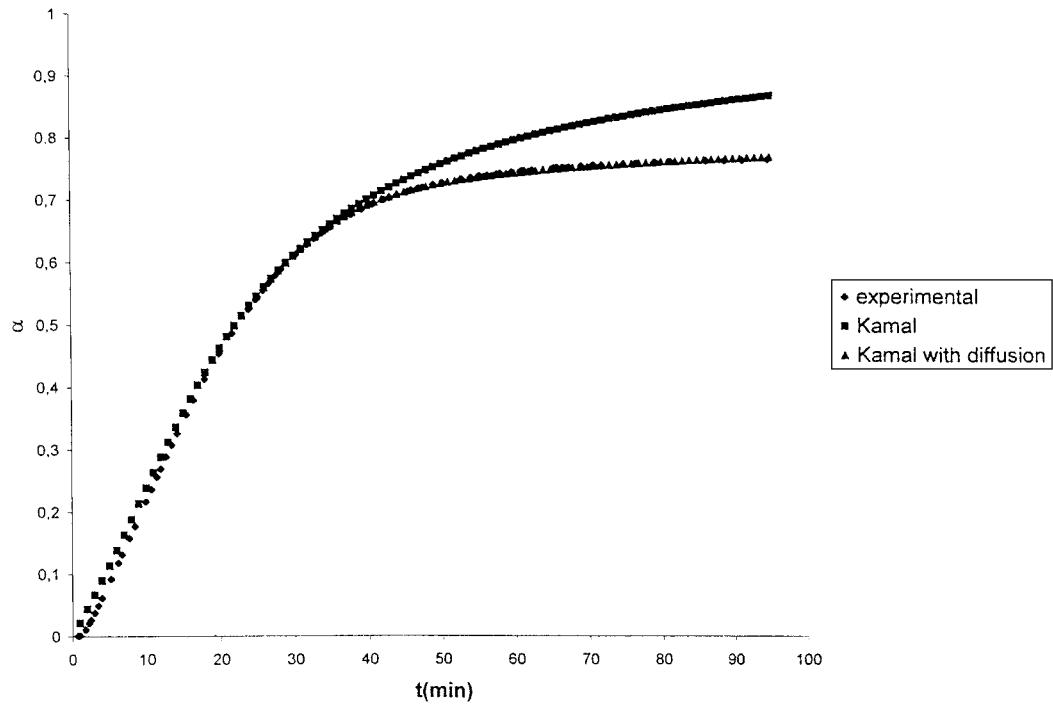
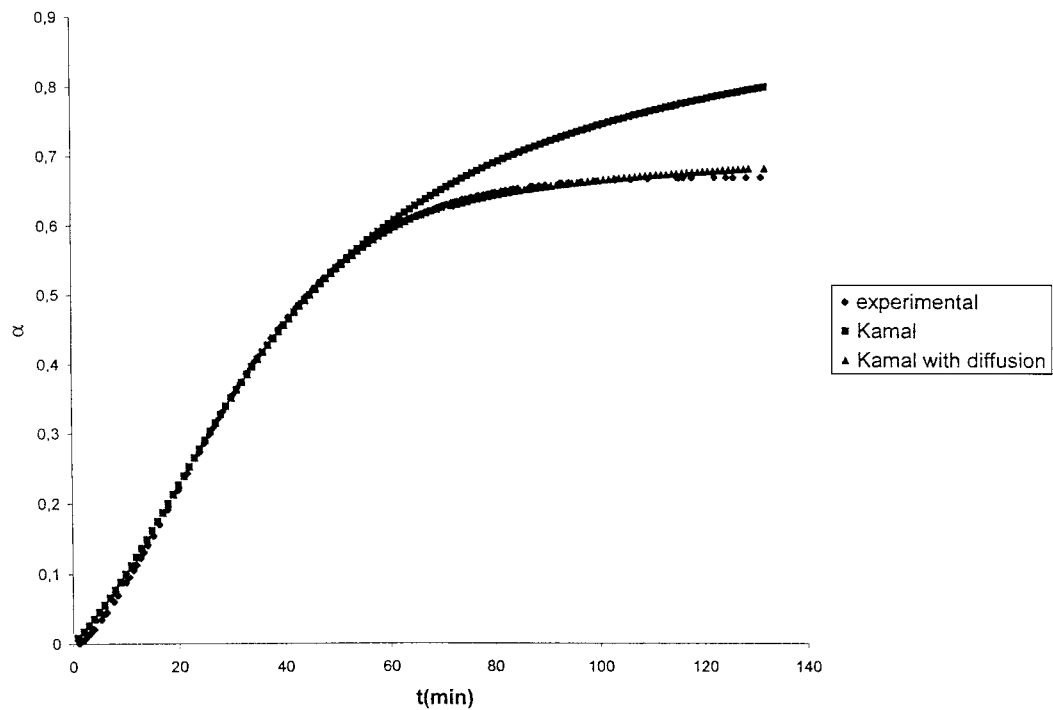


Figure 3 Conversion vs. time for various cure temperatures: (a) 100°C; (b) 90°C; (c) 80°C; (d) 70°C; (e) 60°C; (f) 55°C.



(c)

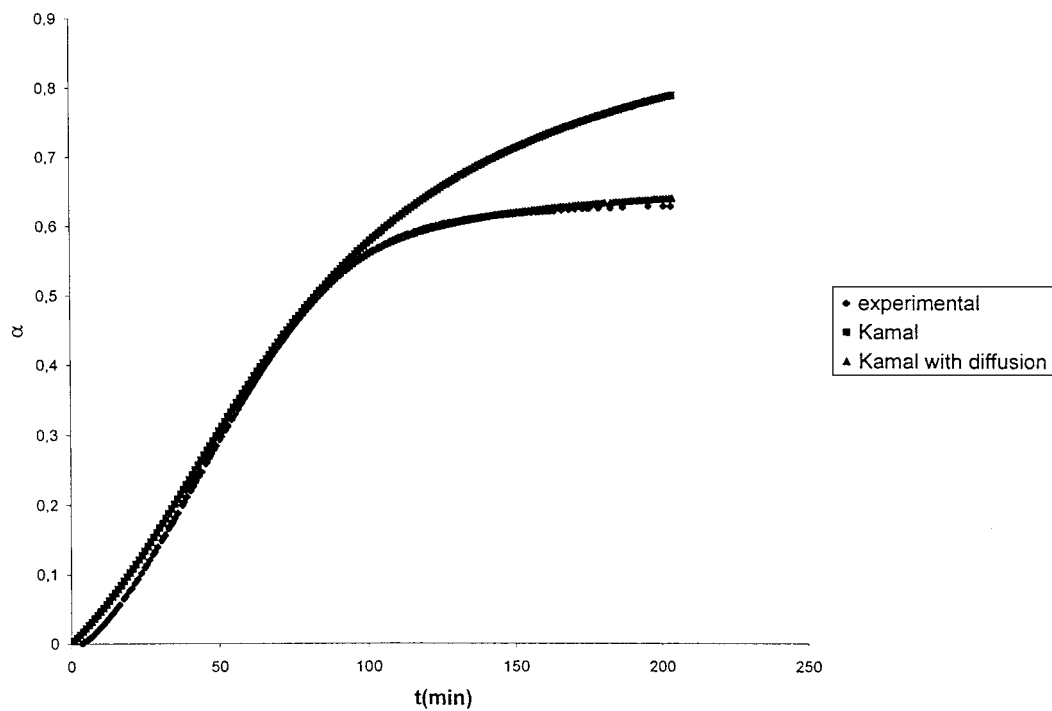


(d)

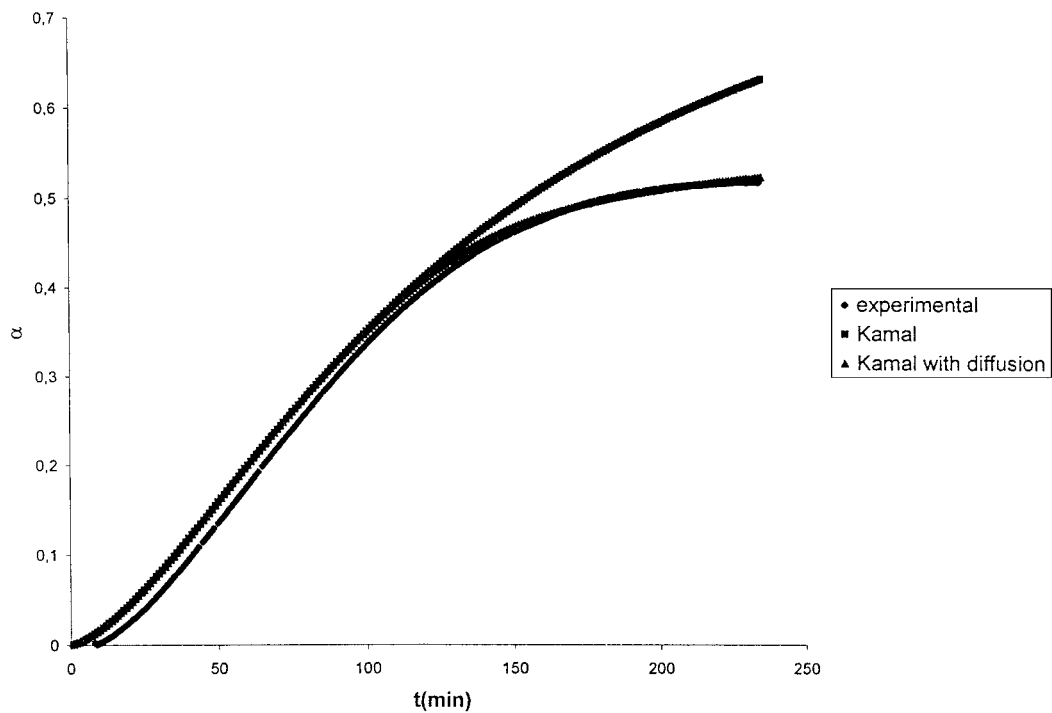
Figure 3 (Continued from previous page)

peratures of isothermal cure. These plots show a similar behavior to that shown by reaction rate vs. time plots. Both plots show large deviations

between experimental data and model predictions at 55°C. Because of this, it may be concluded that 55°C is not an optimum cure temperature for this



(e)



(f)

Figure 3 (Continued from previous page)

type of material. There are two fundamental reasons for discarding this temperature. On the one hand, only low conversions can be achieved, while

on the other hand, the time necessary for curing of the material is very large. From a practical point of view, the optimal cure temperature range

is 60–100°C, and the optimum temperature 100°C. These values coincide with those found for the nonfilled system.^{8,17,18}

CONCLUSIONS

The presence of a filler in the system BADGE ($n = 0$)/1, 2 DCH has no influence on the optimal cure temperature range (60–100°C). The optimum service temperature of the filled material, 100°C, coincides with that found for the system without filler. For the system with filler, vitrification is previous to diffusion control at every temperature. However, this fact does not constitute a disadvantage with respect to the system without filler because, at every temperature, diffusion control takes place at conversion values close to maximum conversion. Temperatures lower than 60°C are not useful for a kinetic study of this epoxy system, owing to low crosslinking and large curing times.

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