Relaxations in Thermosets. XXV. Calorimetric Studies of the Curing Kinetics of Pure and Rubber-Containing Epoxy-Based Thermosets

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SYNOPSIS

The curing kinetics of diglycidyl ether of bisphenol-A, with ethylene diamine, propylene diamine, and hexamethylene diamine, with 60 wt % amine-terminated butadiene acrylonitrile (ATBN) and without, have been measured under both isothermal and ramp-curing conditions. The phase separation of ATBN is undetectable by calorimetry, but has a significant effect on both the rate of curing and the extent of cure. In all cases, its presence decreases the extent of cure and lowers the T_g of the thermoset formed. The total heat of reaction for the curing is 445 ± 15 J/g and remains unaffected by both the presence of an elastomer and the increase in the molecular size of the curing agent. None of the formalisms available for the curing kinetics of epoxy-based thermosets is consistent with the results for the neat thermosets. The average activation energy for the reactions increases from 107 to 150 kJ/mol when ethylene diamine is replaced by hexamethylene diamine, but curing reaches near completion in a shorter time with the latter than with the former. The T_g of the latter thermoset is lower than that of the former and follows a decreasing trend with increase in the molecular size of the curing agent—an effect that is related to the increase in the length of cross-links in the network structure. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The rate at which chemical reactions occur is directly related to the probability of mutual diffusion of the reacting molecules. In the processing of polymers, this probability generally decreases as the viscosity of the reacting mixture increases. Intuitively, one anticipates that this probability would also decrease when foreign, relatively inactive, substances are present in the reacting mixture. Therefore, the properties of a thermoset mixture are expected to depend upon the type and amount of inert additives. Thus, both mechanical and electrical properties of reinforced thermoset composites would depend not only on the volume fraction of the matrix but also on its cross-link density modified by the reinforcing additives.

As part of our studies on rubber-toughened thermosets,[1-5] we have been investigating their curing kinetics by dielectric and ultrasonic measurements. As the chain length of the polymer in such a thermoset, in a homogeneous solution of an elastomer, increases on curing, the elastomer component phase separates while in the liquid state. Thus, as the reacting mixture forms a network structure, thereby lowering the solubility of the elastomer, a new morphology of the elastomer-dispersed-in-a-network structure develops. This morphology of the dispersed phase may be as either discrete particles or continuous structure depending upon the amount of elastomer, the curing temperature, and the rate of chemical reactions. In either case, when phase separation has occurred, the probability of chemical reactions (as a result of molecular diffusion) between the resin and the curing agent is expected to decrease, because the intervening regions of the elastomer phase prevent diffusion by occupying randomly distributed macroscopic sites in the incompletely formed polymer network. This is expected

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therefore to produce a polymer matrix with a lower cross-link density and correspondingly different electrical and mechanical properties.

The main purpose of this study was to investigate the effect of an elastomer's phase separation on the curing kinetics of a thermoset, the glass transition behavior of the elastomer–thermoset composite thus formed, and the effect of chain length of the cross-linking agent on the curing kinetics. We also examine the various formalisms available for the calorimetric effects during a thermoset's curing. For this purpose, the curing kinetics of neat thermosets (containing an epoxy and diamine of three different molecular sizes) were also studied. The study reveals a significant effect of the elastomer's phase separation on the curing kinetics, the cross-link density, and the glass transition temperature of the thermosets.

EXPERIMENTAL

The amines used as curing agents were purchased from Allied Chemical. Their purity was 99% or more. The diglycidyl ether of bisphenol-A or DGEBA was donated to us by Shell Chemical. Its trade name is Epon-828 and it has been characterized by LeMay et al.[6] Its M_n = 380, n = 0.14, T_g = 14°C, and functionality = 2. Amine-terminated butadiene acrylonitrile or ATBN was purchased from B. F. Goodrich Chemical Co. Its trade name is Hycar ATBN-16 with a NH equivalent of 180 g and it contained a residual amount of ≈ 3% by weight of N-(2-amino ethyl)piperizine from its synthesis. Its glass transition temperature is about −50°C. All chemicals were used as such and were kept in dry containers when in storage. The samples were mixed immediately before the measurements. Throughout this paper, EDA refers to ethylene diamine; PDA, to propylene diamine, and HDA, to hexamethylene diamine.

Stoichiometric mixtures of DGEBA and diamines were prepared by weighing, and the required amount of ATBN was added to the mixture. Each thermoset was studied in both its neat state and mixed with ATBN.

For all measurements, a Perkin-Elmer differential scanning calorimeter (DSC 4) with TADS computer-assisted data acquisition was used. Curvature of the DSC scans was eliminated with the SAZ function that substracts during scanning the base line obtained with empty sample pans. Open aluminum pans containing 20–35 mg samples were used under a flow of argon gas. For isothermal measure-

ments, the temperature was raised from 25°C to the curing temperature at the rate of 300°/min. The maximum time taken for the attainment of the isothermal curing temperature was 25 s.

For obtaining DSC scans at controlled heating rates or thermograms, the samples were heated at a rate of 10°C min. In the procedure for measurements of the glass transition temperature, T_g, the sample was first heated to about 20°C above its T_g endotherm, cooled to 25°C at the rate of 10°C min, and thereafter heated at 10°C min. The values of T_g obtained from the scans have an uncertainty of 2°C, which is due mainly to the difficulty in estimating the T_g onset from the broad endotherms.

III. RESULTS

Each thermoset sample, neat or mixed with ATBN, was first studied during its isothermal curing at 50, 60, and 70°C. Typical DSC scans obtained during the isothermal curing for the DGEBA–PDA thermoset here are given in Figure 1, which shows, as for all cases, an exothermic minimum. The integrated area of these plots is equal to ΔH_{iso}, the heat released during the reaction on isothermal curing. Immediately after isothermal curing, the sample was cooled to 25°C and thereafter heated to 240°C at the rate of 10°C min, during which further curing of the thermoset occurred. Typical DSC scans obtained during this controlled heating rate are also shown in Figure 1. These scans show an endothermic step characteristic of the glass → liquid transition, which is followed by an exothermic minimum, indicating further curing of the thermoset. The integrated area bound by this minimum was used to calculate ΔH_{res}, the residual heat of reaction. The total heat of reaction, ΔH_t, thus measured is equal to ΔH_{iso} + ΔH_{res}.

Similar experiments were carried out with thermosets containing 60 wt % ATBN, or 60 g ATBN per 100 g DGEBA. Typical plots for the DGEBA–ATBN mixture and the neat, and ATBN-containing thermosets isothermally cured with EDA, PDA, and HMDA at 50°C, are shown in Figure 2, and the values of ΔH_t at each curing temperature are listed in Table I. Both the plots in Figure 2 and the values given in Table I have been normalized for the weight of DGEBA alone and refer to quantities per gram of DGEBA.

A second set of measurements were made in which each thermoset and its mixture with ATBN was heated from 30 to 240°C at the rate of 10°C/min, during which its thermogram was obtained. Typical
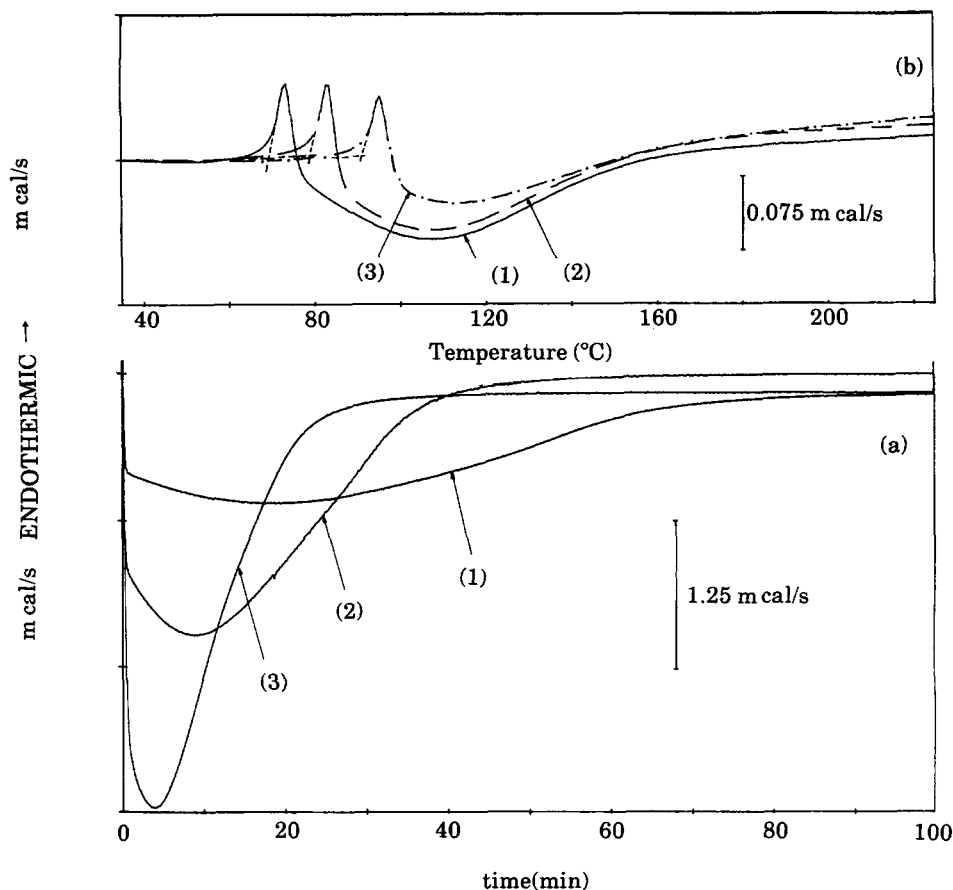
Figure 1   Typical plots of the (a) isothermal heat release during curing of the DGEBA–PDA thermoset at three different temperatures: (1) 50°C, (2) 60°C, and (3) 70°C, and (b) endothermic effect, indicating a glass–liquid transition followed by an exotherm due to postcuring. Curves labeled 1, 2, and 3 were obtained after curing each thermoset for 100 min at 50, 60, and 70°C, respectively. All plots are normalized with respect to the weight of the DGEBA. T_g is indicated by the intersection of dotted lines.

thermograms for the DGEBA–ATBN mixture and the neat and ATBN-containing thermosets are shown in Figure 3. The integrated area bound by the exothermic minimum was then used to calculate ΔH_{ramp}, the total heat of reaction of the thermoset, and these values are also listed in Table I. Both the plots in Figure 3 and the values in Table I are normalized with respect to the weight of DGEBA alone.

The fractional conversion, α, at any instant during the isothermal curing, such as those shown by the plots in Figures 1 and 2, is given by the equation

$$\alpha = \frac{1}{\Delta H_t} \int_0^t \frac{\partial \Delta H}{\partial t} \, dt \qquad (1)$$

From the knowledge of ΔH_t, as described here earlier, and from the partial integration of the plots similar to those shown in Figures 1 and 2, α was

calculated as a function of time. Typical plots of α against time for the neat thermosets for different curing temperatures are shown in Figure 4. The shape of these plots is similar to that observed for thermoset curing in general and are similar to that expected for a chemical process autocatalytic in nature.[7] Because the heat released during the curing of ATBN-containing thermosets contains contributions from the reaction of DGEBA with ATBN, such plots for the ATBN-containing thermosets could not be obtained.

Barton[7] recently reviewed the use of DSC for determining the curing kinetics of thermosets and provided a comparison of the various equations used with both the isothermal and ramp-curing measurements. When the primary and secondary amines are of approximately equal reactivity, a generalized form of the equation[7–9]
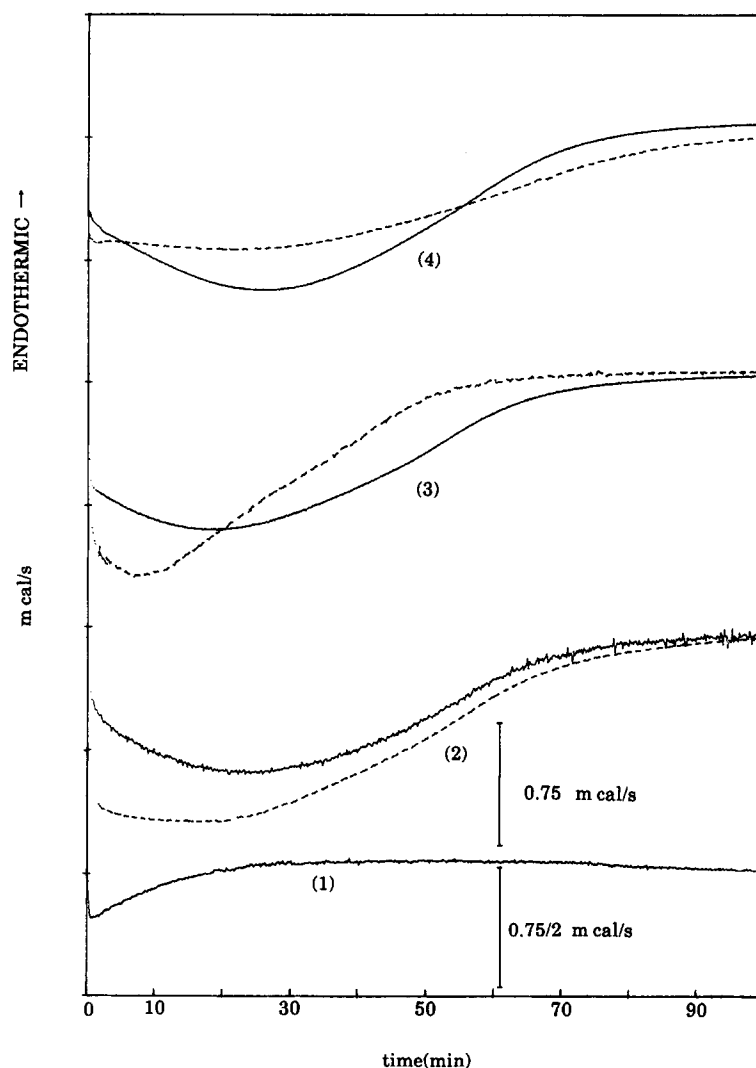
Figure 2 Typical plots of the isothermal heat release against time for the neat thermoset (shown by a continuous line) and that containing 60 wt % ATBN (shown by a broken line). Curve labeled (1) refers to DGEBA-60 wt % ATBN mixture, (2) to DGEBA-EDA, (3) to DGEBA-PDA, and (4) to DGEBA-HMDA thermosets. The plots are normalized with respect to the weight of DGEBA. The curing temperature is 50°C for all cases.

$$\frac{\partial\alpha}{\partial t} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \qquad (2)$$

can be used to fit the data for isothermal curing. Here, K_1 and K_2 are constants related to the rate constants of the two reactions, which were discussed in detail by Horie et al.[9], and m and n are empirical parameters. In several studies[7] of the curing kinetics of DGEBA-diamine thermosets, n has been found to be equal to 1 and $n = 2$. Thus, the reduced rate, r, is given by

$$r = \frac{\partial\alpha}{\partial t}(1 - \alpha)^{-2} = K_1 + K_2\alpha \qquad (3)$$

hence, a plot of r against α should be a straight line with slope K_2 and intercept K_1.

Since the total heat of reaction is determined in our study by two procedures, namely, (i) isothermal curing followed by ramp-curing, and (ii) ramp-curing alone, the fractional conversion, α, calculated from eq. (1) would depend upon the value used for ΔH_t. Thus, for the two different values of ΔH_t two sets of curves of r against α would be obtained. These curves are shown in Figures 5 and 6 for the neat thermosets. Again, similar plots for the ATBN-containing thermosets could not be obtained, because the ΔH_t here contains a contribution from the reaction between ATBN and DGEBA.

Table I   The Parameters for the Curing Kinetics of Pure and 60 wt % ATBN-containing Thermosets

$t_{cure}/°C$	ΔH_t (J/g)	α_{vit} (1)	α_{vit} (2)	t_{min}/min	T_g (iso)	T_g (∞)
DGEBA–EDA						
50	369 (463)	0.86	0.72	23 (14.3)	67 (< 25)	105 (101)
60	436 (445)	0.90	0.89	10 (10)	81 (83)	105 (108)
70	450 (460)	0.92	0.93	5.6 (5)	93 (92)	104 (103)
Ramp	441 (480)[b]	—	—	102 (107)[a]	—	114 (86)
DGEBA–PDA						
50	289 (280)	0.86	0.74	18 (8)	70 (< 25)	102 (74)
60	468 (422)	0.89	0.91	9 (3)	79 (75)	103 (74)
70	450 (415)	0.93	0.91	4 (1.5)	91 (87)	103 (74)
Ramp	459 (449)[b]	—	—	98 (98)[a]	—	91 (73)
DGEBA–HMDA						
50	393 (367)	0.97	0.88	25 (22)	64 (60)	69 (68)
60	403 (462)	0.98	0.92	11.5 (8.7)	69 (67)	69 (69)
70	405 (448)	0.99	0.93	5.1 (2.7)	76 (83)	72 (69)
Ramp	432 (459)[b]	—	—	103 (109)[a]	—	68 (65)

The quantities given in parentheses refer to the ATBN-containing thermosets. α_{max} (1) and α_{max} (2) refer to the values calculated using ΔH_t and ΔH_{ramp}, respectively.

[a] Refers to T_{min}, the temperature in °C.

[b] Refers to ΔH_{ramp}.

For ramp-curing studies of thermosets by DSC, the kinetics of curing can be determined by a method originally given by Barrett.[10] Accordingly, the fractional conversion is given by

$$\alpha = \partial \Delta H(T)/\Delta H_{ramp} \qquad (4)$$

and

$$(\partial \alpha/\partial t) = A f(\alpha) \exp(-E_a/RT) \qquad (5)$$

where $\Delta H(T)$ is the heat evolved up to a certain temperature T and ΔH_{ramp} is the integrated area bound by the DSC thermogram as in Figure 3. E_a is the activation energy for the chemical reactions assumed to be the same for the reaction with primary or secondary amines, and $f(\alpha)$ is a function of α, which has been found in several studies[8,9,11-15] to be of the form $f(\alpha) = (1 - \alpha)^2$. Substituting for $f(\alpha)$ in eq. (5) and solving for the reduced rate, r,

$$\ln(r) = \ln[(\partial \alpha/\partial t)(1 - \alpha)^{-2}]$$
$$= \ln A - E_a/RT \qquad (6)$$

so that a plot of $\ln(r)$ against $(1/T)$ should be straight line with slope $-E_a$ and intercept $\ln A$. The plots of α, or fractional conversion, at different temperatures for the three thermosets are shown in Figure 7, and those of $\ln(r)$ against $(1/T)$ for the three thermosets are shown in Figure 8. Within the experimental uncertainty, the plots in Figure 8 are

linear. The activation energy determined from the plots is 107 kJ/mol of epoxy for DGEBA–EDA, 114 kJ/mol of epoxy for DGEBA–PDA, and 112 kJ/mol of epoxy for DGEBA–HMDA thermosets.

After curing of the neat and 60 wt % ATBN-containing thermosets by both isothermal and ramp-heating procedures, their glass transition temperatures, T_g, were determined by heating at 10°C/min. Typical thermograms thus obtained are shown in Figures 9–11. The T_g was determined as the onset temperature of the endotherm. It is listed in Table I.

IV. DISCUSSION

Chemical reactions between the DGEBA and diamines occur at all temperatures, but the rate of reaction rapidly increases with the temperature of the reactants early during the curing. The result of the reactions is the formation of a macroscopic gel with an infinitely interconnected covalent-bond network with unreacted or partly reacted DGEBA and diamine molecules contained within the network. It is now known that during curing the uncatalyzed reaction of a primary amine with an epoxide first forms a secondary amine, which, in turn, reacts with another epoxide group to form a tertiary amine.[16,17] The reactions seem to be autocatalyzed by hydroxyl groups that are generated in the reactions. The reactions with diamines occur concomi-
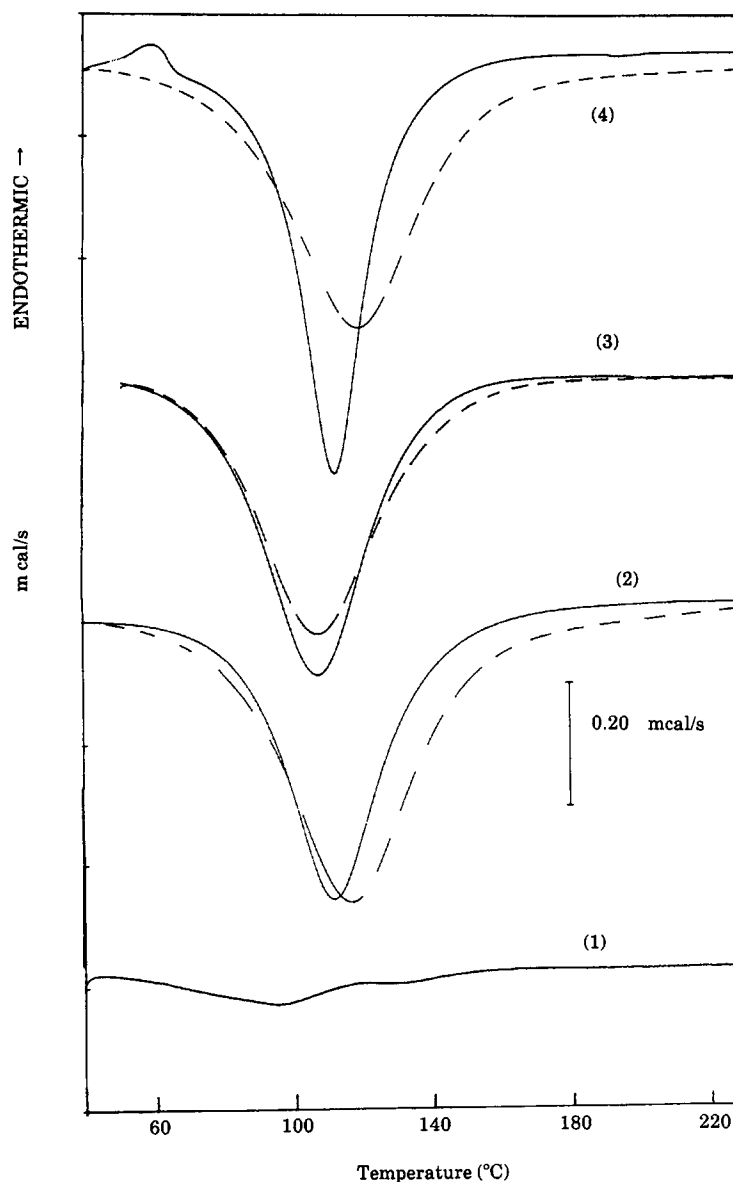
Figure 3   DSC thermograms for the neat thermoset (shown by a continuous line) and that containing 60 wt % ATBN (shown by a broken line). The plots are normalized with respect to the weight of DGEBA. Curves labeled (1) refers to DGEBA–60 wt % of ATBN mixture, (2) to DGEBA–EDA, (3) to DGEBA–PDA, and (4) to DGEBA–HMDA thermosets. The heating rate was 10°C/min in all cases.

tantly with two rate constants and the network forms essentially as a result of cross-linking of linear molecules, when the epoxy group opens to form a hydroxyl group, leading to the formation of a fully connected network at the gel point, which may be reached before the ATBN phase separates, thus decreasing the extent of phase separation. The reactions continue to occur, but thereafter become diffusion-controlled when the internal viscosity of the gel becomes very large. Ultimately, this leads to vit-

rification. The extent of reaction at the time when a thermoset is macroscopically rigid depends upon the temperature of the cure, but its value is typically between 80 and 100%. As the glassy thermoset is now heated above its T_g, reactions occur further, or when a thermoset is aged, its amorphous structure relaxes toward a lower-energy state as a result of slow diffusion of segments within the network. The densification of the structure may, in turn, facilitate further chemical reactions between the remaining
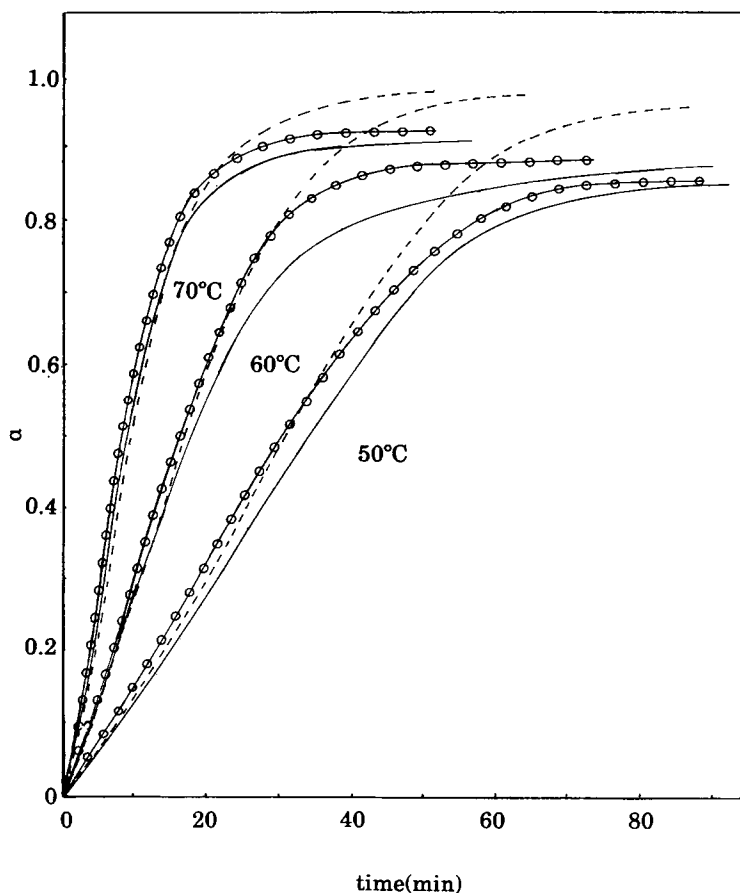
Figure 4   Fractional conversion of DGEBA–EDA, DGEBA–PDA, and DGEBA–HMDA thermosets plotted against the curing time at 50, 60, and 70°C. Continuous line is for DGEBA–EDA, dots are for DGEBA–PDA, and broken line for DGEBA–HMDA thermosets.

unreacted components. Both occurrences of further reactions are known as postcure. In an incompletely cured thermoset, both physical aging and postcure occur simultaneously, but in a fully cured sample, only the former occurs. All these factors determine the curing kinetics and the properties of the ultimately formed thermoset with or without the presence of ATBN and are conveniently discussed separately in the following sections:

1. The Isothermal Curing Kinetics of Thermosets

We first discuss the curing behavior of DGEBA with the three diamines in terms of the above-given formalism. The usefulness of eqs. (2) and (3) as a description of the calorimetric data obtained during the isothermal curing of thermosets has been a subject of recent reviews. These have been based on fitting the data to the generalized eq. (2) with adjustable values of the exponents m and n. For example, Horie, et al.[9] found $m = 1$ and $n = 2$ [which

yields eq. (3)]. These values have been substantiated by the recent analysis by Riccardi and co-workers[15,18] for the DGEBA–EDA thermoset and by several other workers[11-14] who used chemically different thermosets. By assuming that the rate-determining step is the autocatalyzed reaction of a rapidly formed complex of epoxide and amine, Barton[19] showed that $m = n = 1$. Yet, other authors[20-24] observed that although $m + n = 2$, m varies with the temperature and, in particular, Ryan and Dutta[20] showed that m increases from 0.6 to 1.2 with increasing temperature. Thus, both m and n can have fractional values, and an increase in the magnitude of one causes a decrease in that of the other. Most recently, Carrozzino et al.[25] observed that n for the DGEBA–EDA thermoset may be within 1 and 1.5 while $m = 1$.

In an alternative approach. Mijovic et al.[21-24] found that m varies with α itself and increases from 0.5 to 0.7,[22,23] reaches a maximum,[24] and thereafter decreases with increase in the curing temperature.
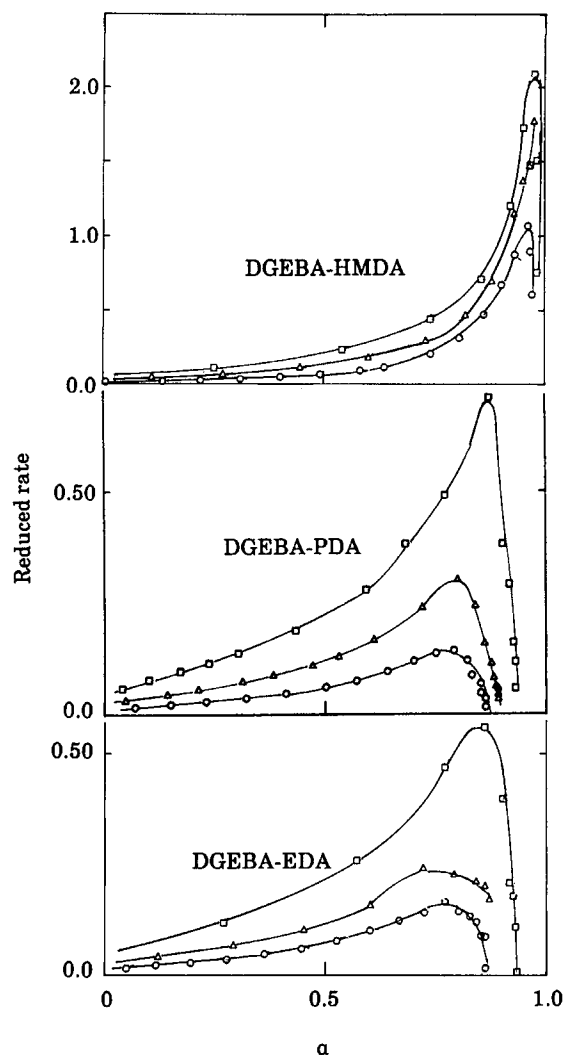
Figure 5   The reduced rate of curing plotted against the extent of conversion or fractional conversion of DGEBA–EDA, DGEBA–PDA, and DGEBA–HMDA thermosets during their isothermal curing. Curing temperatures of (○) 50, (△) 60, and (□) 70°C, respectively. The ΔH_t values used in the calculations were obtained from isothermal-curing experiments.

Its value was interpreted as a measure of the subsequent curing reactions that would follow the autocatalytic behavior for the chemical reactions. The exponent n also varied from 1.1 to 1.3.

Although eqs. (2) and (3) and the relevant parameters m and n are based on the assumption that the reactions follow first- or second-order autocatalytic reaction kinetics, several authors[26–31] justifiably proposed that the average order of reaction may be fractional, with a single rate constant. This average fractional order of reactions has been suggested as 1.64 for DGEBA cured with triethylene

tetramine[28] and 1.70 for DGEBA cured with bis(p-aminocyclo-hexyl)methane.[26,27] These values can also be interpreted to mean a first-order reaction near the vitrification time.

Despite the above-described ambiguities in the validity of eqs. (2) and (3), α_{vit}, the extent of reaction or fractional conversion at vitrification, can still be ascertained from construction of the plots of r against α. This is so because, as the time for vitrification is approached, the rate of reaction, or equivalently $(\partial\alpha/\partial t)$ approaches zero (or $r \rightarrow 0$) as α increases and reaches a value equal to α_{vit}. In the plots of r against α, the value of α_{vit} at $r = 0$ is formally independent of the numerical value of n, but not of m. The values of α_{vit} thus determined are listed in Table I for all the neat thermosets. Since α itself depends upon the measured value of total
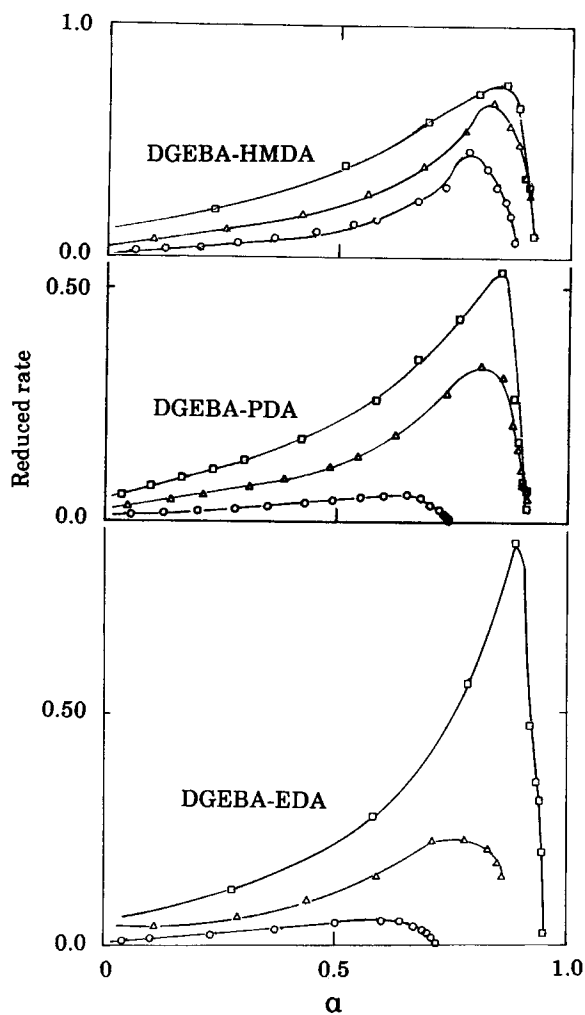

Figure 6   The plots corresponding to Figure 5 but the reduced rate and α were calculated from the ΔH_{ramp} values obtained from ramp-curing experiments.
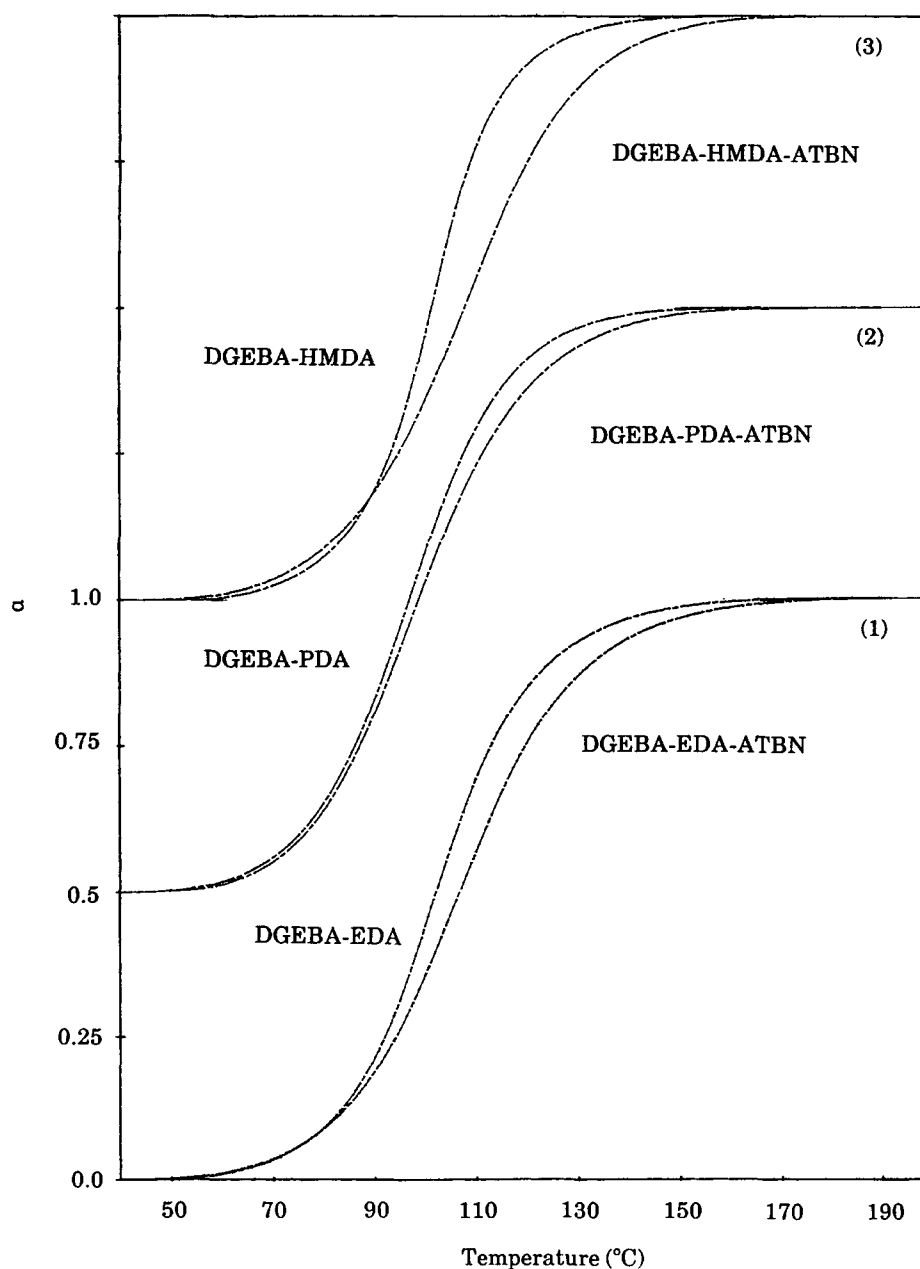
Figure 7   The plots of fractional conversion against the temperature for the (1) DGEBA–EDA, (2) DGEBA–PDA, and (3) DGEBA–HMDA thermosets cured by heating at 10°C/min.

ΔH and since its value, ΔH_t, obtained from isothermal curing and thereafter ramp heating, differs from ΔH_{ramp} obtained only from ramp heating, as is evident in Table I, these values of α_{vit} obtained from the two procedures differ. We suggest that these differences are a reflection of the predominance of certain reactions in the thermosets that differ for the isothermal and ramp-curing processes, an aspect of curing that will be discussed in detail in a later section here.

Figures 5 and 6 clearly show that for the neat thermosets the reduced rate does not increase linearly with α over as wide an α-range as observed by other workers,[8,9,15,18] although the initial increase is linear. Such effects are also evident in Figure 6 of Ref. 15 and have been noted by Carrozzino, et al.[25] Clearly, the values for the exponents m and n are not the same and this implies that the primary and secondary amines are not equally reactive. As mentioned above, values of both m and n have been found
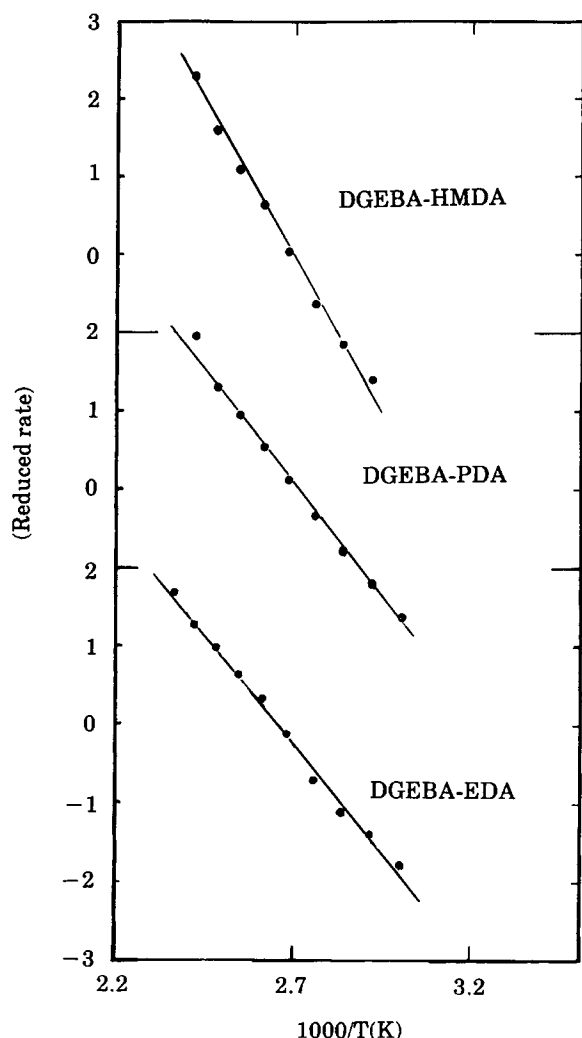
Figure 8 The logarithmic plots of reduced conversion rate against the reciprocal temperature for the various thermosets.

2. The Ramp-Curing Kinetics of Thermosets

It is now known that the kinetic parameters obtained from rate-heating in DSC experiments generally differ from, and are often higher in magnitude than, the corresponding parameters obtained from isothermal experiments.[8,9,15,18] This difference is a reflection of two possible reaction paths, with different kinetic parameters whose relative importance varies with the temperature. These reactions are (i) noncatalytic, with a higher activation energy, and (ii) autocatalytic, with a lower activation energy. The premise for this conclusion is that the activation energy E_A obtained from curing in the rate-controlled heating experiments has been found to differ from that obtained from the isothermal curing experiment at several temperatures[32] and using eq. (3).

As mentioned earlier, for isothermal curing of thermosets, the plots in Figures 5 and 6 do not show a linear increase of r with α over a sufficiently broad region to allow evaluation of the activation energy. Nor do we observe a region of α where this linearity overlaps at different curing temperatures. It is also noteworthy that the corresponding plot for the highest curing temperature in Riccardi et al.'s[15] study seems also to be nonlinear in much the same manner as ours in Figures 5 and 6 here.

The activation energy for the overall reaction, calculated from the plots of reduced rate r against the reciprocal temperature according to eq. (6), increases from 107 to 150 kJ/mol of epoxy when EDA is substituted by HMDA as a cross-linking diamine. Riccardi et al.[15] estimated an activation energy of 102.6 kJ/mol for the DGEBA–EDA reaction. We regard the difference between our result and theirs to be insignificant considering the uncertainty of our respective measurements and the difference between the purity of the chemicals.

3. The Effect of ATBN on the Curing Kinetics

The main purpose of this study was to investigate, as stated earlier, the effect of foreign substances on the curing kinetics of the epoxide resins. We first consider, therefore, whether a significant amount of reaction occurs between DGEBA and ATBN. The plots from experiments carried out to examine this, given in Figures 2 and 3, clearly show that DGEBA and ATBN also react with each other and 65 J/g of DGEBA is the heat released in the ramp-curing process. Because of this reaction, the amount of DGEBA available for reaction with the diamine is reduced and a complete network therefore would not

to be in the range from less than one to two and have been interpreted to indicate the formation of various complexes by H-bonding, hetero and auto-complexes of the reactants with the reaction products, etc. One expects that for all cases the rate constant would depend on the thermodynamics of complex formation, the rate of diffusion of reactants, and the steric hindrance of the reacting groups. Thus, intuitively speaking, a distribution of reaction rates rather than discrete reaction rate processes could become dominant as α increases and this dominance could cause the experimental data to deviate from the generalized eq. (1). It is also conceivable that the discrepancy between the experiments and eq. (2) is caused by a variation of m and/ or n as α increases, as pointed out by Mijovic.[23]
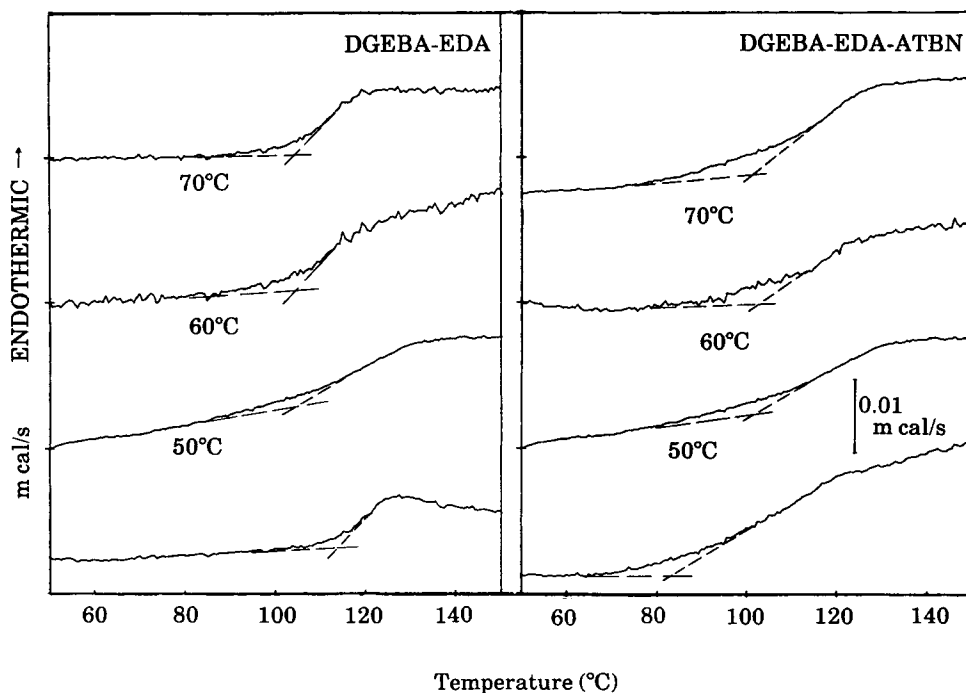
Figure 9 The DSC thermograms of the cured states of neat and 60 wt % ATBN-containing DGEBA–EDA thermosets, showing their glass transition temperatures. Heating rate: 10°C/ min. The curve at the bottom is for a sample obtained by ramp-curing. T_g is indicated by the intersection of the lines drawn.

Figure 10 The DSC thermograms of the cured states of neat and 60 wt % ATBN-containing DGEBA–PDA thermosets showing their glass transition temperatures. Heating rate: 10°C/min. The curve at the bottom is for a sample obtained by ramp-curing. T_g is indicated by the intersection of the lines drawn.
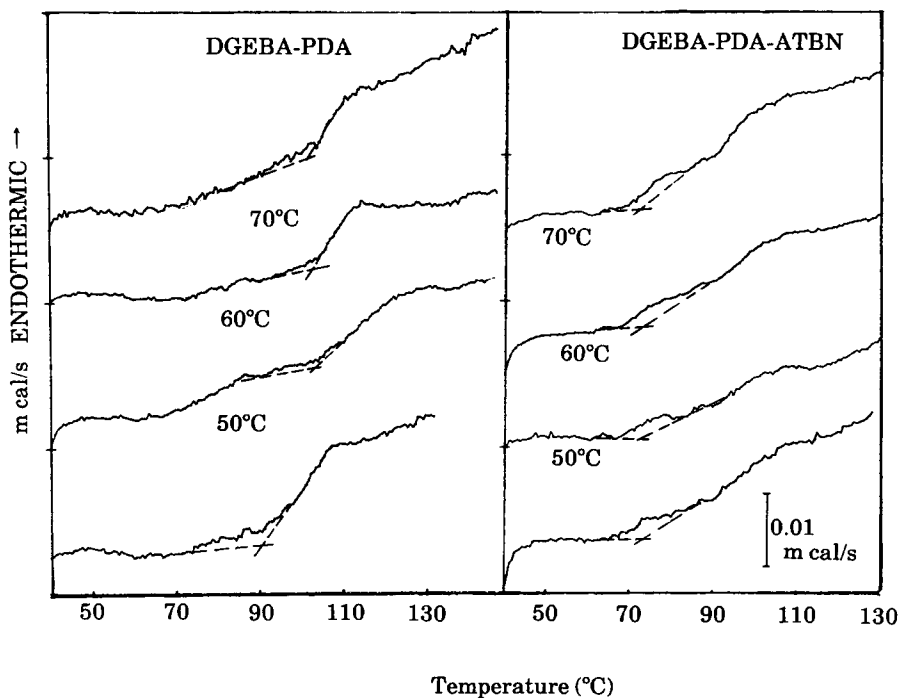
Figure 11 The DSC thermograms of the cured states of neat and 60 wt % ATBN-containing DGEBA–HMDA thermosets showing their glass transition temperature. Heating rate: 10°C/min. The curve at the bottom is for a sample obtained by ramp-curing. T_g is indicated by the intersection of the lines drawn.
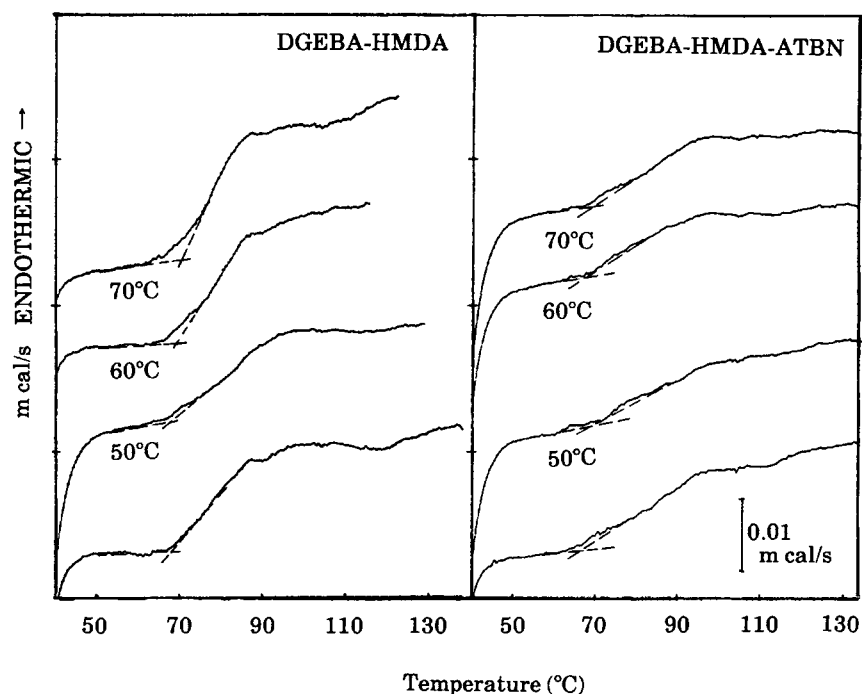
form in the thermoset. Thus, the total heat released in the reaction of ATBN-containing thermosets at any instant is the result of a compensation between the extent of reaction between DGEBA and ATBN and that between the resulting (nonstoichiometric) amounts of DGEBA and diamine. Therefore, the value of α, whose calculation would assume reactions only between the DGEBA and diamine, cannot be easily determined. In a related measurement, Riew[33] found that DGEBA-type epoxy resin can be cured at room temperature with 50% ATBN, and Chan et al.[34] found that the T_g of 15% ATBN-containing DGEBA increases from −12 to +50°C on curing for 2 h at 200°C. Therefore, it was also necessary to determine the extent of reaction between DGEBA and ATBN on isothermal curing at 50, 60, and 70°C. The corresponding typical plot for 50°C is shown in Figure 2. The total heat evolved from isothermal and subsequent ramp-curing is 19 J/g, which is ∼ 4% of the heat evolved during the curing of DGEBA with the diamines used here. Thus, even for isothermal curing conditions, a significant contribution to ΔH_t comes from the reaction between ATBN and DGEBA. But, more significantly, the total heat evolved during the isothermal curing of ATBN-containing thermosets is considerably less

than that obtained by ramp-curing, indicating that the extent of reaction at vitrification for the ATBN-containing thermosets is much less than that for the neat thermosets.

Dielectric[1-3] and microstructure studies[35] of ATBN-containing thermosets show a region where phase-separation of ATBN occurs. This liquid–liquid phase separation of the ATBN from the DGEBA–diamine solution is not evident in the calorimetric measurements here, which agrees with the accepted suggestion that the phase separation involves spinodal decomposition. Nevertheless, the morphology produced on phase separation by spinodal decomposition is generally that of nonspherical regions of high connectivity, and microstructure studies by Yamanaka and co-workers[35,36] show that spherical domains are formed. The apparent conflict between the expected and observed morphology of phase separation can be reconciled by suggesting that nucleation and growth of ATBN that occurs on phase separation involves enthalpy changes that are much smaller than the enthalpy released in the chemical reactions between DGEBA and diamines, and, therefore, the phase separation remains undetectable during the isothermal curing and rate-heating.

A pronounced effect of ATBN on both the isothermal curing and ramp-heating is seen here as the change in t_{min}, the time, and T_{min}, the temperature, of the exothermic minimum whose shape becomes broadened in most cases. The minimum shifts to shorter times of cure for all temperatures, as listed in Table I, and except for PDA cured at 50°C, it becomes shallow for all thermosets at their different isothermal curing temperatures. The corresponding total heat released, which is also listed in Table I for a comparison against that for the curing behavior of neat thermosets, is, in general, higher for ATBN-containing DGEBA–EDA thermosets than for the neat thermosets and lower for the DGEBA–PDA and DGEBA–HMDA thermosets.

For the ramp-curing of thermosets, the shift in the exothermic minimum toward a higher temperature on the addition of ATBN is zero or insignificant for the PDA and highest for the HMDA-cured thermoset, as evident in Figure 3. The total heat of reaction is increased on the addition of ATBN to EDA and decreased for the PDA and HMDA-cured thermoset by an amount that is listed in Table I and is consistent with the observations made from isothermal curing. Here, also, the exothermic minimum for the reaction between DGEBA and ATBN is undetectable in the curing kinetics of the ATBN-containing thermoset, as can be seen in Figure 3.

The shift in the position of the exothermic minimum and the change in its shape on the addition of ATBN indicate a change in the rate of reaction of DGEBA with the diamine. This can be more clearly analyzed in terms of fractional conversion against temperature, whose plots are shown in Figure 7. For the three thermosets, the temperature needed to reach the same extent of cure is increased on the addition of ATBN. Alternatively stated, for a given temperature, the addition of ATBN decreases the extent of conversion. The apparent anomalous behavior of the HMDA-cured thermoset below 20% cure, where α for the ATBN-containing is greater than for the neat thermoset, is probably caused by the heat released on phase-separation of ATBN in the thermoset. These observations may be confirmed by light-scattering measurements that are used for detecting the phase-separation of ATBN as the thermoset curing occurs.[35,36]

4. The Effect of ATBN on the T_g

The DSC thermograms in Figures 9–11 and the T_g data listed in Table I show that the addition of ATBN reduces T_g of the cured thermoset. The de-

crease in T_g of a network polymer is an indication of a decrease in the number of cross-links in the polymer, and this is also the case here as the presence of ATBN retards the chemical reaction, thus preventing the attainment of a stoichiometric concentration of cross-links in the ultimately formed network structure.

The effect of ATBN on T_g is much greater for isothermal curing at low temperatures than at high temperatures, as for curing with both EDA and PDA at 50°C, the T_g of the ATBN-containing thermosets is below room temperature, but increases to 101 and 74°C, respectively, after further curing by rate-controlled heating. Even when almost full cure is achieved on ramp-heating, the T_gs of the ATBN-containing thermosets are lower than those of the corresponding neat thermosets for all cases studied here. The effect may be partly due to the lower cross-link density and partly due to plasticization of the network polymer caused by ATBN molecules that remain dissolved and do not phase separate (this situation may exist when gelation occurs prior to phase-separation). We expect that there is also a third effect that is due to the cross-linking of the ATBN molecules with the DGEBA, which decreases the cross-link density by occupying a greater molecular volume in the network structure. A study that requires variation of the amount of ATBN in the thermoset may be useful in resolving the relative magnitudes of these effects.

5. The Effect of the Chain Length

The probability of reaction between two molecules or two segments of a macromolecule is expected from hydrodynamic considerations to depend on the local diffusion coefficient or internal viscosity and the spatial or conformational degree of freedom of the macromolecule. In addition, this probability is also expected to vary with the steric hindrance of the reacting group. That such differences become prominent in the curing with different lengths of the cross-linking agents is clearly evident in Figure 4, where the extent of reaction at the three temperatures between DGEBA and EDA, PDA, and HMDA are plotted against the curing time.

Similar differences in the curing kinetics are also evident in Figure 7, where the extent of reaction is plotted against the temperature during the ramp-curing of the three thermosets. The rate of change with temperature is lowest for EDA and highest for PDA. For curing with HMDA, the rate of conversion is initially less than that for PDA and becomes

greater than that of PDA after about 30% conversion.

It seems surprising at first that increase in the chain length of a diamine increases the extent of cure at a given time. But consideration in terms of the conformational degrees of freedom of a chain molecule leads us to suggests that the probability of chemical reaction between a second primary amine (of a molecule whose one primary amine group has already reacted with an epoxy group) and the epoxy group would be greater the greater the flexibility of the chain connecting the primary amine groups. It is expected, therefore, to be lowest for ethylene diamine where only one $C-C$ bond separates the NH_2 group and to increase with increase in the number of $C-C$ bonds in the diamine and to be highest for HMDA where five $C-C$ bonds separate the two NH_2 groups.

The maximum or limiting value of the extent of reaction for the thermosets also increases with increase in the length of the curing agent although the total heat of reaction, ΔH_t of 445 J/g, remains constant within about 3%, which is the uncertainty in our calculations. Evidently, the extent of reaction is controlled by the flexibility or conformational freedom of the curing agent.

The T_g of the HMDA-cured thermoset is 20–40°C less than those of the PDA- and EDA-cured thermosets and is not much different from its ATBN-containing cured state. The latter observation implies that the plasticization effect of ATBN is marginal for the HMDA-cured thermoset. Its lower T_g is likely to be due to the increased length of the cross-links that contain five $C-C$ bonds. It is, of course, well known that decrease in the size of the cross-links in a given structure increases its T_g. The trend observed for the decrease in T_g with increase in the number of $C-C$ bonds of the diamines is clearly related to this effect.

V. CONCLUSIONS

A detailed calorimetric study of the reaction kinetics between DGEBA and ATBN, and neat, and ATBN-containing thermosets cured with ethylene diamine, propylene diamine, and hexamethylene diamine shows that the curing is considerably affected by the presence of an elastomer and that the effect can be understood in terms of the changes in the network structure of the matrix formed.

The kinetic equations used for the isothermal curing and ramp-curing yield results that are incon-

sistent with the formalism used in deriving the equations. A variety of effects among which the difference between the reactivity of primary and secondary amines are only one factor are attributable to this discrepancy.

The presence of ATBN slows the reaction rate in both the isothermal curing and ramp-curing experiments and prevents the attainment of maximum conversion attainable in the neat thermoset. It is partly due to the fact that ATBN chemically reacts with the DGEBA, thus depleting the amount available for the chemical reactions with the diamine, and partly due to the hindrance to molecular diffusion caused by its phase-separated, macroscopically randomly distributed state.

The glass transition temperature, T_g, of the polymer matrix containing phase-separated ATBN is consistently lower than that of the matrix of the neat thermoset. Both the plasticizing effect of the dissolved ATBN in the polymer network and decreased number of cross-links per unit volume lower the T_g of the thermoset.

The T_g of both the neat and ATBN-containing thermosets decreases with increase in the $C-C$ linkage of the diamines, but the rate of curing increases. The increased number of $C-C$ bonds in the diamines increases the length of the cross-links, decreases the cross-links density, and thus lowers the T_g. Concurrently, the increased number of $C-C$ bonds in the diamine increases its conformational degree of freedom, which increases the probability of chemical reaction between the epoxide and amine. Thus, both the rate of curing and the extent of reaction at the glass transition temperature are increased. The effect seems to be sufficiently general and can be tested from experiments with other curing agents.

REFERENCES

1. M. Wang, J. P. Szabo, and G. P. Johari, *Polymer,* to appear.
2. M. Wang, G. P. Johari, and J. P. Szabo, *Polymer,* to appear.
3. G. P. Johari and J. P. Szabo, *Plast. Rubber Compos. Process Appl.,* **17,** 299 (1992).
4. M. Wang, G. P. Johari, and J. P. Szabo, *Plast. Rubber Compos. Process Appl.* **17,** 289 (1992).
5. I. Alig, D. Lellinger, and G. P. Johari, *J. Polym. Sci. Polym. Phys. B.,* **30,** 791 (1992).
6. J. D. LeMay, B. J. Swetlin, and F. N. Kelley, in *Characterization of Highly Crosslinked Polymers,* ACS Symp. Ser. 243, S. S. Labana and R. S. Dickie, Eds.,

American Chemical Society, Washington, DC, 1984, p. 65.

7. J. M. Barton, *Adv. Polym. Sci.,* **72,** 111 (1985) and reference therein.

8. S. Souror and M. R. Kamal, *Thermochim. Acta,* **14,** 41 (1976).

9. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci. A-1,* **8,** 1357 (1970).

10. K. E. J. Barrett, *J. Appl. Polym. Sci.,* **11,** 1617 (1967).

11. S. Charlesworth, *J. Polym. Sci. Polym. Chem. Ed.,* **18,** 1621 (1980).

12. M.-F. Grenier-Loustalot and P. Grenier, *Crosslinked Epoxies,* B. Sedlacek and J. Kahovec, Eds., Walter de Gruyter, Berlin, 1987.

13. M. F. Grenier-Loustalot, L. Orozco, and P. Grenier, *Makromol. Chem.,* **188,** 2559 (1987).

14. M. F. Grenier-Loustalot, P. Grenier, P. Horny, and J.-Y. Chenard, *Br. Polym. J.,* **20,** 463 (1988).

15. C. C. Riccardi, H. E. Adabbo, and R. J. J. Williams, *J. Appl. Polym. Sci.,* **29,** 2481 (1984).

16. C. A. May and Y. Tanaka, Eds., *Epoxy Resins, Chemistry and Technology,* Marcel Dekker, New York, 1973.

17. S. Candau, J. Bastide, and M. Delasanti, *Adv. Polym. Sci. (Polym. Networks),* **44,** 27 (1982).

18. C. C. Riccardi and R. J. J. Williams, *J. Appl. Polym. Sci.,* **32,** 3445 (1986).

19. J. M. Barton, *Polymer,* **21,** 603 (1980).

20. C. M. Ryan and A. Dutta, *Polymer,* **20,** 203 (1979).

21. C. C. Foun, A. Moroni, E. M. Pearce, and J. Mijovic, *Polym. Mater. Sci. Eng.,* **51,** 411 (1984).

22. J. Mijovic, J. Kim, and J. Slaby, *J. Appl. Polym. Sci.,* **29,** 1449 (1984).

23. J. Mijovic, *J. Appl. Polym. Sci.,* **31,** 1177 (1986).

24. A. Moroni, J. Mijovic, E. M. Pearce, and C. M. Foun, *J. Appl. Polym. Sci.,* **32,** 3761 (1986).

25. S. Carrozzino, G. Levita, P. Rolla, and E. Tombari, *Polym. Eng. Sci.,* **30,** 366 (1990).

26. J. B. Enns and J. K. Gillham, *J. Appl. Polym. Sci.,* **28,** 2567 (1983).

27. G. Wisanrakkit, J. K. Gillham, and J. B. Enns, *Polym. Mater. Sci. Eng.,* **57,** 87 (1987).

28. D. H. Kim and S. H. Kim, *Polym. Bull.,* **18,** 533 (1987).

29. D. J. Glover, J. V. Duffy, and B. Hartmann, *J. Polym. Sci. Polym. Chem. Ed.,* **26,** 79 (1988).

30. V. Spacek, J. Poucly, and J. Biros, *Eur. Polym. J.,* **23,** 377 (1987).

31. H. J. Flammersheim, H. H. Harhold, K. Bellsted, and J. Klee, *Makromol. Chem.,* **184,** 113 (1983).

32. R. B. Prime, *Polym. Eng. Sci.,* **13,** 365 (1973).

33. C. K. Riew, *Rubber Chem. Technol.,* **54,** 374 (1981).

34. L. C. Chan, J. K. Gillham, A. H. Kinloch, and S. J. Shaw, in *Rubber-Modified Thermosets Resins,* Adv. Chem. Ser. 208, American Chemical Society, Washington, DC, 1984, Chap. 15.

35. K. Yamanaka, Y. Takagi, and T. Inoue, *Polymer,* **83,** 2687 (1989).

36. K. Yamanaka and T. Inoue, *J. Mater. Sci.,* **25,** 241 (1990).

37. K. Hofer and G. P. Johari, *Macromolecules,* **24,** 4978 (1991).