

Relaxations in Thermosets. XXIX. Calorimetric Studies of the Curing Kinetics of Nonstoichiometric Diamine–Epoxy Mixtures

S. WASSERMAN* and G. P. JOHARI†

Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, L8S 4L7 Canada

SYNOPSIS

The curing kinetics of nonstoichiometric mixtures of diglycidyl ether of bisphenol A, with ethylene diamine, propylene diamine, and hexamethylene diamine have been measured under both isothermal and ramp-curing condition. Their kinetics are faster than for stoichiometric compositions and the reactions reach completion. The total heat evolved for the amine-rich composition is greater than for the amine-deficient. None of the available formalisms is consistent with the results. This and the variation in the heat of reaction indicate that steric effects are important for both the reaction rate and the heat evolved. It is argued that the standard heat of reaction of primary amine with the epoxide group differs from that of secondary amine. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The rate of a chemical reaction is directly related to the probability of mutual diffusion of the reacting species and inversely to their diffusion coefficient. The first can be altered by increasing the concentration of one of the species; both are altered by change in the viscosity. In polymer processing, both occur until the viscosity increases beyond a certain value. In an earlier study¹ we had investigated the effects of phase separation of an elastomer dissolved in diamine–diepoxide thermosetting mixture on the reaction kinetics of the thermoset; it generally slowed the rate. Phenomenological equations for the rate kinetics were also critically examined¹ and found to be less satisfactory than generally accepted.

The two reactions, namely, the primary amine's with an epoxide and the secondary amine's, have different rates because of the different steric hindrances and probably different standard heats of reaction. The less than satisfactory data fit to the phenomenological equations¹ can be attributed to

both. Here we examine this issue from a study of the nonstoichiometric compositions of several diamines and diepoxides.

Numerous studies of curing kinetics of diamine–diepoxide thermosets have appeared in the literature.^{2–8} Stoichiometric and nonstoichiometric compositions of a catalyzed reaction of butylamine with phenylglycidyl ether in the original studies by Horie, et al.⁸ gave the same heat of reaction. It was therefore concluded that the standard heat of reaction of an epoxide group with a primary amine is the same as with a secondary amine. We also examine the validity of this conclusion.

EXPERIMENTAL

The 99±% pure amines used as curing agents were purchased from Aldrich Chemicals. Diglycidyl ether of bisphenol A, or DGEBA (EPON 828), was donated to us by Shell Chemicals. Its $M_n = 380$, $n = 0.14$, $T_g = -14^\circ\text{C}$, and functionality = 2. All chemicals were mixed at room temperature, 2–3 min before the measurements.

A Perkin-Elmer differential scanning calorimeter, DSC 4, with TADS computer-assisted data acquisition was used. Curvature of the DSC scans was eliminated by the SAZ function, which subtracts,

* On sabbatical leave (1990–91). Permanent address: Armament Development Authority, P.O. Box 2250, Haifa 31021, Israel.

† To whom correspondence should be addressed.

during scanning, the baseline obtained with empty sample pans. Open aluminum pans containing 20–35 mg samples were used under the flow of Ar gas. For isothermal measurement, the temperature was raised from ambient to the curing temperature at the rate of 80°/min. The maximum time taken for attaining the curing temperature was 50 s.

DSC scans were obtained during heating at 10°/min. For measuring its T_g , the sample was first heated to 20° above its T_g endotherm, cooled to 25°C at 10°/min, and thereafter reheated at 10°/min. Because of the broadness of the endotherms, T_g is uncertain by $\sim 2^\circ\text{C}$.

RESULTS

Thermosets of two compositions, one with half the stoichiometrically required diamine (2 : 0.5) and the second with twice (2 : 2), were studied. Data for the stoichiometric compositions (2 : 1) are taken from Ref. 1. Representative scans for isothermal curing of each of the three compositions containing ethylene diamine (EDA), propylene diamine (PDA), and hexamethylene diamine (HMDA) are shown in Figure 1. Integrated area of these scans is equal to ΔH_{iso} . Immediately after the isothermal curing, the samples were cooled to 25°C and reheated to 240°C at 10°/min. These DSC scans showed, except for the 2 : 0.5 compositions, an endothermic broad feature characteristic of the glass-liquid transition, followed by an exothermic minimum indicating further curing of the thermoset, similar to Figure 1(b) in Ref. 1. The integrated area of this minimum was used to calculate $\Delta H_{\text{postcure}}$, the residual heat of reaction. The heat of reaction, ΔH_{tot} , is equal to $\Delta H_{\text{iso}} + \Delta H_{\text{postcure}}$; ΔH_{tot} and $\Delta H_{\text{postcure}}$ per gram of the sample for all compositions cured at different temperatures are given in Table I.

In the second set of measurements each mixture was heated from 25 to 240°C at 10°/min and its DSC scans obtained. Representative scans are shown in Figure 2. ΔH_{ramp} per gram of the sample determined from the integrated area of the scans is given also in Table I.

The fractional conversion α , at a time t during the isothermal curing, was calculated from the plots in Figure 1 and ΔH_{tot} in Table I from:

$$\alpha(t) = \frac{1}{\Delta H_{\text{tot}}} \int_0^t \frac{\partial \Delta H}{\partial t} dt \quad (1)$$

α is plotted against the reaction time t , in Figures 3–5. The plots are similar to those observed for time-

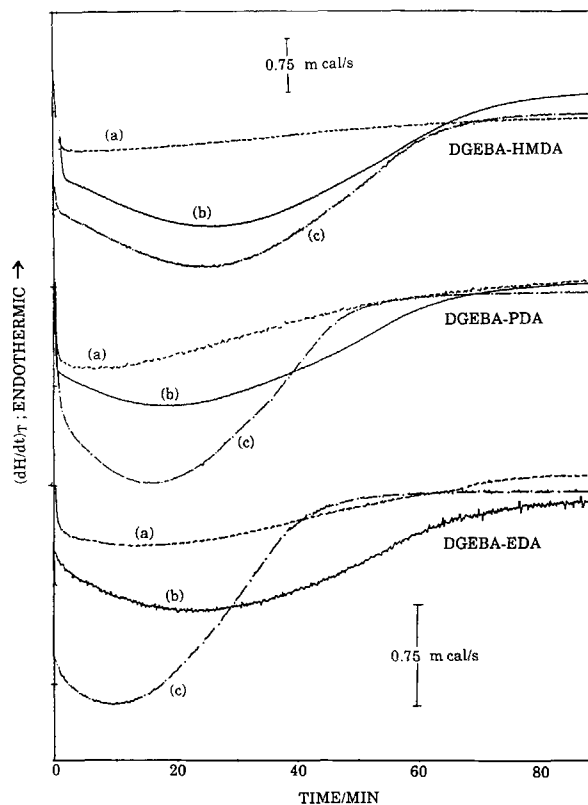


Figure 1 Representative DSC scans of DGEBA-diamine compositions during their isothermal curing at 50°C. Plots are labeled (a) for 2 : 0.5, (b) for 2 : 1, and (c) for 2 : 2 (DGEBA-diamine) compositions. They are normalized with respect to the sample's mass. Plots for 2 : 1 are from Ref. 1. Baseline for integration was for the (dH/dt) values as $t \rightarrow \infty$.

dependent, irreversible chemical and physical (e.g., crystallization,⁹ grain growth^{9–11} and structural relaxation^{11–13} in glasses) processes. For the curing of thermosets, it is seen as characteristic of an autocatalytic chemical reaction, although autocatalysis does not occur in the physical processes.

In a review of the use of DSC for determining the curing kinetics of thermosets, Barton² compared the various equations for fitting isothermal and ramp curing data. He concluded that if the primary and secondary amine (formed after one proton of the NH_2 group has reacted with the epoxy group) are of equal reactivity,

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

where K_1 and K_2 are constants related to the rate constants of the two reactions, and m and n are empirical parameters ($m + n = 2$). This relation was

Table I Parameters for the Ramp Curing and Isothermal Curing Kinetics of Thermosets of Various Compositions at Different Temperatures^a

Thermoset Composition	$\Delta H_{\text{tot}} (\Delta H_{\text{postcure}}) (\text{J/g})$			ΔH_{ramp} (J/g)	t_{min} at T_{cure} (min)			$T_{\text{min,ramp}}$ (°C)
	50°C	60°C	70°C		50°C	60°C	70°C	
DGEBA-EDA (2:0.5)	175 (9)	226 (1.5)	266 (1.5)	272	13.2	5.6	4.0	104
DGEBA-EDA (2:1) ^b	370 (49)	436 (38)	450 (28)	441	23.5	10.6	5.6	102
DGEBA-EDA (2:2)	389 (0)	443 (0)	461 (0)	407	9.5	7.0	3.1	95
DGEBA-PDA (2:0.5)	264 (7)	207 (5)	215 (4)	264	7.0	5.0	2.6	104
DGEBA-PDA (2:1) ^b	489 (55)	468 (49)	450 (30)	459	18.2	9.1	4.0	98
DGEBA-PDA (2:2)	465 (6)	426 (0)	390 (0)	465	16.2	5.9	2.0	96
DGEBA-HMDA (2:0.5)	190 (10)	204 (4)	222 (4)	278	4.6	2.9	2.0	105
DGEBA-HMDA (2:1) ^b	393 (10)	403 (6)	405 (4)	432	25.4	11.7	5.1	103
DGEBA-HMDA (2:2)	410 (5)	486 (3)	452 (0)	487	25.0	10.7	4.0	102

^a Values in parenthesis are for $\Delta H_{\text{postcure}}$ measured on postcure.

^b Data taken from Ref. 1. In Fig. 3 of Ref. 1, the temperature scale for plot (1) is as shown; other plots were shifted to the right by 10°C. Tabulated values and text are correct in Ref. 1.

originally used by Horie, et al.⁸ for fitting the DSC data for stoichiometric thermosets including the EDA, PDA, and HMDA compositions.

Barton pointed out that, for curing kinetics of a variety of stoichiometric diamines, DGEBA mixtures $m = 1$ and $n = 2$. Thus, the reduced rate,

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

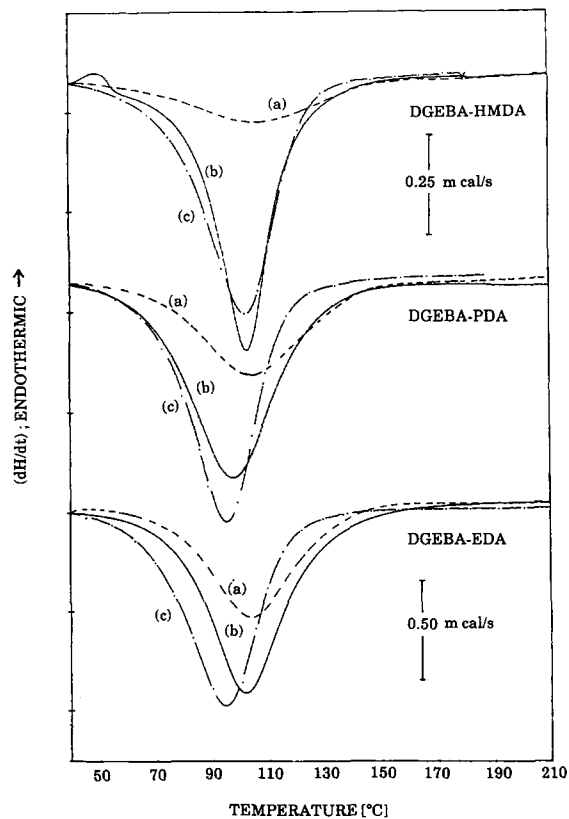


Figure 2 Representative DSC scans of DGEBA-diamine compositions during their temperature ramp curing at 10°/min. Other descriptions are as in Fig. 1.

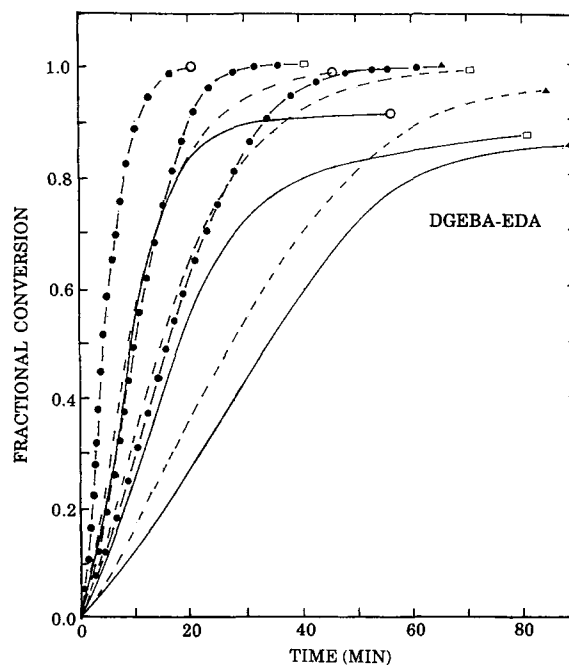


Figure 3 Fractional conversion of DGEBA-EDA compositions plotted against the curing time at 50, 60, and 70°C. Dashed line is for 2 : 0.5, continuous line for 2 : 1, and line through the dots for 2 : 2 composition. Lines ending at (▲) are for 50°C cure, at (□) for 60°C cure, and at (○) for 70°C cure.

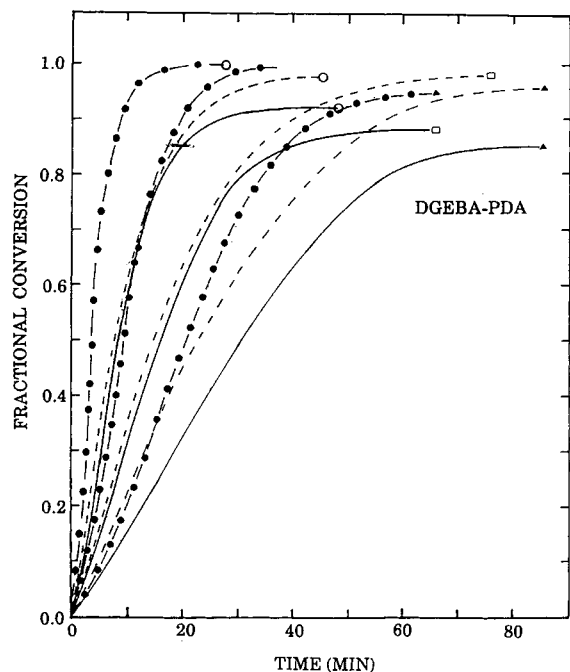


Figure 4 Fractional conversion of DGEBA-PDA mixtures plotted against the curing time at 50, 60, and 70°C. For notations, see Fig. 3.

so that the plot of r against α should be a straight line with intercept K_1 and slope K_2 . As before,¹ our attempts to fit the data to Eq. (3) were again unsuccessful. The plots were nonlinear with r reaching a maximum value and then abruptly decreasing at a rapid rate with increasing α . As discussed in our earlier studies¹ of stoichiometric compositions, the plot of r against α will not be linear because as vitrification is reached, the rate of reaction, or $(\partial\alpha/\partial t)$, approaches zero (as does r). This occurs as α reaches a value equal to α_{vit} . In such plots, α at $r = 0$ is formally independent of n in Eq. (2) but not of m . Thus m is not equal to 1. Modifications to this value by others have also been discussed in Ref. 1.

For DSC scans obtained by rate heating, a general equation for fractional conversion (chemical or physical processes) is,

$$\alpha = \Delta H(t) / \Delta H_{ramp} \quad (4)$$

or²

$$(\partial\alpha/\partial t) = A(1 - \alpha)^2 \exp(-\Delta E_a/RT) \quad (5)$$

where A is a constant, $\Delta H(t)$ is the heat evolved up to a certain temperature T , ΔE_a is the activation energy and R the gas constant. ΔE_a is assumed to be the same for the reaction with primary and sec-

ondary amines. By combining Eqs. (3) and (5), the reduced rate,

$$\begin{aligned} \ln(r) &= \ln[(\partial\alpha/\partial t)(1 - \alpha)^{-2}] \\ &= \ln A - \Delta E_a/RT \end{aligned} \quad (6)$$

so that a plot of $\ln(r)$ against T^{-1} should be a straight line with slope ΔE_a and intercept $\ln A$. Although portions of the $\ln(r)$ against T^{-1} plot could be seen as linear, over a broad temperature range they were convex to the axis. Therefore, a meaningful value of E_a could not be obtained.

DISCUSSION

During the curing of these thermosets, uncatalyzed reaction of a primary amine with an epoxide first forms a secondary amine. This in turn reacts with another epoxide group to form a tertiary amine.^{14,15} The reactions are seen to be autocatalyzed by hydroxyl groups that are generated in the reactions. As the network structure produced by crosslinking reaction densifies, internal viscosity increases and molecular diffusion slows. This ultimately leads to vitrification. At vitrification α is typically between 80 and 100%. It increases further when the vitrified

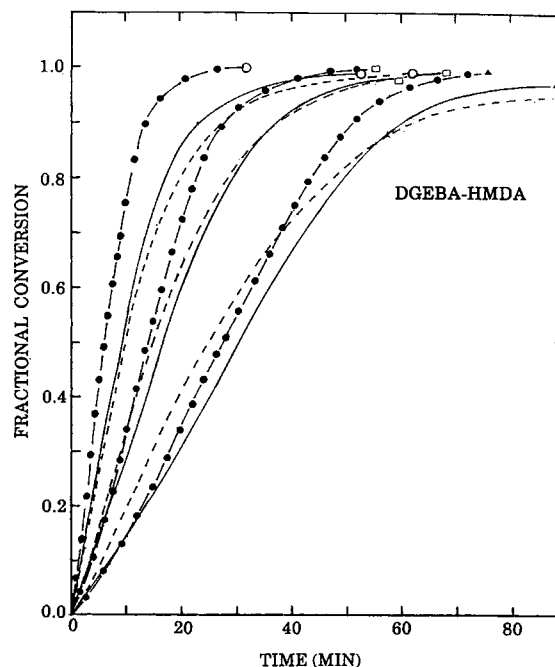


Figure 5 Fractional conversion of DGEBA-HMDA mixtures plotted against the curing time at 50, 60, and 70°C. For notations, see Fig. 3.

thermoset is heated above its T_g or aged (for a substantial period) at temperatures below T_g , a process known as postcure.

The above processes do not occur if the amine-DGEBA mixture is nonstoichiometric. For example, both primary and secondary amine reactions should reach completion in a reasonable time in an amine-deficient mixture, and the faster of the two reactions reach completion in an amine-rich mixture, neither of which reach vitrification at the curing temperature. In Table I, the heat evolved (values given in parentheses) on postcuring are 1-5% of the ΔH_{tot} for 50°C cure and zero for 70°C cure. These values remain higher for 2 : 1 compositions except for the DGEBA-HMDA, whose reactions reach almost completion in 100 min at 70°C. Since aging effects on the properties of a thermoset involve both chemical reactions (which densify it by crosslinking and remove certain dipolar and other end groups) and a physical process of structural relaxation, we deduce that the effect from the first would be vanishingly small for the cured nonstoichiometric compositions when kept at a temperature below their T_g , than for the cured stoichiometric compositions kept at a corresponding temperature. Data in Table I also indicate that the effect will be relatively less for a diamine with a longer CH_2 chain between the NH_2 groups.

For the conditions listed in Table I, T_g of the cured 2 : 0.5 compositions are less than 40°C for all DGEBA-diamines. For the 2 : 2 compositions T_g 's are 68°C for DGEBA-EDA, 66°C for DGEBA-PDA, and 66°C for DGEBA-HMDA. These values are significantly less than the corresponding values: 104-114°C, 91-103°C, and 68-77°C for the cured stoichiometric composition, except for DGEBA-HMDA.¹ The similarity between the T_g 's of the 2 : 2 and 2 : 1 DGEBA-HMDA composition is remarkable for it implies that the relaxation time of a network with a lower crosslink density of an amine-rich composition (not each amine molecule is expected to form four covalent bonds with four DGEBA molecules) is close to that of a network with a higher crosslink density of the cured stoichiometric composition. Without a chemical analysis for the unreacted HMDA in the cured amine-rich composition, it is not possible to resolve whether this similarity can be attributed to antiplasticization of the structure by HMDA or to more efficient molecular packing of the incompletely formed HMDA-DGEBA network containing less than the expected number (four) of covalent bonds between one diamine and four (different) DGEBA in a stoichiometric composition.

As mentioned earlier, there are two chemical reactions that form the network: first between the primary amine and epoxide group and the second between the secondary amine (formed after the removal of one proton by the first reaction) and another epoxide group. It is intuitively expected that the steric hindrance for the second reaction would be much greater than for the first and will increase with increase of the amine's chain length and the size of the R and R' groups in the reacting structure, $R-\text{CH}(\text{OH})-\text{CH}_2-[\text{NH}-(\text{CH}_2)_n-\text{NH}]-\text{CH}_2-\text{CH}(\text{OH})-R'$. Figures 3-6 show that 2 : 0.5 compositions, in which all secondary amines react with the epoxide, take longer to reach complete cure than 2 : 2 compositions despite the former's low viscosity and T_g , or that the rate of the secondary amine's reaction is slower than that of the primary amine's owing to this steric hindrance and/or slower diffusion. Furthermore, for 70°C cure, the reactions in 2 : 0.5 compositions are slower to reach completion than in 2 : 1 compositions for HMDA than EDA

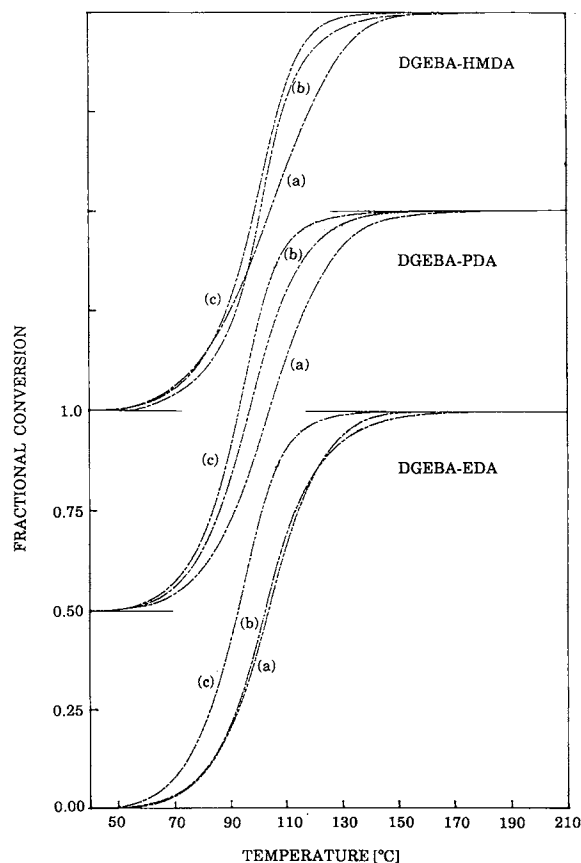


Figure 6 The plots of fractional conversion against the temperature for the various DGEBA-diamine compositions.

and PDA, confirming the above-mentioned effects of the CH₂ chain length.

The heat evolved, ΔH° , in the curing process is also from two reactions of DGEBA: (i) with primary amine and (ii) with the secondary amine formed after one proton from the primary amine is lost to the epoxy group. Horie et al.⁸ concluded that the two reactions (between phenylglycidyl ether and butylamine) have the same ΔH° of 102 ± 2.5 kJ/mol of DGEBA (more recent experiments on DGEBA-EDA give 117 kJ/mol¹⁶). Hence, ΔH° for 2 : 0.5 composition should be one-half of that for 2 : 1, which in turn should be equal to that of the 2 : 2 composition, since any catalyzed reaction between the DGEBA molecules themselves does not contribute to ΔH at these temperatures.¹ Table I shows that ΔH° ($= \Delta H_{\text{ramp}}$) measured for the 2 : 0.5 and 2 : 2 compositions is generally greater than for the 2 : 1 compositions ($\Delta H_{\text{ramp}} = 542 \pm 14$ (2×271) for 2 : 0.5, 445 ± 15 for 2 : 1, and 475 ± 12 J/g for 2 : 2 compositions). This also indicates, as in earlier studies,¹ that the reactions for 2 : 1 DGEBA-EDA and PDA compositions did not reach completion, but did for 2 : 0.5 and 2 : 2 compositions. Why is then ΔH° for the 2 : 0.5 composition 14% greater than for the 2 : 2 composition? We tentatively attribute it to a higher ΔH° for the secondary amine's reaction than for the primary amine's with DGEBA (the former reactions must occur in 2 : 0.5 composition, but not necessarily in 2 : 2 composition).

Here, we differ from Horie et al.'s⁸ conclusion that the heat released on DGEBA's reaction with primary and secondary amines is the same. In amine-rich compositions, the amine left after the reaction may be entirely either the primary amine, or the secondary amine (formed on reaction of the primary amine) or a mixture of the two. For 2 : 2 composition, this would be one mole of the primary or 2 moles of secondary amine or any combination of the two that satisfies complete bonding with the epoxy groups. In their original work, Horie et al.⁸ reported the total amount of unreacted primary and secondary amines, not the separate amounts. So an ambiguity remains in the proton state of the amine left after the reaction for their 2 : 2 and 2 : 4 compositions. These differences may be resolved by chemical or other analysis or alternatively by separately determining ΔH° for the DGEBA's reactions with a secondary amine alone. As the reaction of DGEBA with a primary amine—and not with the secondary amine formed after this reaction—will produce a linear chain polymer instead of a network, measurement of the mechanical modulus can also indicate the state of amine in the cured 2 : 2 compositions. We tentatively conclude that a difference

between ΔH° of the two reactions may partly be the reason for the observed differences in the heat evolved for the same extent of cure under different conditions.

CONCLUSIONS

Isothermal and temperature ramp curing studies of three diamine-DGEBA compositions containing lesser, and greater, than the stoichiometric amounts of diamines, show that the reaction with the stoichiometric amount is slower than with the nonstoichiometric, for which it reaches completion. The heat of reaction of DGEBA with a primary amine significantly differs from that with secondary amine. This difference is partly the reason for the inadequacy of the data fits to the generally available calorimetric equations.

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