Study of an Epoxy System Cured with Different Diamines by Differential Scanning Calorimetry

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ABSTRACT: Kinetic and cured reaction experiments for five systems based on the epoxy resin diglycidyl ether of bisphenol A (DGEBA) cured with the diamines 1,3-bisaminomethylcyclohexane, 4-4'-diaminediphenylmetane, 1,4-phenylediamine, 4-4'(1,3-phenylenediisopropylidene) bisaniline, and 4-4'metilenebis(2,6-dietilaniline) were carried out by differential scanning calorimetry. Kinetic analysis was performed using dynamic experiments through the Kissinger and Flynn–Wall–Ozawa methods. The isothermal experimental data showed an autocatalytic behavior compared with the model proposed by Kamal. Activation energy and kinetic parameters were determined by fitting experimental data. This model provided a good description of the cure kinetics up to onset of vitrification. Diffusion control was incorporated to describe the postvitrification region. By combining the autocatalytic model and the diffusion factor, it was possible to predict the cure kinetics over the whole conversion range. The behavior of the cure kinetics of the DGEBA was similar with all the diamines used. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1759–1768, 2007

Key words: differential scanning calorimetry (DSC); diffusion; kinetics (polym.); resins

INTRODUCTION

The study of the reaction kinetics of epoxy cured with an amine as hardener by differential scanning calorimetry (DSC) has been discussed in the literature.[1–3] Assuming the heat evolved during cure is proportional to the extent of reaction, kinetic parameters have been determined from both isothermal and dynamic experimental data.

Epoxy-aromatic diamines reactions usually follow the scheme of Horie et al.[4] The autocatalytic behavior of epoxy cures has also been discussed,[1,2] and it has been suggested that the curing process is governed by more than a single rate constant.

Despite considerable current research of diglycidyl ether of bisphenol A (DGEBA) cured with diamines,[5–9] its kinetics with several different diamines, 1,3-BAC,[10–12] DDM,[13] pPDA,[14] MDEA,[15] and BSA, was investigated, and to add a third component-forming ternary system later, some have been studied with thermoplastics[16,17] and with polyhedral oligomeric silsesquioxanes (POSS).[18,19]

In contrast, calorimetry is a powerful method for directly measuring the rate of exothermic polymerization. The differential scanning calorimetry technique has the advantage of being the only reaction rate method that allows the reaction rate, the degree of conversion, as well as the temperature gradient of the vanished DSC cell to be measured with great accuracy. Therefore, DSC kinetics provide the variables required for solution of the heat/mass transfer equations, namely, heat flow (proportional to the rate of reaction) and heat generation (proportional to the degree of conversion).

In this work, isothermal and dynamic experiments by DSC were used to study the Kissinger and Flynn–Wall–Ozawa dynamic kinetic models and the Kamal isothermal method. The change from chemical kinetic control to control by diffusion with advancement of curing was also analyzed.

Theoretical

It is well known that the curing of epoxy resin is complex, including several reaction processes. Isothermal and dynamic models may be used to characterize the curing behavior for the attainment of some parameters including reaction activity energy, frequency factor, and reaction order.

Kinetic analysis was performed using three kinetic models: the Kissinger method,[20] the Flynn–Wall–Ozawa method,[21,22] and the Kamal-method phenomenological model.[23]

If it is assumed that the extent of reaction, α, is proportional to the heat generated during the reaction, the reaction rate can be expressed by the general law

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where t is the time, $k(T)$ is the rate constant, and $f(\alpha)$ is a function of the dependence of conversion.

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TABLE I
Characteristics of Different Diamines Used

Diamine	Molecular weight (g/mol)	Melting point (°C)	Molecular formula
1,3-BAC	142.25		
DDM	198.26	88–92	
p-PDA	108.14	138–143	
BSA	344.50	110–114	
MDEA	310.48	88–90	

The rate equation for dynamic curves in its integrated form can be expressed as

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T)t \qquad (2)$$

The dependence of the rate constant, $k(T)$, on temperature may be described by the Arrhenius expression

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \qquad (3)$$

where A is the frequency factor, E is the activation energy, and R is the universal gas constant.[3,24]

The Flynn–Wall–Ozawa and Kissinger methods assume that the DSC exothermal peak is isoconversional and that its value is independent of the heating rate.

The values of the second member [eq. (2)] can be expressed through a polynomial function. Using a Doyle's approximation,[25] a constant conversion, it will be fulfilled as
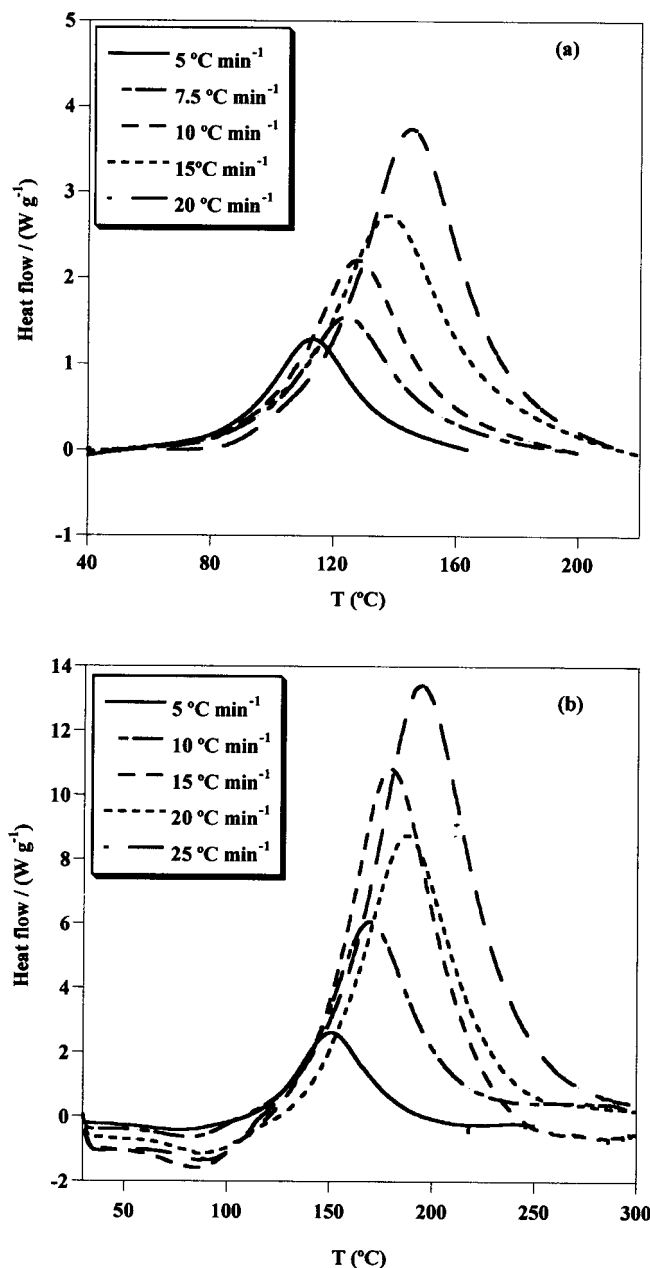
$$\log q = A' - 0.457 \frac{E}{RT} \qquad (4)$$

where for each degree of conversion, A' is a constant that takes the value of

$$A' = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 \qquad (5)$$

and q is the reaction rate.

Using eq. (4), E and the constant A' can be determined from the slope and from extrapolation with the horizontal axis of the linear fitting of $\log q$ against the inverse temperature, respectively.

Figure 1 Heat flow measured by DSC cured under various heating rates for the DGEBA/pPDA and DGEBA/BSA systems.

TABLE II
Peak Temperatures of All Systems Measured by DSC in Dynamic Scans

q (°C/min)	DGEBA/1,3-BAC (°C)	DGEBA/DDM (°C)	DGEBA/p-PDA (°C)	DGEBA/BSA (°C)	DGEBA/MDEA (°C)
2.5	70.3	—	—	—	—
5	81.2	139.6	113.1	151.4	203.5
7.5	98.7	150.1	123.8	—	—
10	106.4	156.7	127.9	170.7	223.1
15	—	169.1	138.5	180.1	233.3
20	—	177.7	145.0	188.2	243.0

Assuming that when the exothermic peak is reached, the degree of conversion is independent of the heating rate, eq. (4) can be applied directly,[26] performing log q against the inverse of the temperature of the exothermic peak, T_p.

According to the Kissinger method, the activation energy can be obtained from the maximum reaction rate, where $[d(d\alpha/dt)]/dt$ is zero at a constant heating rate. The resulting relation can be expressed as

$$\frac{d\left[\ln\left(q/T_p^2\right)\right]}{d\left(1/T_p\right)} = -\frac{E}{R} \quad (6)$$

Therefore, a plot of $\ln(q/T_p^2)$ versus the reciprocal of T_p gives the activation energy without the need to make any assumption about the conversion-dependent function.

As the curing process had a finite reaction rate at time zero, a rate equation proposed by Sourour and Kamal[1] was used for the treatment of the isothermal experiments:

$$\frac{d\alpha}{dt} = \left(k_1 + k_2\alpha^m\right)(1-\alpha)^n \quad (7)$$

where, as in other works,[10,17,27] k_1, and k_2 are constants related to the rate constants of the two reactions with two different activation energies, and m and n and $m + n$ are the two empirical preexponential factors, the reaction order and the overall reaction order, respectively.

EXPERIMENTAL

Materials

The studied systems were based on a commercial diglycidyl ether of bisphenol A (DGEBA), Araldite/GY260, from Ciba-Geigy (Barcelona, Spain) that had a weight per epoxy equivalent of 188 g/eq. Five diamines were used as curing agents: 4-4′-diaminediphenylmetane (DDM), from Fluka (Buchs, Switzerland); and 1,4-phenylediamine (pPDA), 4-4′(1,3-phenylenediisopropylidene) bisaniline (BSA), 1,3-bisaminomethylcyclohexane (1,3-BAC), and 4-4′metilenebis(2,6-dietilaniline) (MDEA), all from Aldrich Chemical

(Milwaukee, WI). All components were commercial products with more than 98% purity and were used without further purification. The characteristics and
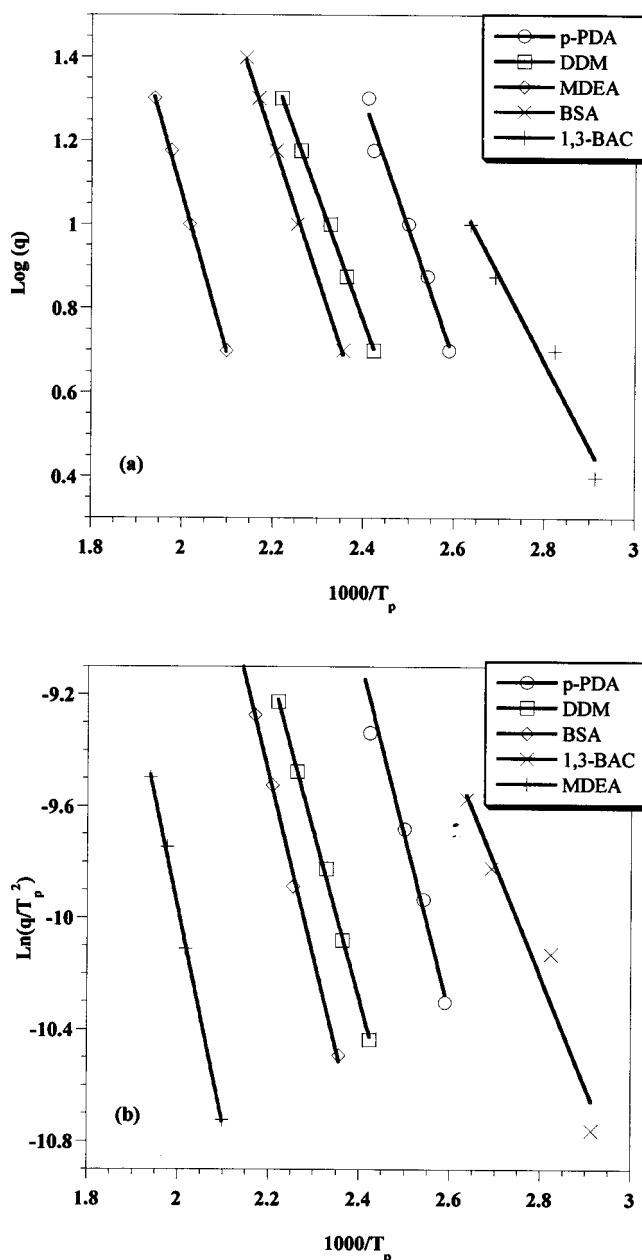

Figure 2 (a) Flynn–Wall–Ozawa plots and (b) Kissinger plots for the DGEBA/diamine systems applied at the exotherm peak.

System	E_K (kJ/mol)	R^2 Kissinger	E_O (kJ/mol)	R^2 Ozawa
DGEBA/1,3-BAC	32.92	0.946	28.32	0.961
DGEBA/DDM	49.80	0.998	51.42	0.998
DGEBA/pPDA	52.20	0.993	55.96	0.994
DGEBA/BSA	54.75	0.998	59.11	0.998
DGEBA/MDEA	64.23	0.998	71.57	0.999

molecular formulas of these diamines are shown in Table I.

Epoxy resin/diamine mixtures in a stoichiometric amine/epoxy ratio of 1 were prepared. The DGEBA/ 1,3-BAC system was stirred at room temperature and quickly was enclosed because the reaction was very fast. The diamines DDM and pPDA were dissolved in tetrahydrofuran at room temperature and heated in
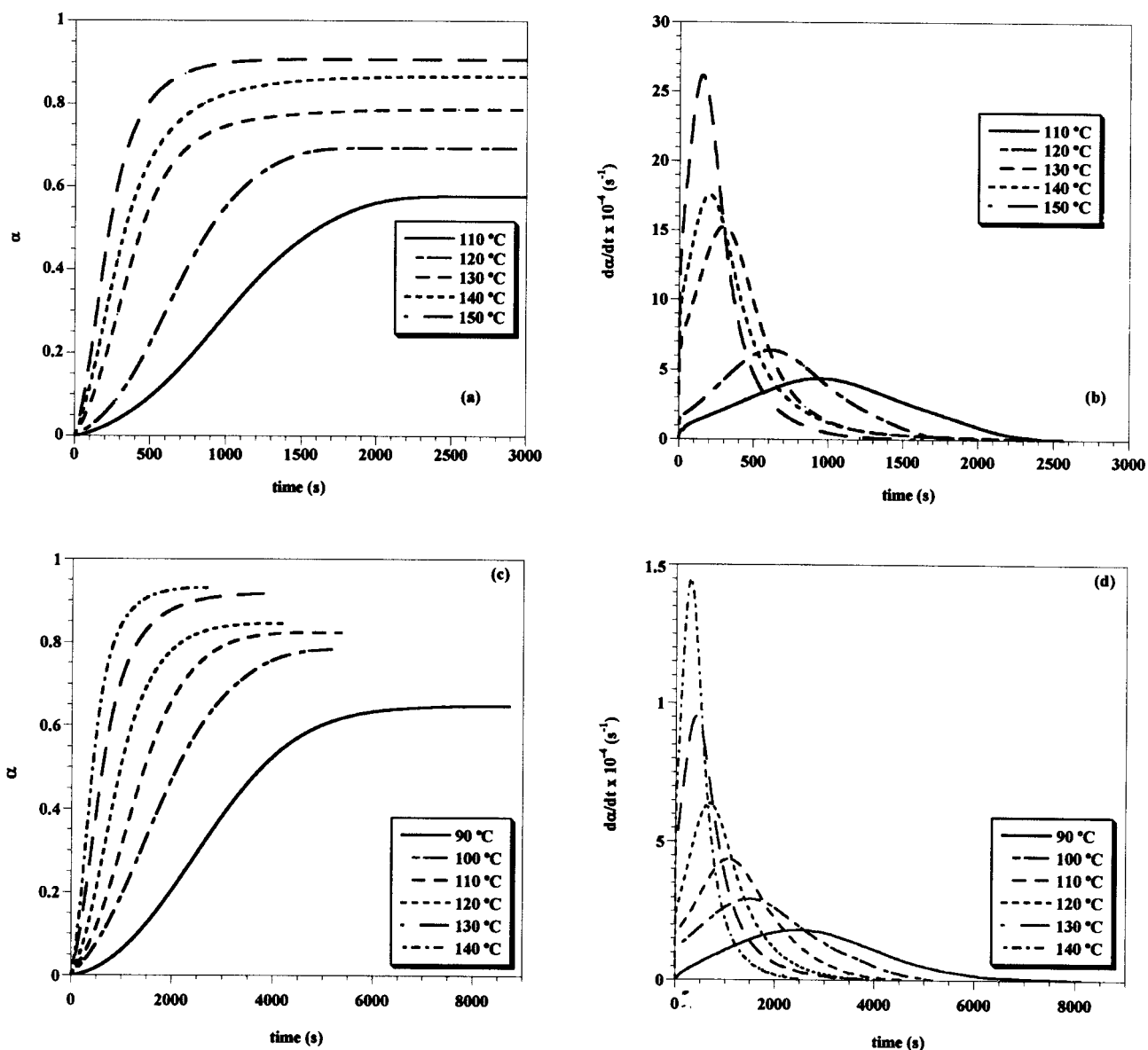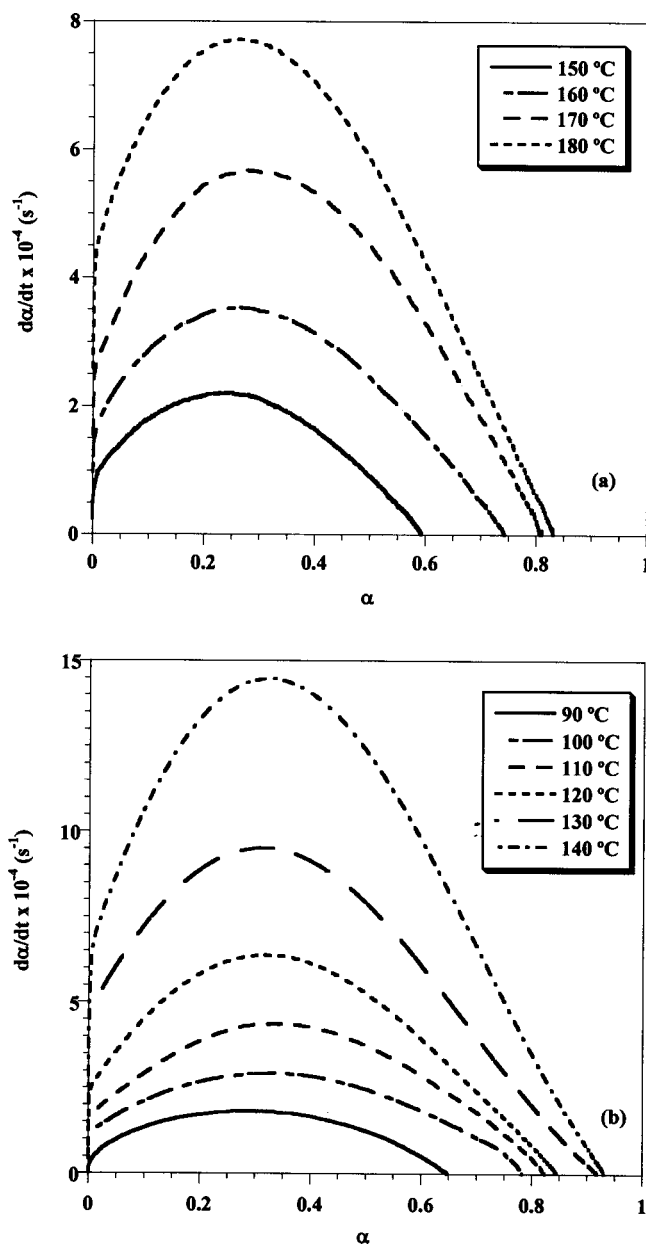

Figure 3 Curves at curing temperature studied of (a) reaction rate versus time for DGEBA/DDM, (b) conversion versus time for DGEBA/DDM, (c) reaction rate versus time for DGEBA/BSA, and (d) conversion versus time for DGEBA/BSA.

Figure 4 Curves of reaction rate, $d\alpha/dt$, versus conversion, α, at different temperatures: (a) DGEBA/MDEA and (b) DGEBA/BSA.

an oven to 60°C, and then the DGEBA was mixed in. For the preparation of the DGEBA/BSA and DGEBA/MDEA systems, the epoxy resin was heated in an oven to 120°C and 100°C, respectively, and diamine was added, always with continuous stirring for several minutes.

Instrumentation

A differential scanning calorimeter (DSC7, Perkin–Elmer, Norwalk, CT) equipped with an intracooler and supported by a Perkin–Elmer computer for data acquisition/analysis was used for the dynamic and

isothermal cure experiments and data analysis. Termal response and temperature were calibrated with the heat of fusion and melting point of pure indium. A dry nitrogen flow of 40 mL/min was used as the purge sample. Samples of 5–8 mg were enclosed in aluminum DSC capsules.

For the dynamic heating experiments, heating rates between 2.5°C/min and 25°C/min were investigated in order to calculate the total heat of reaction, ΔH_0, and were generated to reach full conversion. A second scan was performed to determinate the glass-transition temperature. Figure 1 shows the heat flow measured by DSC at various heating rates for the DGEBA/pPDA and DGEBA/BSA systems.

Isothermal experiments were carried out from 60°C to 170°C, according to the system, in order to obtain cure rate and extent of cure as a function of time. The reaction was considered complete when the signal leveled off to baseline. A second scan was performed to determinate the right baseline for each experiment. The isothermal conversion at time t was defined as $\alpha(t) = \Delta H_t/\Delta H_0$, where ΔH_t is the heat under the exotherm curve at time t, calculated by interpolation of the DSC isothermal signal.

RESULTS AND DISCUSSION

Dynamic methods

The Kissinger and Flynn–Wall–Ozawa methods assume that the DSC exothermic peak is isoconversional and that its value is independent of the heating rate. These two methods were applied to the data obtained in the dynamic heating experiments, which are shown in Table II for all systems. The temperature of the maximum rate increased with an increase in the heating rate. The fastest reactions were with 1,3-BAC as hardener, and the slowest were with MDEA as hardener.

By applying these methods, represented in eqs. (4) and (6) (Fig. 2), the activation energies could be determined from the slopes, with the values obtained by the Flynn–Wall–Ozawa method slightly higher but not significantly different than those obtained by the Kissinger method for the four systems.[7,28] The DGEBA/1,3-BAC system showed higher activation energies with the Kissinger method than with the

TABLE IV
Activation Energies and Preexponential Factors for All Epoxy/Diamine Systems

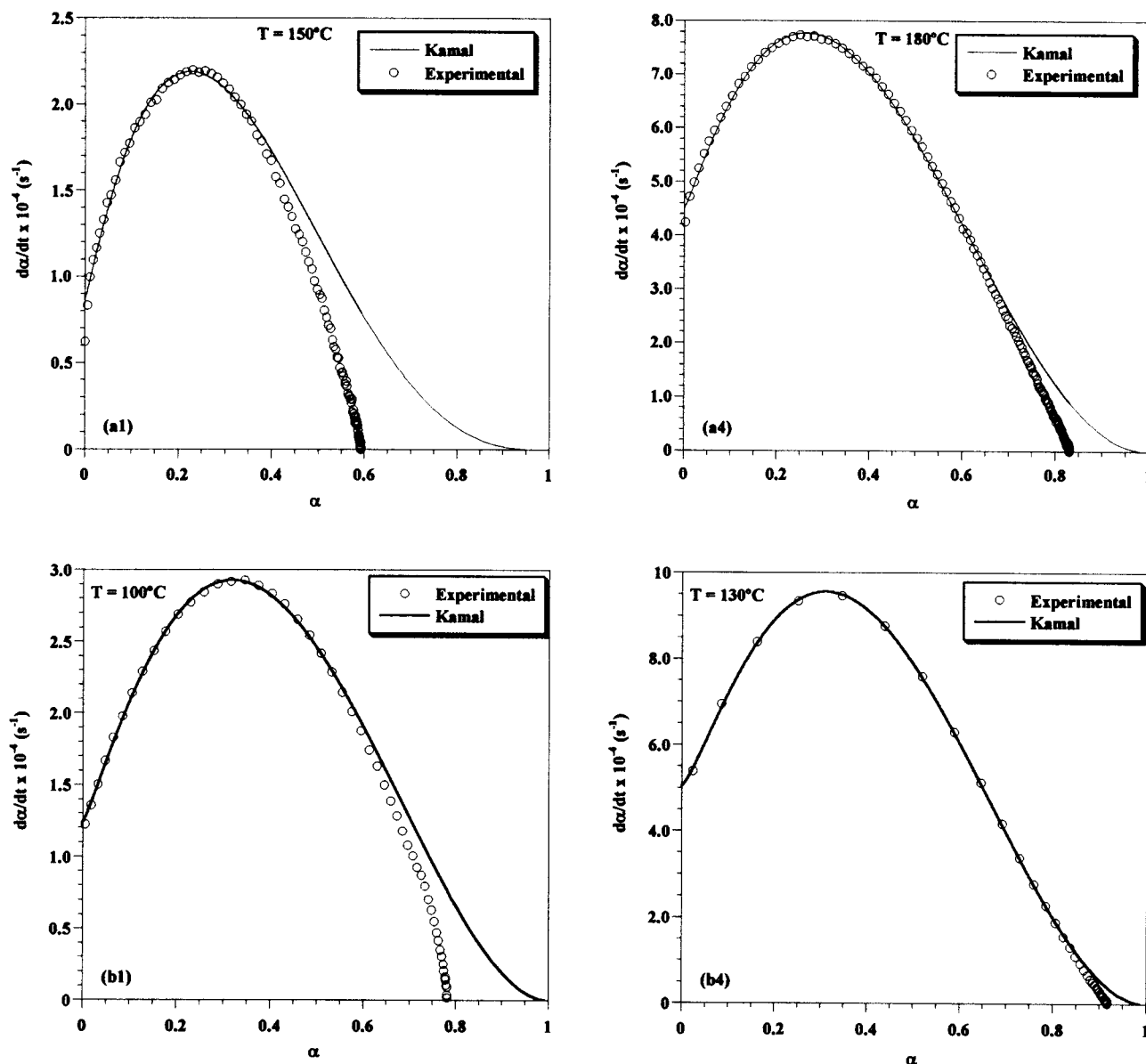| System	E_1 (kJ/mol)	E_2 (kJ/mol)	$\ln A_1$	$\ln A_2$
DGEBA/1,3-BAC	44.0	57.0	8.69	14.12
DGEBA/DDM	94.3	61.5	20.49	13.61
DGEBA/p-PDA	81.9	44.3	18.62	9.84
DGEBA/BSA	58.8	43.3	9.87	7.90
DGEBA/MDEA	86.5	47.5	15.27	7.19

Figure 5 Curves of reaction rate versus conversion with model predictions for (a) DGEBA/MDEA and (b) DGEBA/BSA.

Flynn–Wall–Ozawa method, but they were comparable (see Table III).

Isothermal method

For determination of the cure kinetics first through an autocatalytic model (initial reaction rate was not zero), the isothermal cure in DSC was performed at several temperatures. Then the experimental rate equation [α, $d\alpha/dt$] was determined for the complete course of the reaction, and finally, the experimental results were fitted with the kinetic equation. Thus, the reaction orders and rate constant for each temperature were obtained, and the activation energies and frequency factors were determined.

The kinetics of epoxy–amine reactions have been well established in the literature.[5–7] On the basis of the results

shown in Figure 1, the isothermal curing temperatures for the DGEBA/BSA system from 90°C to 140°C were determined. A similar procedure was followed for the other systems. Figure 3 shows isothermal reaction rate versus time for the DGEBA/DDM and DGEBA/BSA systems and conversion versus time. The autocatalytic nature of each system studied was similar, with a maximum rate of conversion after the start of the reaction.

The overall heat evolved in the reaction was determined as the average reaction heat calculated in each thermogram. The overall heat evolved was 495.5 J/g for DGEBA/1,3-BAC, 539.1 J/g for DGEBA/DDM, 526.3 J/g for DGEBA/pPDA, f 367.2 J/g or DGEBA/BSA, and 378.3 J/g for DGEBA/MDEA.

The parameters of eq. (7) were obtained from experimental data through the use of a method proposed by Kamal.[23] The parameters m, n, k_1, and k_2 were esti-
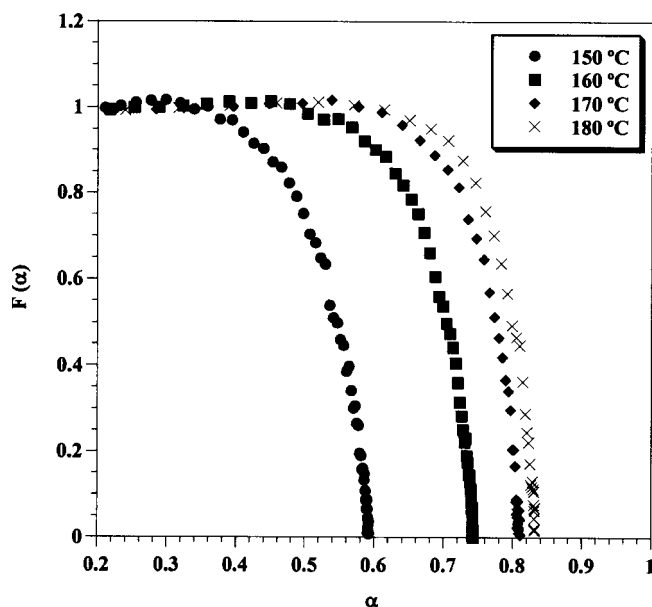
Figure 6 Plot of diffusion factor, $f(\alpha)$, versus conversion, α, for DGEBA/MDEA.

mated without any constraints on them by fitting the experimental data shown in Figure 4 to eq. (7) using a least-squares method. The values of m and n were based on the assumption that the reactions followed first- or second-order autocatalytic reaction kinetics.

Barton[29] showed that $m = n = 1$. However other authors observed that $m + n = 2$, but m increases from 0.6 to 1.2 with increasing temperature.[2] Thus, both m and n can have fractional values. Our systems yielded values of m from 0.6 to 1.3, in good agreement with other systems, and these values remained constant or decreased with an increase in the curing temperature. The values of n were more variable, varying from 2 to 3, which yielded $m + n$ values from about 2.6 for the system with 1,3-BAC and to close to 4 for the system with p-PDA.

In eq. (7), the rate constants k_1 and k_2 are temperature dependent through an Arrhenius relationship as eq. (3). From these two kinetic constants, k_1 and k_2, two activation energies, E_1 and E_2, could be obtained by plotting $\ln k_1$ and $\ln k_2$, respectively, versus reciprocal temperature. E_1 and E_2 and the preexponential factors associated with parameters k_1 and k_2 obtained for all the systems are listed in Table IV.

It is generally accepted that progress of the curing of thermosetting resins has two distinct stages: a chemically controlled stage and a diffusion-controlled stage. In the early stage of curing (before gel or vitrification), cure reactions are mainly controlled by the kinetic rate of the chemical reaction. Subsequently, the cure reaction reaches higher conversions, where the reaction gradually becomes diffusion controlled.[30–32] When a system reaches the gel point, a network is gradually formed with an infinite molecular weight, the viscosity

of the system increases significantly, and the system is transformed from a liquid/rubbery state to a glassy state. Generally, formation of macromolecular networks is accompanied by a considerable increase in the glass-transition temperature of the reacting system. In such a case, segmental motion of the system is slowed, and the chemical reaction is controlled by these mechanisms rather than by reactivity. Therefore, to model a reaction or a cure process, the diffusion control mechanism must be taken into account.

Figure 5 shows a comparison of the DGEBA/MDEA and DGEBA/BSA experimental data and the model-fitted results of the Kamal model [eq. (7)]. It can be seen that the results agreed well in the initial stage of the reaction. The data from the Kamal model were greater than the experimental results. These results show that a deviation from the prediction by the original model will occur if diffusion control in the latter stage of the reaction is not considered. The other systems behaved in a similar manner.

As the cure process proceeds and the resin crosslinks, the glass-transition temperature, T_g, of the system rises. When it approaches the curing temperatures, 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 experimental conversion and reaction rates being lower than those predicted by eq. (7). In

TABLE V
Critical Conversion, α_c, and Parameter C Values for Each Epoxy System

System	Temperature (°C)	α_c	C
DGEBA/1,3-BAC	70	0.68	14.78
	80	0.71	18.10
	90	0.79	25.33
	100	0.86	20.02
	110	0.86	43.24
DGEBA/DDM	110	0.55	18.27
	120	0.67	16.65
	130	0.72	18.18
	140	0.85	20.55
	150	0.90	22.54
DGEBA/pPDA	80	0.66	56.94
	90	0.69	83.87
	110	0.76	38.74
	120	0.82	36.02
DGEBA/BSA	90	0.60	21.05
	100	0.78	19.06
	110	0.81	35.62
	120	0.83	30.96
	130	0.90	52.98
	140	0.92	43.91
DGEBA/MDEA	150	0.55	22.15
	160	0.71	22.76
	170	0.78	24.95
	180	0.80	25.71
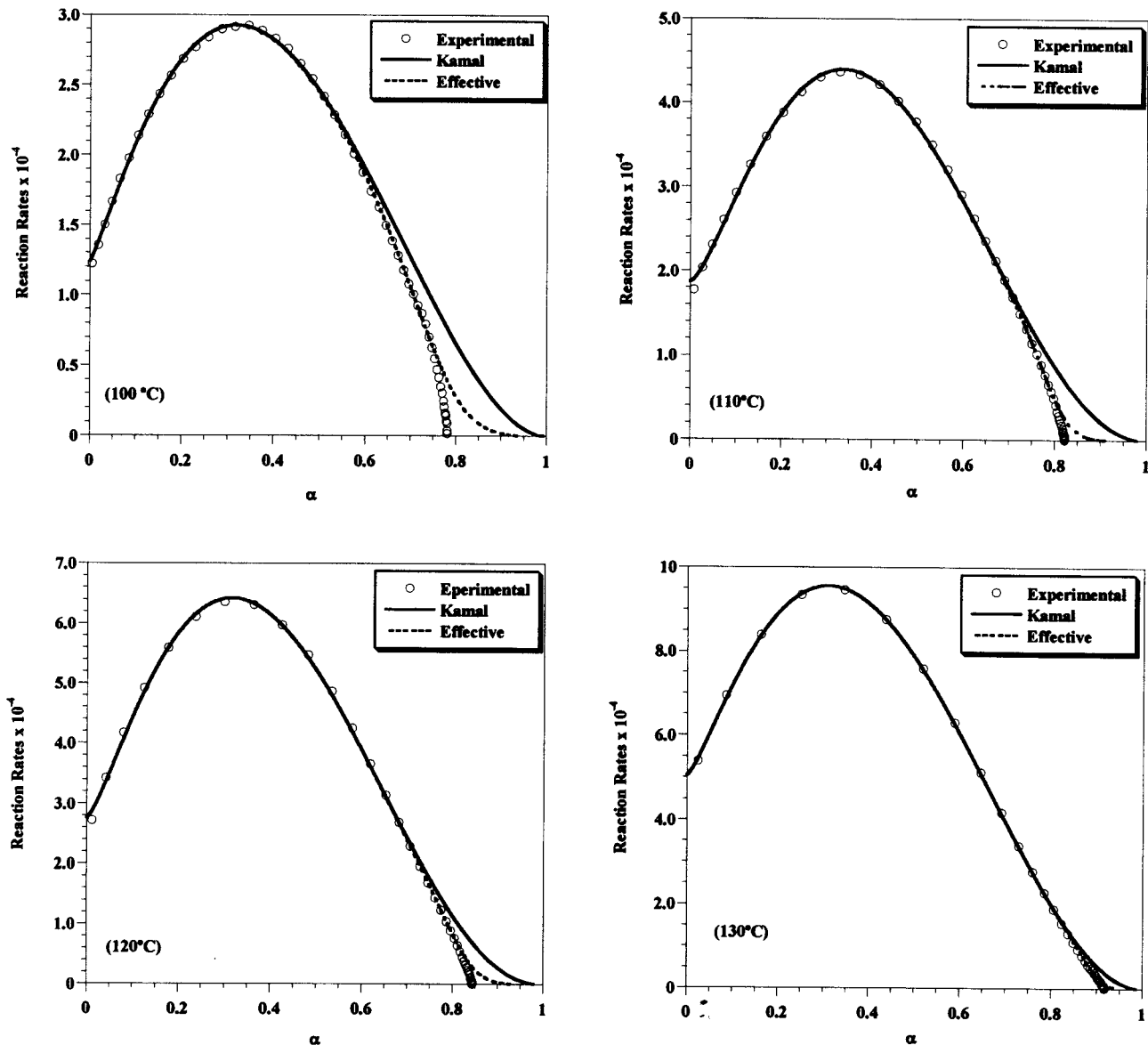
Figure 7 Curves of reaction rates versus conversion with model predictions. The solid lines represent the autocatalytic model (DGEBA/BSA).

the present work, this change in the controlling mechanism was observed in all cases, necessitating modification of the autocatalytic relationship by inclusion of a diffusion term. A typical approach[33] 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 the difference $T - T_g$ by a Williams–Landell–Ferry-type equation. To consider the diffusion effect, a semi-empirical relationship based on free-volume considerations was used. So when the degree of cure reached a critical value, α_c, diffusion became controlling, and the rate constant, k_d, could be given by

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \tag{8}$$

where k_c is the rate constant for the chemical kinetics and C is a fitted parameter. This equation corresponds

to the region where both chemical and diffusion factors are controlling with $\alpha = \alpha_c$ as the theoretical point where the reaction changes. The diffusion factor, $f(\alpha)$, is defined as the ratio k_e/k_c, with k_e the overall effective rate constant, which includes both effects. This diffusion factor is

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{9}$$

For $\alpha \ll \alpha_c$, $f(\alpha)$ approximates unity and the effect of diffusion is negligible. As α approaches α_c, $f(\alpha)$ begins to decrease and approaches zero as the reaction effectively stops. The effective reaction rate at any conversions equals the chemical reaction rate multiplied by $f(\alpha)$. The diffusion factor was obtained as the ratio of the experimental reaction rate to the reaction rate pre-
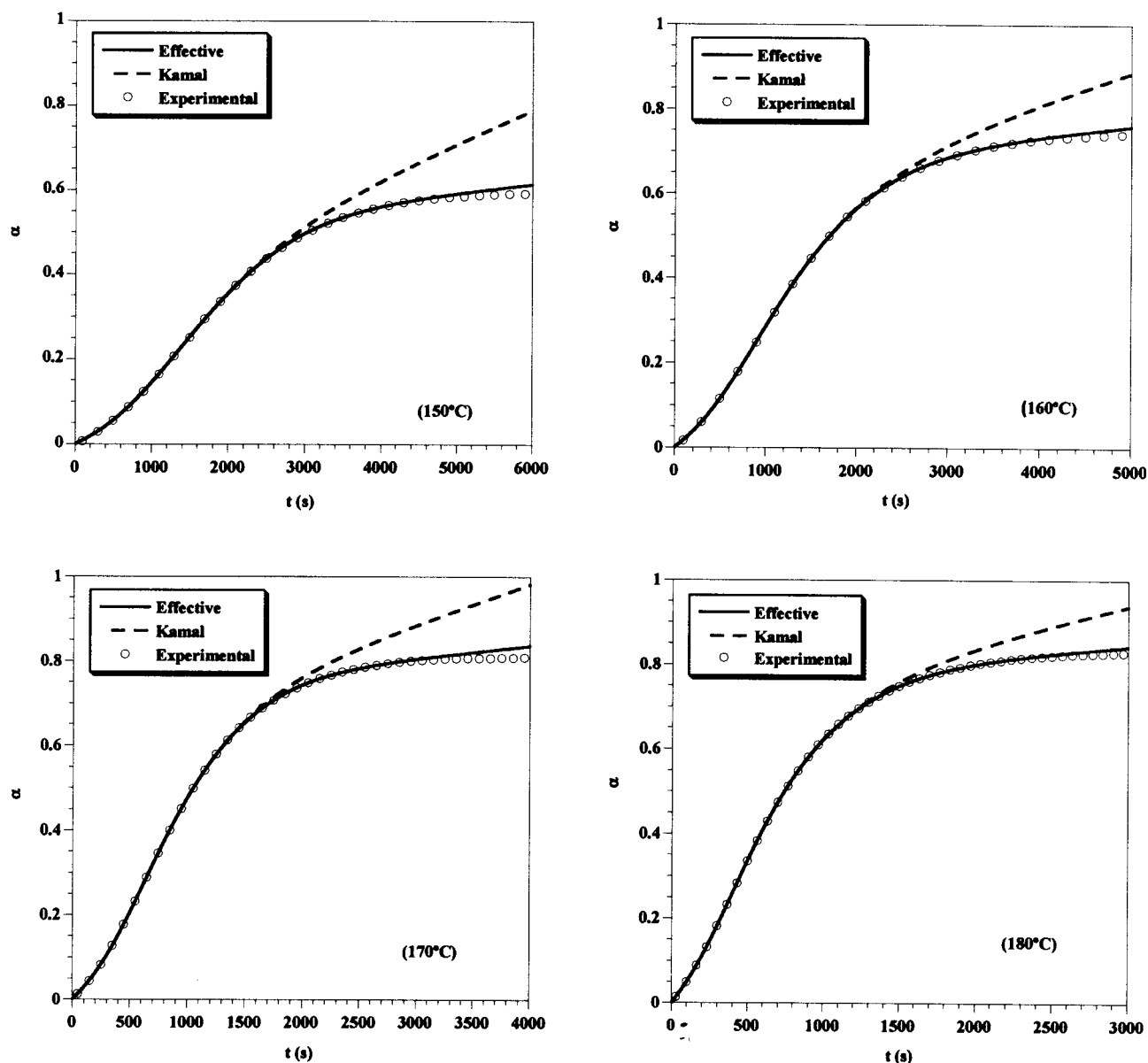
Figure 8 Comparison of experimental data with model prediction at different temperatures for DGEBA/MDEA. Conversion α versus time: (xxx) experimental, (—) autocatalytic model, (—) autocatalytic model with diffusion.

dicted by the autocatalytic model in eq. (7). Figure 6 shows the behavior of $f(\alpha)$ with conversion for the DGEBA/MDEA system at all curing temperatures. A decrease in $f(\alpha)$ and, consequently, in the effective reaction rate arising from the onset of diffusion at higher conversions was seen before the behavior of the other systems DGEBA/diamine demonstrated similar trends.

The values of α_c and C obtained by applying nonlinear regression to $f(\alpha)$ versus α data are listed in Table V. The α_c increased with the cured temperature, but for coefficient C no discernible trend emerged.

Figure 7 shows the results for DGEBA/BSA 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. (9). Figure 8 displays the curves of α versus time comparing the data also calculated by the autocatalytic model for the DGEBA/MDEA system. Similar agreement between the experimental and predicted values was obtained for the other resin compositions used.

CONCLUSIONS

Differential scanning calorimetry (DSC) can be successfully used over a wide temperature range to obtain isothermal cure data for epoxy polymers. Dynamic testing was performed to obtain the overall

heat of reaction. Application of the Kissinger and Flynn–Wall–Ozawa method to the exothermic peak showed similar activation energies, except for the liquid diamine 1,3-BAC, which were lower.

The simple-mechanism kinetic model developed by Kamal for describing the initial stages of cure of epoxy/diamine systems was found to be consistent for the five systems in this work. This model was not valid for the later stages of cure, where the reaction mechanism was diffusion controlled. The maximum experimental values of conversion were reached by the system cured with BSA. The conversion of the epoxy systems was not connected with the melting temperature nor was the molecular weight of the diamines. The values found for the reaction order, m, of about 1 agreed with those for epoxy/diamine systems reported in the literature. The values of n, however, show more variation.

Introducing the diffusion factors, the five systems were adjusted over the whole range of conversion. The epoxy resin diglycidyl ether of bisphenol A cured with any diamine showed similar behavior, which was useful for modifying with thermoplastics or polyhedral oligomeric silsesquioxanes.

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