Kinetics of Anhydride Curing of Isophthalic Diglycidyl Ester Using Differential Scanning Calorimetry

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SYNOPSIS

The cure reaction of a model diglycidyl ester, bis-(2,3-epoxypropyl)-1,3-benzenedicarboxylate, with hexahydrophthalic anhydride as the curing agent and benzyldimethylamine as the catalyst, was studied by differential scanning calorimetry using an isothermal approach over the temperature range 100–135°C. The results indicate that the cure reaction is autocatalytic in nature and does not follow simple nth-order kinetics. A semiempirical equation for autocatalytic systems containing two rate constants and two reaction orders, viz., 0.5 and 1.5, provided a good phenomenological description of the cure kinetics up to the point of vitrification. With the inclusion of a diffusion factor into this model, it was, however, possible to predict with precision the cure kinetics over the whole range of conversion covering both pre- and postvitrification stages and over the entire temperature range of 100–135°C employed for isothermal curing. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Interest in the kinetics and mechanism of anhydride curing of epoxy resins largely derives from the usage of these materials in reinforced composites. Anhydride curing agents find use in most of the important applications of epoxy resins, particularly in casting and laminates. Chemical reactions that take place during cure determine the resin morphology, which, in turn, determines the properties of the cured thermoset. The understanding of the mechanism and kinetics of cure is thus the first essential step in the process of evaluation of processing–morphology–property relationships in thermosets and their composites.

Excellent reviews of the mechanisms and kinetics of thermoset cure have appeared in the literature.[1-3] However, in spite of considerable current research activity in the field of epoxy resin cure, numerous questions are yet to be answered. This is particularly true for catalyzed curing reactions of epoxy resins and cyclic anhydrides, as is evident from the fact that a number of partially conflicting

reaction mechanisms have been proposed in recent years to account for the observed reaction kinetics of an anhydride-cured epoxy system.[4-13]

With the growth of computer-aided design and manufacturing, there has been an increased interest in modeling the processing of epoxy-based composites.[14] The object is to optimize the processing parameters to obtain high-quality parts with greater consistency and to minimize the experimental work required to establish a cure cycle for any new parts. A good model enables one to predict how the system will behave during cure and what its final condition will be. One of the most important components of such a model is an accurate description of the kinetics of cure. With the chemistry of epoxy curing being rather complex and not completely understood, the cure kinetics are not easily elucidated.

Phenomena such as autocatalysis in the early stages[15] and onset of gelation at later stages[16,17] can further complicate the kinetic modeling. Determination of the reaction order from experimental data can be difficult and confusing in some reaction systems. Thus, reaction kinetics differing from first to third order have been reported.[16-18] In an important investigation of curing of a diglycidyl ether of bisphenol A-based epoxide resin with methylnadic anhydride using the FTIR technique, it is reported[8]

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that the overall kinetics are first order but the data can fit to zero- and second-order kinetics almost as well.

Most of the investigations on anhydride curing of epoxy resins reported in the literature have been on bisphenol A diglycidyl ether or model compounds like phenyl glycidyl ether, but very little is known about the anhydride curing of diglycidyl esters, which are important for the fabrication of electroinsulators. This prompted Steinman[19] to study the kinetics and mechanism of the anhydride curing of a diglycidyl ester. We also took up for investigation a diglycidyl ester–cyclic anhydride–tertiary amine system and studied the reaction of the model compound isophthalic diglycidyl ester (IPDGE) with hexahydrophthalic anhydride (HHPA), catalyzed by benzyldimethylamine (BDMA). Of the three ester isomers (*ortho, meta,* and *para*), IPDGE, which is the *meta* isomer, was chosen as the epoxide monomer since its amine-cured product is reported[20] to have the highest T_g. A variety of experimental techniques has been developed to follow the cure reaction of thermosetting systems, one of them being differential scanning calorimetry (DSC). In this article, we have used the DSC technique to investigate the cure kinetics of the BDMA-catalyzed IPDGE–HHPA resin system. The basic assumption used is that the heat evolution monitored and recorded by DSC is proportional to the extent of consumption of the epoxide group in the epoxy resin or the anhydride group in the curing agent. Rate laws are derived in agreement with the data generated from both dynamic and isothermal DSC measurements during cure.

EXPERIMENTAL

Materials

The epoxy compound used in the study was bis-(2,3-epoxypropyl)-1,3-benzenedicarboxylate (IPDGE), as shown in Figure 1. This was synthesized by the Schotten–Baumann reaction using isophthaloyl dichloride (Aldrich, 98%) and glycidol (Aldrich, 96%), according to the method of Galy et al.[20] In a typical procedure, isophthaloyl dichloride (12.68 g) dissolved in toluene (10 mL) was added dropwise to a mixture of glycidol (10.8 mL), triethylamine (19.3 mL), and toluene (150 mL) and stirred at −10°C, the stirring being continued for 2 h at −10°C after the addition was complete. The organic layer was separated and dried using anhydrous sodium sulfate. The solvent was distilled off and the residue recrystallized twice from a mixture of ethyl acetate and
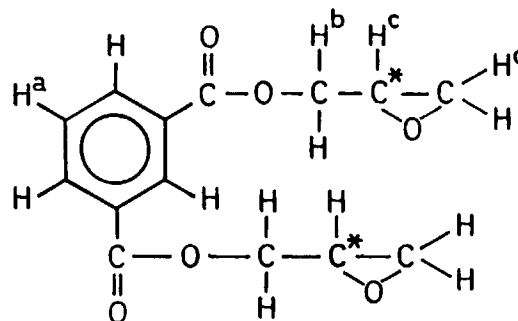

Figure 1 Structure of bis-(2,3-epoxypropyl)-1,3-benzenedicarboxylate (IPDGE).

hexane. The microanalysis of the epoxide product (IPDGE) gave C, 60.23%; H, 5.19%; and O, 33.91%, in good agreement with the expected values of C, 60.43%; H, 5.04%; and O, 34.53%. The ^{1}H-NMR spectrum of the product (Fig. 2) shows signals for the protons labeled (a)–(d) in Figure 1, namely, (a) four aromatic protons at 7.4–8.8 ppm, (b) four methylene protons attached to oxygen of the ester group at 4.1–4.8 ppm, (c) two protons attached to the asymmetric carbons of the epoxide rings at 3.4 ppm, and (d) four protons attached to the two epoxide rings at 2.6–3.0 ppm. The integration curve, showing the number of protons, confirms the structure shown in Figure 1.

Hexahydrophthalic anhydride (HHPA) (Ciba-Geigy, mp 35–36°C) and benzenedimethylamine (BDMA) (Aldrich, 99%) were used as received.

Apparatus and Procedure

The Rigaku 8230 calorimeter coupled with the TAS 100 data storage station was used for data acquisition and analysis by DSC. The DSC was calibrated with high-purity indium.

The reactants IPDGE and HHPA were mixed at room temperature in a 1:1 equivalent ratio. An appropriate quantity of BDMA was then transferred with a microsyringe and mixed thoroughly in a dry chamber. The concentrations of BDMA used were 0.10, 0.25, and 0.50 parts per hundred grams of resin (phr). Approximately 20–30 mg samples of the mixture were weighed accurately to the nearest 0.1 mg into an aluminum DSC sample pan and covered with an aluminum lid. The entire operation was carried out in a dry chamber.

For dynamic cure, the sample was heated using a fully cured mixture as the reference at a rate of 10°C/min from room temperature until 270°C, beyond which decomposition was observed. The com-
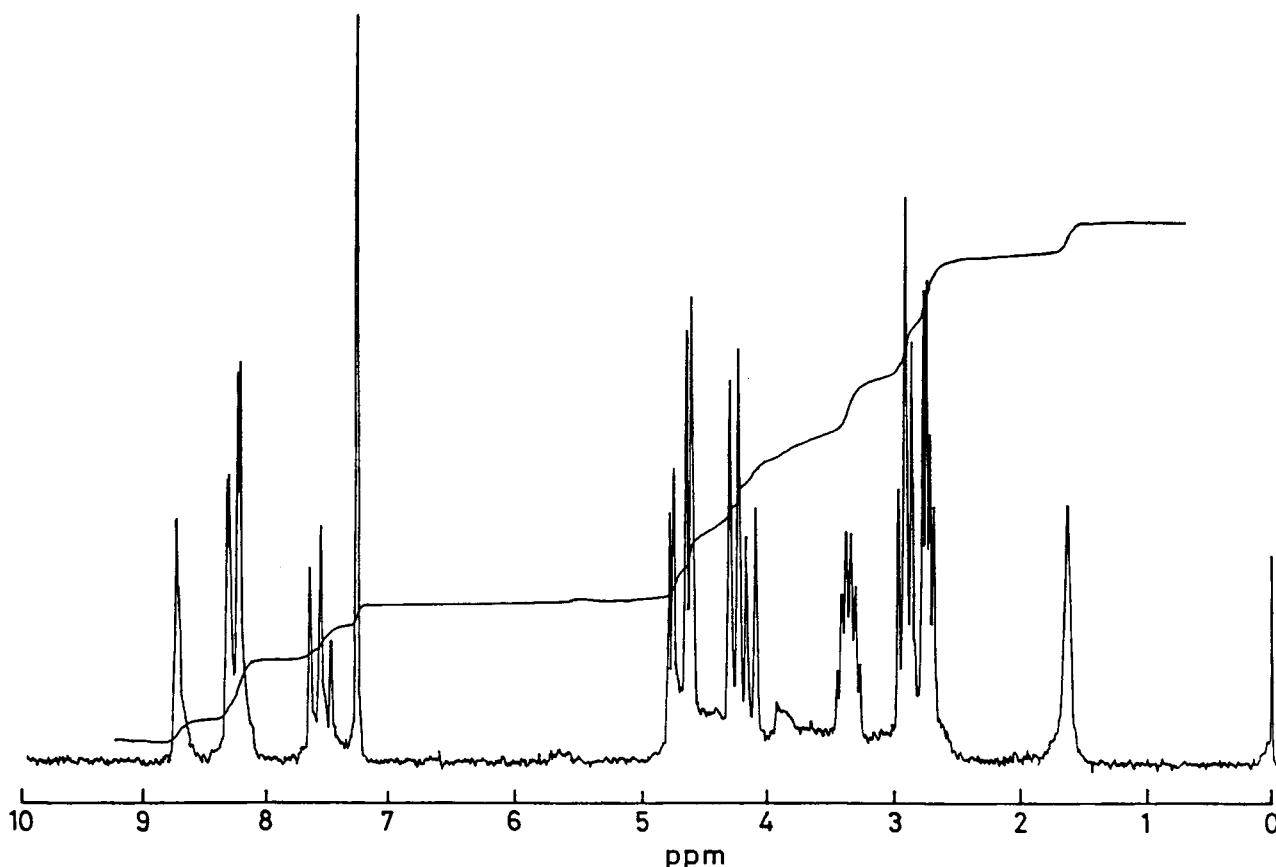
Figure 2 ¹H-NMR spectrum of IPDGE.

plete heat of cure was estimated as the area under the cure exotherm, measured with a planimeter.

A simple procedure was employed in the DSC experiments to minimize the error caused by the unrecorded heat of reaction. The DSC cell was equilibrated at a predetermined temperature before the sample was inserted. A fully cured mixture was used as the reference. A temperature drop of 10–30°C was noticed immediately after insertion of the sample. The data acquisition was started after the DSC cell temperature equilibrated, which usually took about 1 min or less. Since the time lapse was short, it could be reasonably assumed that experimental error due to an unrecorded exotherm was negligible. The exothermic signal was recorded until a steady base line was obtained. The DSC cell was flushed with nitrogen at a flow rate of 30 mL/min.

The isothermal temperatures for each concentration of BDMA were determined from the corresponding dynamic curves. The temperatures were selected from an interval defined between 10°C below the onset of cure and a point midway to the peak maximum. The selected temperatures in each in-

terval were 5°C apart. The isothermal runs were repeated at a number of temperatures and these showed excellent reproducibility.

RESULTS AND DISCUSSION

Figure 3 shows the DSC thermograms for dynamic cure of the IPDGE/HHPA system with 0.10, 0.25, and 0.50 phr BDMA at a heating rate of 10°C/min. The total area under the thermogram, based on the extrapolated base line at the end of reaction, was used to calculate the total heat of reaction ΔH_r. Replicate experiments were performed at each concentration of BDMA and the average values of ΔH_r obtained for each BDMA concentration are shown in Table I.

Figure 4 shows some typical isothermal DSC curves for IPDGE/HHPA system with 0.25 phr BDMA. If the cure reaction is the only thermal event, then the reaction rate $d\alpha/dt$ is directly proportional to the rate of heat generation dH/dt (which is the ordinate of a DSC trace):
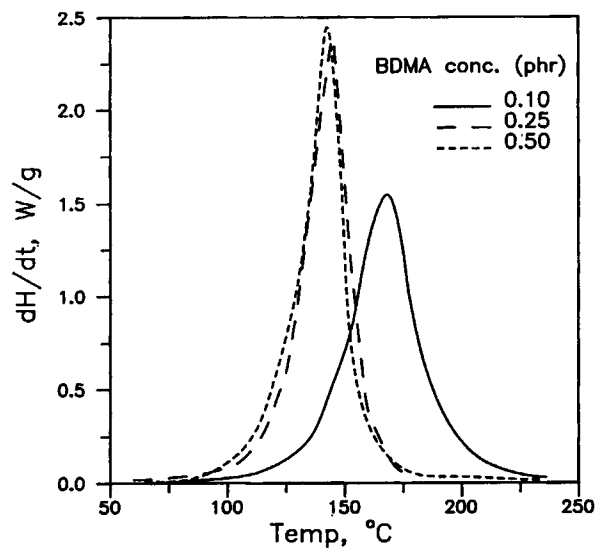
Figure 3 Dynamic DSC curves at a heating rate of 10°C/min for various BDMA concentrations.

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H} \frac{dH}{dt} \qquad (1)$$

where $\Delta H = (\Delta H_r)$ (wt of sample). The extent of reaction, α, is given by

$$\alpha = \frac{\Delta H_t}{\Delta H} \qquad (2)$$

where ΔH_t is the partial area under a DSC trace up to time t.

Figure 5 shows typical plots of reaction rate, $d\alpha/dt$, vs. time, t, at different isothermal temperatures for a given BDMA concentration. The reaction rate at any temperature is seen to increase with time and passes through a maximum while the reaction rate peak becomes higher and shifts to lesser times with an increase in isothermal temperature. A comparison of such curves for different BDMA concentrations at the same temperature, shown in Figure 6, reveals that there is no significant change in reaction rate at BDMA concentrations greater than 0.25 phr.

Table I Total Heat of Reaction of IPDGE/HHPA System Catalyzed by BDMA

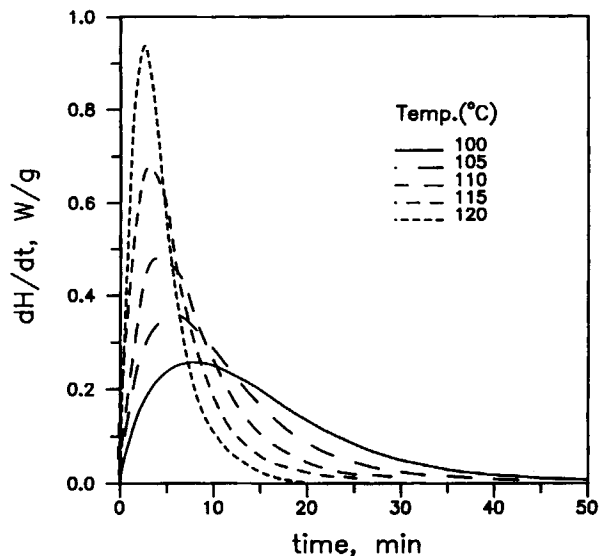| BDMA Concn (phr)	T_{peak} (°C)	ΔH_r (J/g)
0.10	167	291.0
0.25	143	322.6
0.50	141	313.0

Figure 4 Isothermal DSC curves for BDMA concentration of 0.25 phr at different temperatures.

To model the kinetics, it is necessary to derive an equation expressing the rate of conversion, $d\alpha/dt$, as a function of α and temperature. For thermosets that follow nth-order kinetics, $d\alpha/dt$ is proportional to the fraction of material unreacted $(1 - \alpha)$, usually expressed as

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \qquad (3)$$

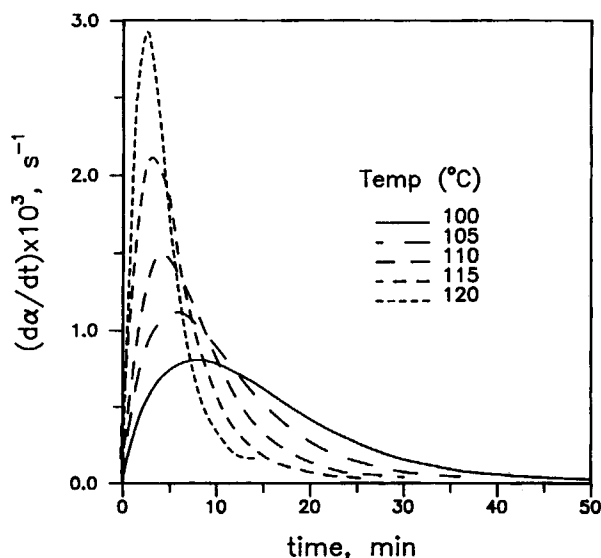where n is the reaction order and k is the specific

Figure 5 Reaction rate, $d\alpha/dt$, vs. time curves at different temperatures for BDMA concentration of 0.25 phr.
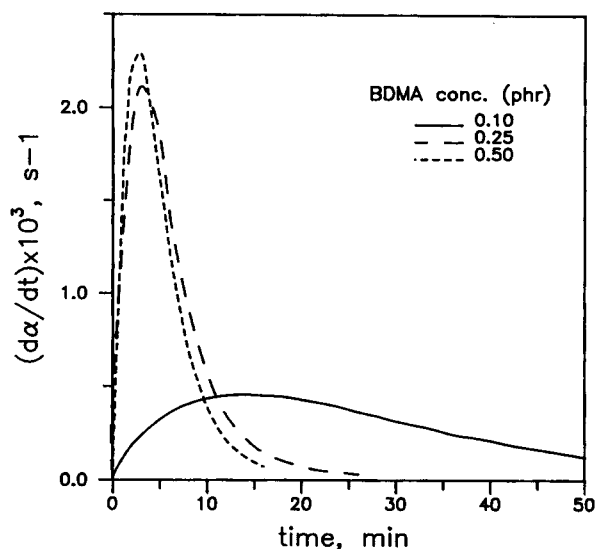
Figure 6 Reaction rate, $d\alpha/dt$, vs. time curves for different BDMA concentrations at 115°C.

rate constant. Systems obeying nth-order kinetics will obviously have the maximum reaction rate at $t = 0$.

Cure reactions that are autocatalyzed can be described by relations such as

$$\frac{d\alpha}{dt} = k'\alpha^m(1 - \alpha)^n \qquad (4)$$

where m and n are the reaction orders and k' is the specific rate constant. According to this model, the rate is zero initially and attains a maximum value at some intermediate conversion. An autocatalyzed thermoset usually has its maximum heat evolution at 30–40% conversion.

The initial rate of autocatalytic reactions is not necessarily zero, since there is a possibility that reactants can be converted into products via alternative paths. To take into account these autocatalytic characteristics, Kamal[21] proposed a generalized expression:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (5)$$

The introduction of four parameters (k_1, k_2, m, n) makes it possible to obtain a good fit to experimental data, and the equation has found successful application for both epoxy and polyester systems. The exponents m and n are often found to be temperature-dependent, so the dependency must be determined over the whole range of temperature.

Figure 7 shows DSC data on the IPDGE/HHPA system with 0.25 phr BDMA plotted as $d\alpha/dt$ vs. α at different temperatures. The plots show a maximum reaction rate at time greater than zero, thereby negating simple nth-order kinetics. Further, the maximum rate is observed at conversions around 30–40%, as expected for an autocatalytic reaction.

The isothermal curves obtained in the present study always gave a finite value of reaction rate when extrapolated to zero time. Such an occurrence of nonzero initial reaction rate in autocatalyzed curing has been reported by several workers.[22,23] Mijovic et al.[22] attributed this to some reactions that are dominant only in the early stages of cure.

Taking into account the above observations, eq. (5), representing autocatalytic systems, was chosen to test the rate data. It may be noted, however, that earlier workers[19] studying the cure of epoxy–anhydride systems have employed nth-order kinetics [eq. (3)] even though isothermal curves showed distinct autocatalytic behavior.

At the start of cure reaction, $t = 0$, $\alpha = 0$; so eq. (5) simplifies to

$$\left.\frac{d\alpha}{dt}\right]_{t=0} = k_1 \qquad (6)$$

Therefore, k_1 can be obtained directly from isothermal reaction rate curves. In the present study, the k_1 values observed were negligibly small, ranging from 1.0×10^{-5} to 1.6×10^{-5} s^{-1} and did not show
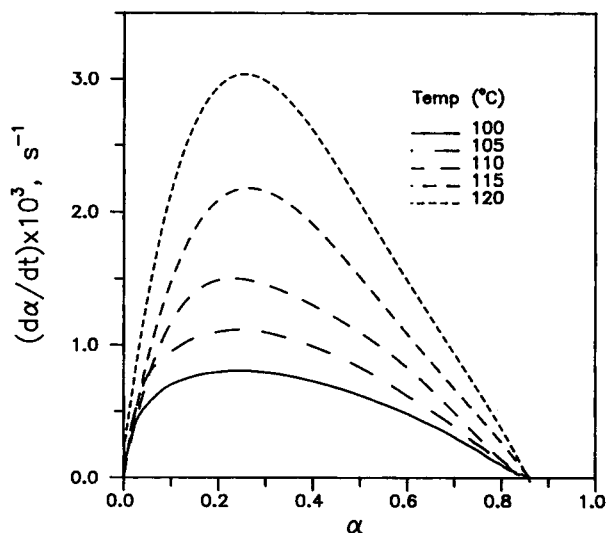

Figure 7 Reaction rate, $d\alpha/dt$, vs. conversion, α, curves at different temperatures for BDMA concentration of 0.25 phr.

any discernible trend with temperature. Since k_1 is very small, the initial reaction rate can be considered to be negligible, suggesting that conversion of reactants into products via alternative paths, if any, is insignificant.

For epoxy–amine systems, Mijovic et al.[22] and Ryan and Dutta[23] determined the remaining parameters assuming that $m + n = 2$. Former workers observed m to increase with increasing temperature, whereas the latter found a decreasing trend. In the present study, the parameters m, n, and k_2 were estimated without any constraints on them, using Marquardt's regression technique.[24] The values of m and n obtained are shown in Table II, whereas k_2 is shown as an Arrhenius plot in Figure 8, which yielded a value of 76 kJ/mol for the associated activation energy. Table II shows that the sum of the exponent factors $(m + n)$ is a constant and approximates to 2, with $m \simeq 0.5$ and $n \simeq 1.5$. The overall reaction order of 2 is in agreement with the observation of Tanaka and Kakiuchi[25,26] that the reaction kinetics of a variety of epoxy–anhydride systems obey second-order kinetics.

Since $k_2 \gg k_1$ and m has a fractional value, the reaction rate at higher conversions $(\alpha > 0)$ can be approximated by

$$\frac{d\alpha}{dt} \simeq k_2 \alpha^m (1 - \alpha)^n \qquad (7)$$

Table II   Values of m and n Estimated at Different Temperatures for Various BDMA Concentrations

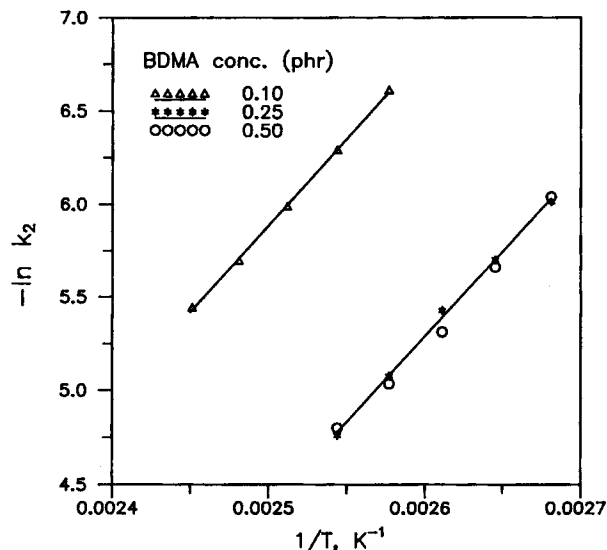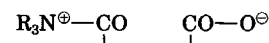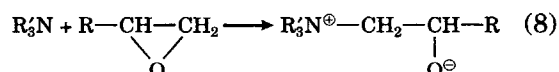| BDMA Concn (phr)	Temperature (°C)	m	n
0.10	115	0.509	1.67
	120	0.490	1.38
	125	0.488	1.58
	130	0.491	1.42
	135	0.549	1.68
0.25	100	0.480	1.52
	105	0.502	1.66
	110	0.491	1.54
	115	0.578	1.78
	120	0.576	1.66
0.50	100	0.463	1.53
	105	0.509	1.57
	110	0.516	1.45
	115	0.559	1.47
	120	0.528	1.43

Figure 8   Arrhenius plot of rate constant k_2 for different BDMA concentrations.

with reaction orders m and n being 0.5 and 1.5, respectively. The order of reaction, according to definition, indicates the number of atoms, molecules, or reactive groups whose concentrations determine the reaction rate. Though it is generally not possible to infer a mechanism from the reaction order alone, it is usually possible to evaluate the order of the reaction if the mechanism is known. Thus, eq. (7) can be shown to be qualitatively in agreement with the general mechanism of tertiary-amine-catalyzed epoxy–anhydride reactions.
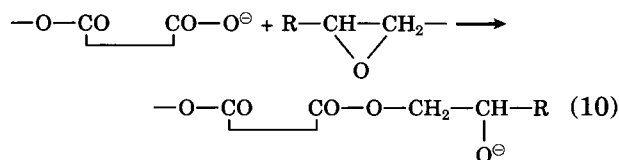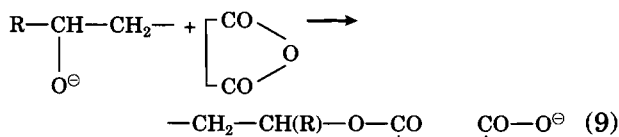
Most authors agree that the mechanism of the reaction is an anionic one. According to Fischer,[27] the reaction is initiated by the anion,

$$R_3N^{\oplus}\text{—}\underset{\underline{\hspace{1.5cm}}}{CO \qquad CO}\text{—}O^{\ominus}$$

formed in a reaction between anhydride and tertiary amine. Tanaka and Kakiuchi[28] said that the propagation is initiated by a reaction between tertiary amine and epoxide, whereas Fedtke and Mirsojew[29] reported that tertiary amine is chemically bound to epoxide. Irrespective of the detailed mechanism, it can be stated that (1) the reaction is initiated by tertiary amine and/or anion formed due to interaction of the tertiary amine with anhydride or epoxy [eq. (8)]:

$$R_3'N + R\text{—}\underset{O}{\underset{\diagdown\diagup}{CH\text{—}CH_2}} \longrightarrow R_3'N^{\oplus}\text{—}CH_2\text{—}\underset{O^{\ominus}}{\overset{|}{CH}}\text{—}R \qquad (8)$$

and (2) propagation proceeds via two reactions involving acylation and esterification in sequence:

$$R-CH-CH_2- + \left[\begin{array}{c}CO\\\\CO\end{array}\right.O \longrightarrow$$
$$\qquad\qquad O^\ominus$$

$$-CH_2-CH(R)-O-\underline{CO\qquad CO}-O^\ominus \quad (9)$$

$$-O-\underline{CO\qquad CO}-O^\ominus + R-CH-CH_2- \longrightarrow$$
$$\qquad\qquad\qquad\qquad\qquad\qquad O$$

$$-O-\underline{CO\qquad CO}-O-CH_2-CH-R \quad (10)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad O^\ominus$$

Thus, although at any stage of reaction both the reacted epoxide and anhydride are present partly as constituents of the alkoxide and partly as carboxylate, the former can react only with anhydride [eq. (9)] and the latter only with epoxide [eq. (10)]. Hence, a fractional order with respect to reacted epoxide and equivalent anhydride [m in eq. (7)] could arise. A fractional order is suggestive of the fact that what we observe is the overall effect of a sequence of elementary reactions and not of a single elementary reaction step. In the present study, m is found to be approximately 0.5, showing a half-order with respect to reacted functional groups. Moreover, since $m + n = 2$, an overall order of 2 is indicated, which is in agreement with the reaction mechanisms reported by several workers.[25,26]
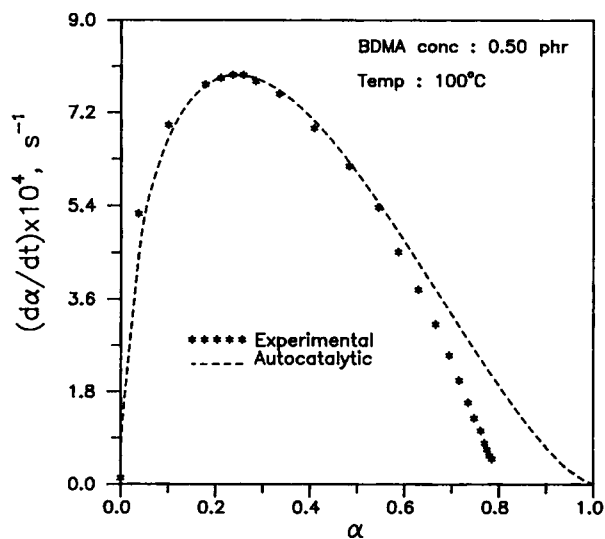
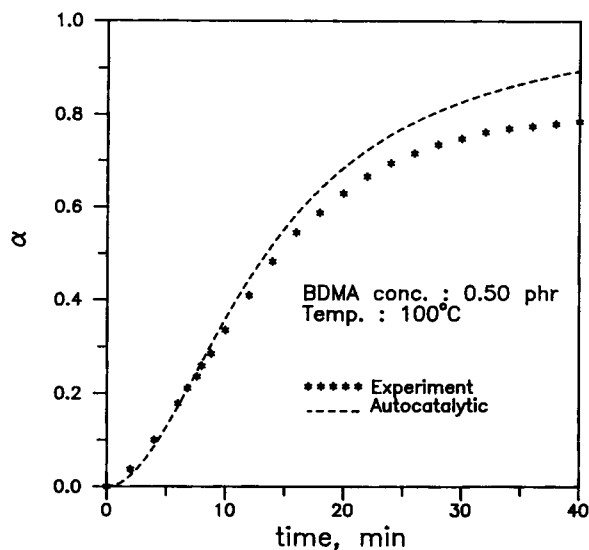Figures 9 and 10 present typical comparisons be-

Figure 10 Comparison of experimental data with autocatalytic model: conversion, α, vs. time.

tween experimental data and predictions of the autocatalyzed model [eq. (5)], with values of model parameters determined above. A good agreement is observed up to 60% conversion, after which significant deviations are observed due to the onset of gelation. As the cure progresses and the resin crosslinks, the glass transition temperature, T_g, of the system rises. When it approaches the curing temperature, the resin passes from a rubbery state to a glassy state. At this stage, the mobility of the reacting groups is hindered and the rate of conversion is controlled by diffusion rather than by chemical factors. This accounts for the fact that the experimental conversion and reaction rates are lower than those predicted by eq. (5). In the present work, this change in the controlling mechanism is observed in all cases, necessitating modification of the autocatalytic relationship by inclusion of a diffusion term.

Various workers have attempted mathematical treatment of the above type of diffusion phenomenon.[30–36] A typical approach[32] is to express T_g in terms of α using DiBenedetto's equation and then to express the diffusion-controlled rate constant in terms of $T - T_g$ by a Williams–Landell–Ferry-type equation. This leads to a rather complex relationship. Chern and Poehlein[31] proposed a somewhat simpler semiempirical relationship based on free-volume considerations to explain the diffusion control in cure reactions.

When the degree of cure reaches a critical value α_c, diffusion becomes controlling and the rate constant k_d is then given by

Figure 9 Comparison of experimental data with autocatalytic model: reaction rate, $d\alpha/dt$, vs. conversion, α.
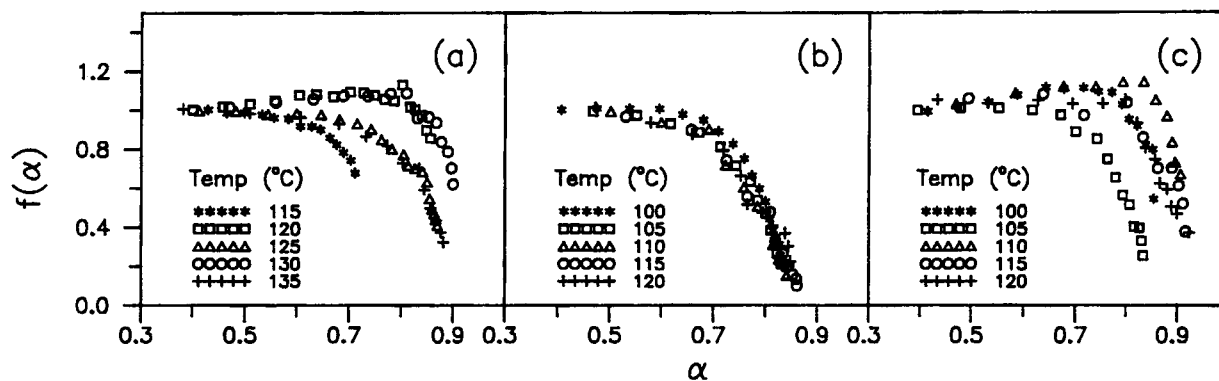
Figure 11   Plots of diffusion factor, $f(\alpha)$, vs. conversion, α, at different temperatures for various BDMA concentrations: (a) 0.10 phr; (b) 0.25 phr; (c) 0.50 phr.

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \qquad (11)$$

where k_c is the rate constant for chemical kinetics and C is a constant. Equation (11) corresponds to a rather abrupt onset of diffusion control at $\alpha = \alpha_c$, though, in reality, the onset is somewhat more gradual and there is a region where both chemical and diffusion factors are controlling. According to Rabinowitch,[37] the overall effective rate constant, k_e, can be expressed in terms of k_d and k_c as follows:

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \qquad (12)$$

Combining eqs. (11) and (12), a diffusion factor $f(\alpha)$ can be defined as follows:

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \qquad (13)$$

For $\alpha \ll \alpha_c$, $f(\alpha)$ approximates unity and the effect of diffusion i? negligible. As α approaches α_c, $f(\alpha)$ begins to decrease, reaching a value of 0.5 at $\alpha = \alpha_c$ and beyond this point approaches zero as the reaction effectively stops. The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$.

In this study, $f(\alpha)$ was obtained as the ratio of experimental reaction rate to the reaction rate predicted by the autocatalytic model [eq. (5)]. Figure 11 shows the behavior of $f(\alpha)$ with increasing conversion at different temperatures, for the epoxy–anhydride system using different BDMA concentrations. The decrease in $f(\alpha)$ and, hence, in the effective reaction rate due to onset of diffusion at higher conversions is clearly seen. Values of α_c and C obtained by applying nonlinear regression to $f(\alpha)$ vs. α data are listed in Table III. For α_c, temperature

variations over the limited range (20°C) studied showed little effect. For the coefficient C, on the other hand, there was scatter and no discernible trend emerged. It may also be noted that Cole et al.[38] in their studies on epoxy–amine curing did not observe any trend for variations of C with temperature, though α_c was found to increase by 30% for a 40°C increase in temperature.

It may be noted that the critical conversion is not an adjustable parameter because it reflects the onset of diffusional limitation that occurs only in the later stages of reaction. It is also not an observable quantity since the transition to the diffusion regime is gradual. As cure proceeds, the mobility of the reacting species is reduced and this leads to diffusional

Table III   Values of Critical Conversion, α_c, and the Constant C at Different Temperatures for Various BDMA Concentrations

BDMA Concn (phr)	Temperature (°C)	α_c	C
0.10	115	0.758	18.2
	120	0.864	17.2
	125	0.861	19.7
	130	0.811	17.7
	135	0.856	19.7
0.25	100	0.766	22.8
	105	0.785	22.9
	110	0.774	22.1
	115	0.778	19.4
	120	0.765	20.2
0.50	100	0.741	22.3
	105	0.804	26.5
	110	0.842	32.2
	115	0.903	27.6
	120	0.894	26.9

effects. Hence, α_c would reflect the state of cure of the system rather than the temperature of cure.

Figures 12 and 13 show the results for one resin composition at each temperature, where the experimental values of $d\alpha/dt$ are compared with those calculated by the autocatalytic model, coupled with the diffusion factor, according to eq. (13). The agreement is excellent. A similar agreement between experimental and predicted values was obtained for the other resin compositions used.

CONCLUSIONS

A phenomenological kinetic model has been proposed with which it is possible to calculate accurately

the degree of conversion of catalyzed epoxy–anhydride systems over the whole range of cure. The epoxy resin used is a model diglycidyl ester, bis-(2,3-epoxypropyl) - 1, 3 - benzenedicarboxylate, hitherto not studied from a kinetic viewpoint. Hexahydrophthalic anhydride has been used as the curing agent and benzyldimethylamine as the catalyst. Since all isothermal DSC cure curves for the system show the maximum rate of heat evolution only around 30–40% conversion, a mathematical expression representing autocatalytic kinetics instead of the nth-order kinetics has been used. Previous workers,[19] however, adopted nth-order kinetics to explain the anhydride cure of similar diglycidyl esters, though DSC curves had autocatalytic features in them.
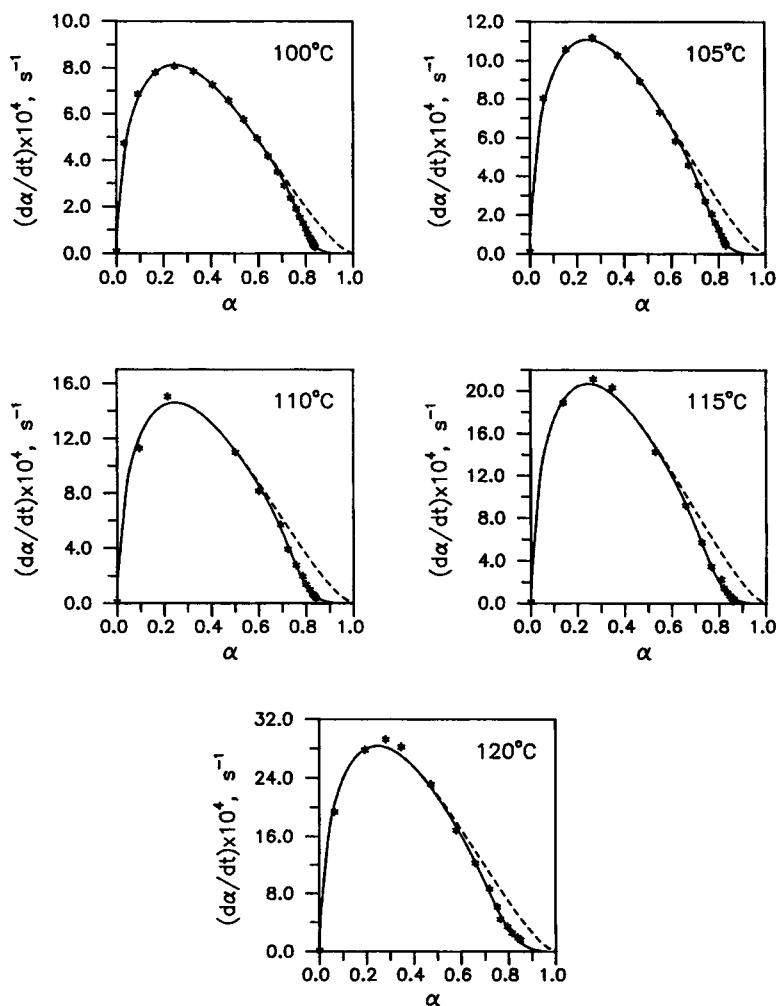
A four-parameter semiempirical equation for au-

Figure 12 Comparison of experimental data with model predictions at different temperatures for BDMA concentration of 0.25 phr: reaction rate, $d\alpha/dt$, vs. conversion, α: (∗∗∗) experimental; (----) autocatalytic model [eq. (5)]; (——) autocatalytic model with diffusion [eqs. (5) and (12)].
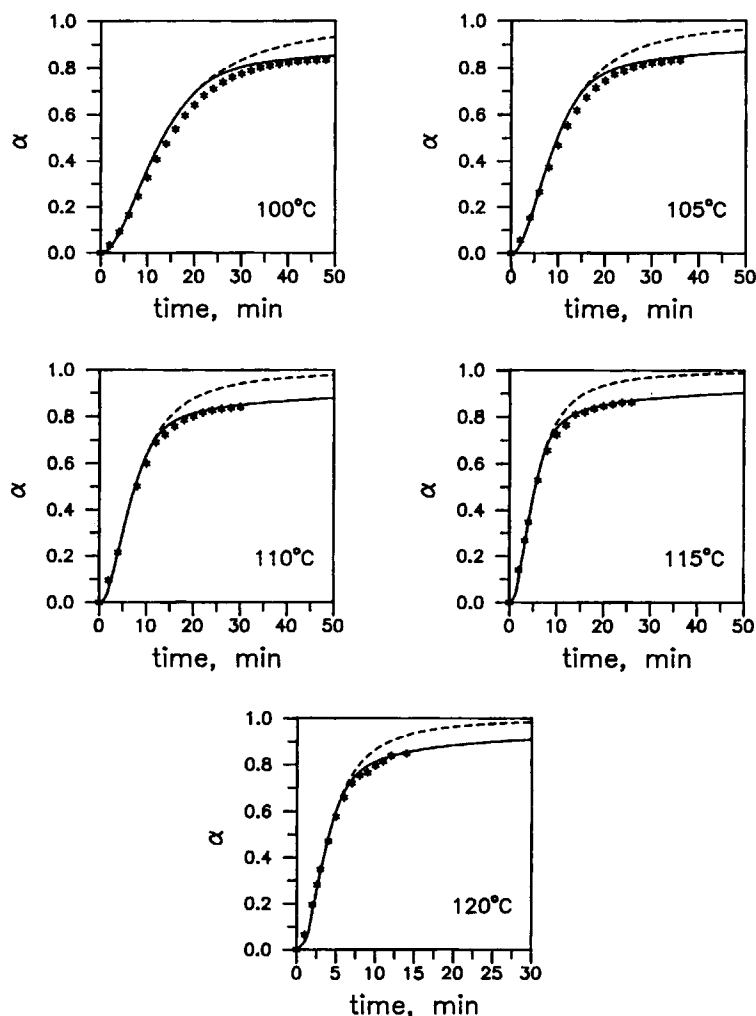
Figure 13 Comparison of experimental data with model predictions at different temperatures for BDMA concentration of 0.25 phr: conversion, α, vs. time: ($***$) experimental; (----) autocatalytic model [eq. (5)]; (——) autocatalytic model with diffusion [eqs. (5) and (12)].

tocatalytic systems proposed by Kamal[21] that contained two rate constants, k_1 and k_2, and two reaction orders, m and n, provided a good fit to the experimental data up to the point of vitrification. The rate constant k_1 was found to be negligibly small, being two orders of magnitude smaller than k_2. The predominant rate constant k_2 showed an excellent Arrhenius fit to temperature, yielding a value of 76 kJ/mol for activation energy. The orders m and n, determined without imposing any constraint, did not vary with temperature. They averaged to a value of 0.5 and 1.5, respectively. The above equation is thus ideal as a kinetic model for the present resin system at conversions below the point of vitrification.

To describe the cure in the postvitrification region, a diffusion factor has been introduced on the

basis of a combination of two equations proposed by other workers.[31,37] With the inclusion of this factor, it is possible to calculate with excellent precision the degree of conversion over the whole range of cure and temperature ($100-135°C$) studied.

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