Competitive Primary Amine/ Epoxy and Secondary Amine/ Epoxy Reactions: Effect on the Isothermal Time-to-Vitrify

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SYNOPSIS

The effect of temperature on the ratio of the kinetic rate constants, k_2/k_1, has been investigated using FTIR spectroscopy for the competing reactions of epoxy with secondary amine (k_2) and primary amine groups (k_1) in a trimethylene glycol di-p-aminobenzoate/ diglycidyl ether of the bisphenol A system. The ratio of the rate constants increases from 0.16 to 0.33 in the temperature range 100–160°C. The corresponding difference in the activation energies for the competing reactions is about 3.7 kcal/ mol. The effect of the ratio on the time-to-vitrify contour of the isothermal time–temperature–transformation (TTT) cure diagram is discussed: The effect is more significant at higher curing temperatures.

INTRODUCTION

Prediction and determination of the relationships between the cure process of thermosetting resins and the final macroscopic properties is complicated by the complex changes (both physical and chemical) that can potentially occur during their cure. A framework for understanding these relationships is the isothermal time–temperature–transformation (TTT) cure diagram.[1] The diagram (Fig. 1) displays the states of the material which are encountered during isothermal cure vs. time[1-6]: These include liquid, sol glass, sol/ gel rubber, gel rubber, sol/ gel glass, gel glass, and char. The various changes occurring in the material during isothermal cure are characterized by contours of the times to reach the various events. Recently, quantitative modeling of the TTT diagram has been reported under both kinetic and diffusion control[3] for the difunctional epoxy/ tetrafunctional aromatic diamine system shown in Figure 2. However, the effect of the different reactivities of the primary amine and the secondary amine with epoxide was only briefly considered in that report.[3] The ratio of the rate constants, k_2/ k_1, where k_1 is the rate constant defined for the

reaction of epoxy with a primary amine group and k_2 is the rate constant for the reaction of epoxy with secondary amine, is generally reported to be in a range of 0.1–1.0.[3,7-10] Note that for equal reactivity of amine hydrogen atoms $k_2/k_1 = 0.5$.

However, the effect of temperature on the ratio, k_2/ k_1, has rarely been discussed, the ratio being assumed to be independent of temperature in most kinetic analyses.[3,4,7-16] The ratio is predicted to have consequences on the chemical and physical properties of curing systems, because the reaction of secondary amine with epoxy is the principal factor for introducing branching points and crosslinking points into the developing molecular network.

The experimental methods used most often for the determination of k_2/ k_1 are DSC,[3,4,10] GPC,[11,16] and swollen titration.[12,13] For a curing system, it is difficult to measure the conversion after the gel point by means of the GPC and swollen titration techniques. DSC has the disadvantage of not monitoring changes of individual reactive functional groups during cure.

Fourier transform infrared spectroscopy (FTIR) was chosen for this research as being potentially more discriminating. The ratio k_2/ k_1 is studied versus temperature for the difunctional aromatic epoxy/ tetrafunctional aromatic diamine used in earlier research.[3,4] The results obtained from FTIR show that k_2/ k_1 changes with cure temperature. The
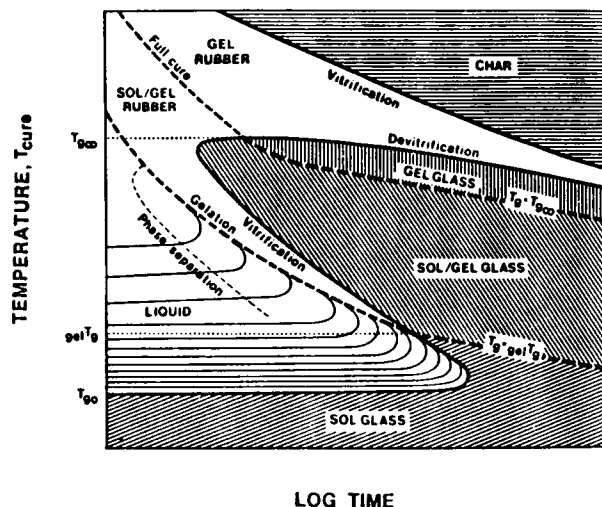

LOG TIME

Figure 1 A generalized isothermal time–temperature–transformation (TTT) cure diagram for a thermosetting system.[5] Relevant contours: gelation (corresponding, for the simplest system, to the unique conversion at the molecular gel point), vitrification (corresponding to T_g of isothermal curing system rising to the cure temperature T_{cure}), devitrification (corresponding to T_g decreasing to the cure temperature T_{cure}), and vitrification leading to char.

consequence of the ratio on the physical and chemical properties of the material during cure is discussed in terms of the isothermal TTT cure diagram. A preliminary report has been published.[17]

MATERIALS AND EXPERIMENTAL PROCEDURE

The chemical system used was a mixture of a liquid difunctional epoxy [diglycidyl ether of bisphenol A, DER 332 (DGEBA) Dow Chemical Corp.] and a tetrafunctional aromatic diamine [trimethylene glycol di-p-aminobenzoate (TMAB), Polaroid Corp.] (Fig. 2). The epoxy monomer is a viscous liquid with an epoxide equivalent weight (EEW) of 174 g/ eq. The amine curing agent is a crystalline solid (melting point = 125°C) with amine hydrogen equivalent weight = 78.5 g/ eq. The chemicals were stoichiometrically mixed at 100°C for 15 min with vigorous stirring in order to dissolve the amine in the epoxy resin.[3,4] Immediately after mixing, the warm liquid was degassed for 10 min under vacuum in an oven held at room temperature. The resulting clear viscous liquid mixture was stored at −15°C. The glass transition temperature of the initial mixture, T_{g0} = 0°C. The glass transition temperature for the fully cured material, $T_{g\infty}$ = 180°C.
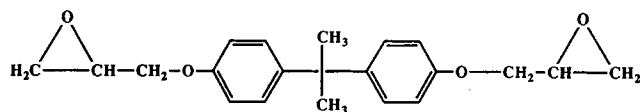
Diglycidyl Ether of Bis-phenol A
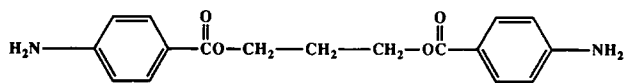
Trimethylene Glycol Di-p-aminobenzoate

Figure 2 Chemical reactants.

Infrared analysis was performed using a Fourier transform infrared spectrometer (Nicolet 170SX) equipped with a temperature-controlled cell which was continuously purged with nitrogen gas. A series of spectra on specimens sandwiched between two sodium chloride plates was obtained versus time at each cure temperature T_{cure}, which ranged from 100 to 160°C. Each spectrum from 4900 to 400 cm^{-1} was averaged over 32 scans taken at 4 cm^{-1} resolution. The methyl group absorbance peak, ν_{C-H} = 2962 cm^{-1}, was used as an internal standard. Important absorbances of relevant functional groups are listed in Table I. Figure 3 shows the FTIR spectrum of the initial mixture. The conversion of a functional group versus time is calculated by

$$1 - p = \frac{I_{(t)} \times I_{(0)\text{standard}}}{I_{(0)} \times I_{(t)\text{standard}}}$$

where I = absorbance, subscripts (t) and (0) refer to time t and initial time, subscript "standard" refers

Table I Important Absorbances in TMAB-Cured DGEBA System

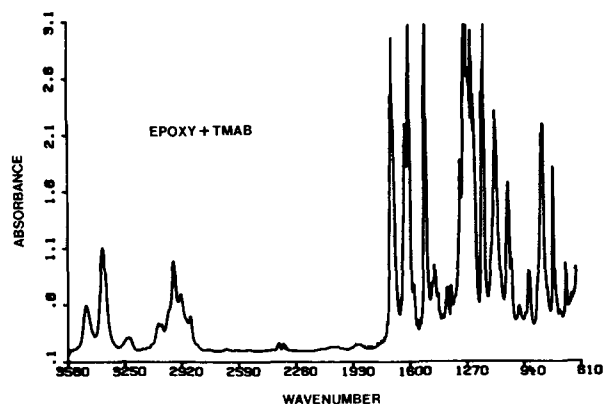| Peak or Band (cm^{-1})	Assignment
3581–3430	Hydroxyl stretching vibration
3545	Isosbestic point of OH
3480–3310	N — H stretching vibration
2962	Methyl C — H assym stretching
1710	C = O vibration
1618	NH$_2$ deformation vibration
1590	Substituted aromatic ring
1360	Ether methylene C — H
1036	Aromatic deformation
915	Epoxide ring deformation

Figure 3 FTIR spectrum of the unreacted formulation: DGEBA/TMAB (stoichiometric mixture).

to the internal standard, p = the fractional conversion; for the fractional yield of hydroxyl group, Y_{OH},

$$Y_{OH} = \frac{I_{(t)} \times I_{(\infty)\text{standard}}}{I_{(\infty)} \times I_{(t)\text{standard}}}$$

where subscript (∞) refers to the fully cured specimen.

RESULTS AND DISCUSSION

Kinetic Ratio k_2/k_1

The spectroscopy of hydroxyl-containing compounds is frequently complicated by the occurrence of hydrogen bonding. Hydrogen bonding may occur both intramolecularly and intermolecularly, the ratio being influenced by temperature. Figure 4, for the fully cured material, is presented as evidence that OH intramolecular hydrogen bonding (absorbance at 3581 cm^{-1}) increases with increasing temperature, whereas OH intermolecular hydrogen bonding (3430 cm^{-1}) decreases with increasing temperature.[18] When the spectra obtained at different temperatures for a fully cured specimen are superimposed (normalized by using the methyl ν_{C-H} peak at 2962 cm^{-1}), the composite graph obtained shows that the curves intersect at one point (3545 cm^{-1}). The point is known as the isosbestic point (3545 cm^{-1}) and has been used to monitor the concentration of OH groups in epoxies.[19] Figure 5 shows that the isosbestic point is just beyond the amine N—H peaks (i.e., 3480–3310 cm^{-1}). The isosbestic point is assumed to not change significantly during cure. The change of OH group concentration is therefore monitored by measuring the absorbance intensity at the isosbestic point. The decrease of
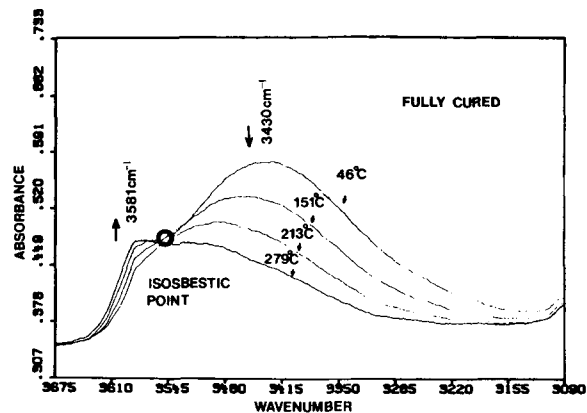

Figure 4 Superimposed FTIR spectra (fully cured system) from 46 to 279°C. OH intramolecular hydrogen bonding (absorbance at 3581 cm^{-1}) increases with increasing temperature, whereas OH intermolecular hydrogen bonding (3430 cm^{-1}) decreases with increasing temperature.

epoxy (915 cm^{-1})^2 and amine (1618 cm^{-1})[15] bands are also monitored during cure.

Generally, the reactions of the aromatic diamine-cured difunctional epoxy which can occur are listed in Figure 6. If only reactions (a) and (b) occur in the curing system, the sum of hydroxyl and epoxy groups should remain constant: i.e., $Y_{OH} + p_A$ = const, where p_A is the fractional conversion of epoxide. However, the occurrence of reactions (c) + (d) would decrease the sum of hydroxyl and epoxy groups.

Experimental data at 145°C are presented in Figure 7. Since the sum of hydroxyl yield and epoxy conversion is a constant during cure, it follows that
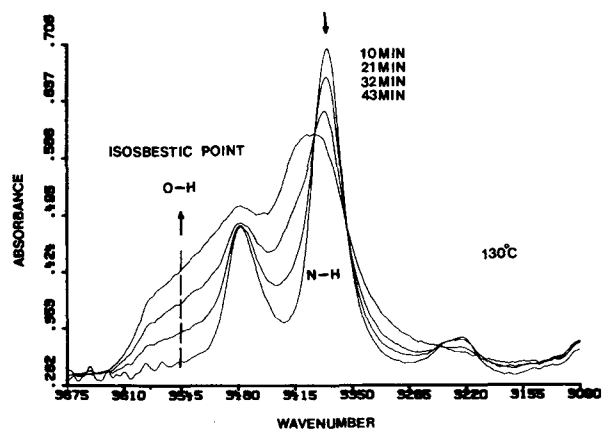

Figure 5 IR spectra at 130°C vs. time during cure. The isosbestic point is related to the hydroxyl content during cure. The isosbestic point (3545 cm^{-1}) is just beyond the N—H peaks (3480–3310 cm^{-1}).
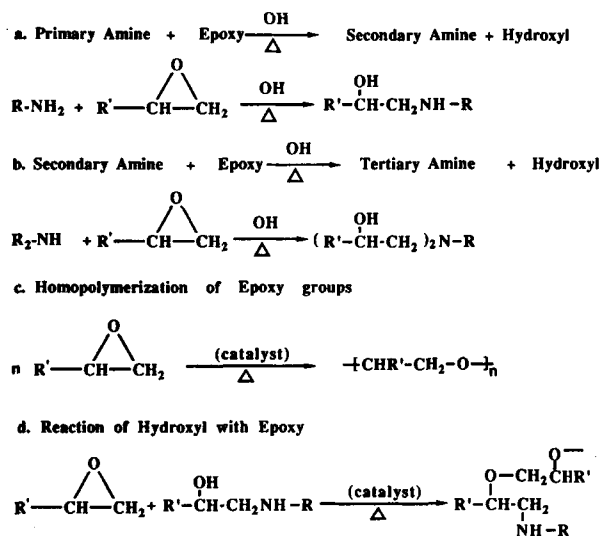
Figure 6 Epoxy/amine reaction scheme: (1) amino hydrogen with epoxide (a, b); (2) homopolymerization of epoxide (c); (3) epoxide with hydroxyl (d).

the homopolymerization of epoxy and the reaction of epoxy with hydroxyl do not occur, or can be neglected, in the 1:1 stoichiometric TMAB/DGEBA system under the present experimental conditions. Other researchers have reached the same conclusion when using stoichiometric quantities without catalyst in other aromatic amine/aromatic epoxy sys-

tems.[15] Figures 8 and 9 show the conversion of epoxy and primary amine, respectively, versus time of cure for temperatures from 100 to 160°C. All of the experimental data obtained are in the kinetically controlled region (i.e., before vitrification, see Table II).[3] If A, B, B', and B" represent epoxy, primary amine, secondary amine, and tertiary amine groups, respectively, and (HX) relates to hydroxyl, then, the hydroxyl-catalyzed reactions of (a) and (b) in Figure 6 can be represented as follows:

$$A + B + (HX) \xrightarrow{k_1} B' + (HX) \qquad (1)$$

$$B' + A + (HX) \xrightarrow{k_2} B'' + (HX) \qquad (2)$$
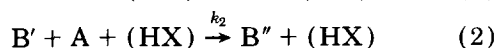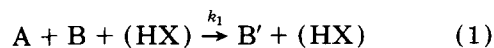
Although there is much experimental evidence[20] that the reactions of diamine-cured epoxy resins are autocatalyzed by OH, it has often been assumed that the reaction is first or second order.[9,11–13,15,16,21,22] Another assumption often made to simplify the mathematical treatments is that the ratio k_2/k_1 is independent of temperature. In the kinetically controlled region, if the activation energies of the two competitive reactions are different, the ratio must be influenced by the cure temperature. The effect of the cure temperature on the ratio is relevant to the effect of the cure temperature on the developing network structure, and on the physical properties of the curing system.
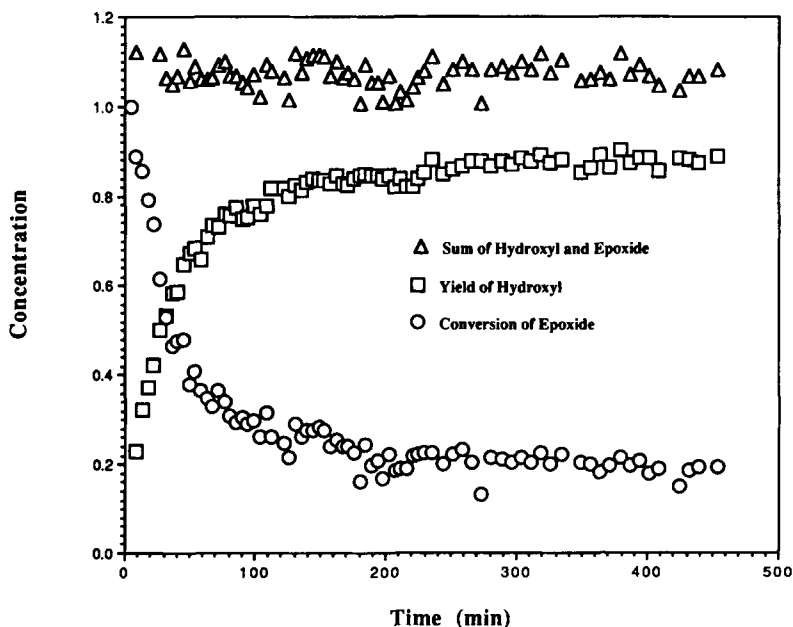

Figure 7 Comparison of hydroxyl and epoxide concentrations during cure. The epoxide concentration decreases, whereas the hydroxyl concentration increases; however, the sum of hydroxyl yield and epoxy conversion is constant during cure. Therefore, the homopolymerization of epoxide and the epoxide/hydroxyl reaction can be neglected.
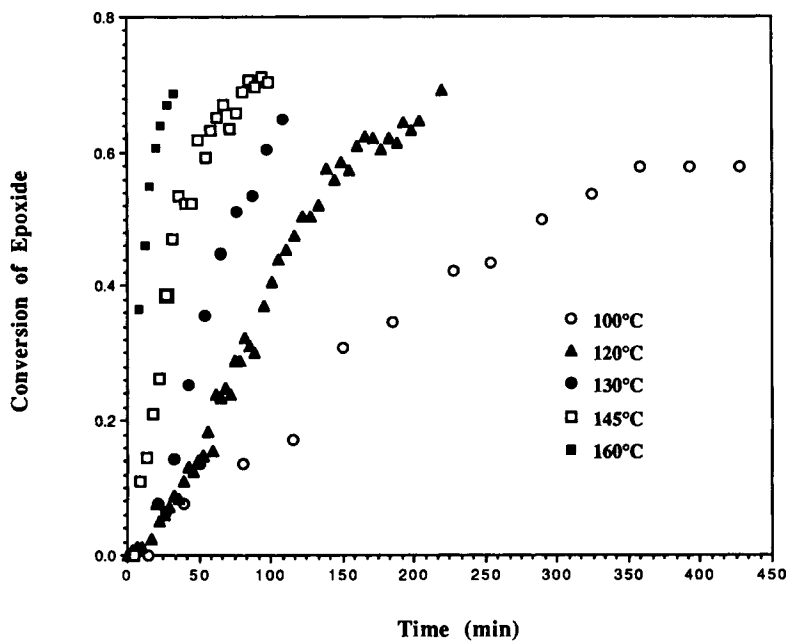
Figure 8   Conversion of epoxide vs. time at different cure temperatures: 100, 120, 130, 145, and 160°C.

The kinetic equations for the mechanism of the autocatalytic reaction can be written as follows:

For consumption of primary amine:

$$\frac{dp_B}{dt} = k_1[\text{A}]_0(1 - p_A)(1 - p_B)[\text{OH}] \qquad (3)$$

For yield of tertiary amine:

$$\frac{d(p_B q_B)}{dt} = k_2[\text{A}]_0(1 - p_A)p_B(1 - q_B)[\text{OH}] \qquad (4)$$
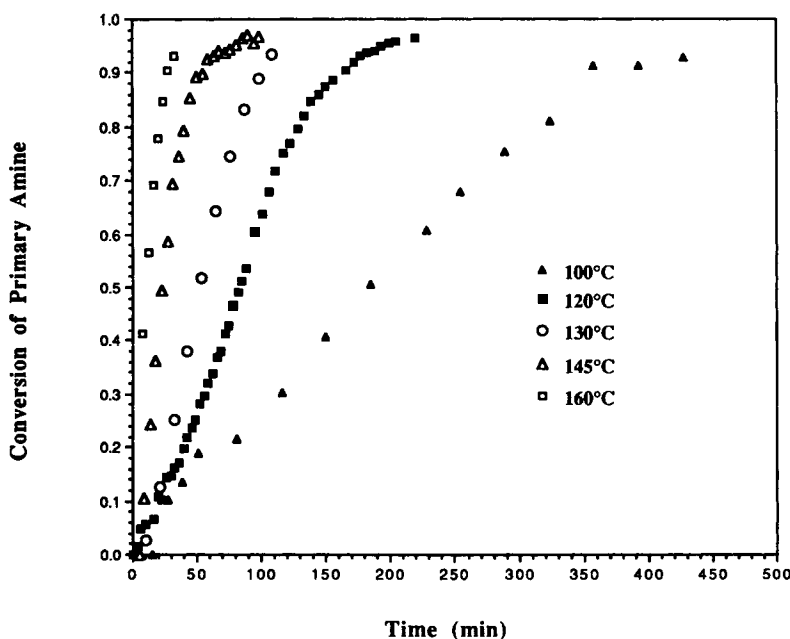
where [OH] is the concentration of hydroxyl in the

Figure 9   Conversion of primary amine vs. time at different cure temperatures: 100, 120, 130, 145, and 160°C.

Table II Limits of Kinetic Control

	Temperature (°C)	100	120	130	145	160
Time to vitrification[a] (min)		960	430	290	160	220
Time of FTIR experiments[b] (min)		0–450	0–250	0–135	0–120	0–50

[a] Data from Ref. 3, obtained from DSC for the same system (1 : 1). Diffusion control becomes important after vitrification (i.e., after $T_g = T_{cure}$).

[b] Present data.

curing system; p_A, p_B, and q_B represent the fractional conversions of epoxide, primary amine, and secondary amine, respectively, and are defined as follows:

$$p_A = \frac{[A]_0 - [A]}{[A]_0}, \quad p_B = \frac{[B]_0 - [B]}{[B]_0}$$

$$q_B = \frac{[B]_0 - [B] - [B']}{[B]_0 - [B]} = \frac{[B'']}{[B]_0 - [B]}$$

$[A]_0$ and $[B]_0$ are the initial concentrations of epoxide and primary amine groups, respectively; $[B]$, $[B']$, and $[B'']$ are the concentrations of primary amine, secondary amine, and tertiary amine groups during cure, respectively.

Several relationships between p_B, q_B, and k_2/k_1 can be derived[23] from eqs. (3) and (4). Dividing eq. (4) by eq. (3) yields

$$\frac{d(p_B q_B)}{dp_B} = \frac{k_2}{k_1} \cdot \frac{p_B - (p_B q_B)}{(1 - p_B)} \quad (5)$$

It should be noted that eq. (5) applies for any order of reaction as long as the exponent for the amine concentration is 1.[24-26]

Integrating eq. (5) from 0 to p_B yields eqs. (6) and (7), depending on the value of the ratio $k_2/k_1 \equiv K$:

$$\frac{(1 - p_B q_B)}{(1 - p_B)} = \frac{[K - (1 - p_B)^{K-1}]}{(K - 1)}, \quad K \neq 1 \quad (6)$$

and

$$\frac{(1 - p_B q_B)}{(1 - p_B)} = [1 - \ln(1 - p_B)], \quad K = 1 \quad (7)$$

Let r_B = [initial primary amine groups]/[initial epoxide groups]. It follows that for the reactions in the amine-cured epoxy system:

$$p_A = r_B p_B + r_B p_B q_B \quad (8)$$

Substituting $p_B q_B$ into eqs. (6) and (7) from (8) yields

$$\left[1 - \left(\frac{p_A - r_B p_B}{r_B}\right)\right] \bigg/ (1 - p_B)$$

$$= \frac{K}{K - 1} - \frac{1}{K - 1}(1 - p_B)^{K-1} \quad K \neq 1 \quad (9)$$

and

$$\left[1 - \left(\frac{p_A - r_B p_B}{r_B}\right)\right] \bigg/ (1 - p_B)$$

$$= [1 - \ln(1 - p_B)], \quad K = 1 \quad (10)$$

Figure 10 shows that the experimental data obtained at 120°C do not fit the relationship derived from eq. (10) with $K = 1$; rather, the experimental points lie between the curves for $K = 1$ and for $K = 1/10$ derived from eq. (9). It is clear that the reactivities of primary amine and secondary amine with epoxy are different.

However, Figure 10 also shows that the lower the conversion, the more insensitive the effect of the ratio. Therefore, the method chosen for studying the kinetic ratio should not be limited to low conversions, such as at the gelation point (which limits application of the methods of GPC and titration).

By suitably choosing the parameter K and using eq. (9), a straight line relationship between $[1 - (p_A - r_B p_B)/r_B]/(1 - p_B)$ and $(1 - p_B)^{K-1}$ is obtained. Figures 11 and 12 show that the experimental data fit the theoretical curve well when $K = 0.238$ and 0.281 for $T_{cure} = 120$ and $145°C$, respectively.

In this research, the best value of the ratio K is obtained from regression of experimental data (from $p_B = 0.0$ to $p_B = 0.93$). The ratio for various cure temperatures is listed in Table III; the ratio changes from 0.158 to 0.330 for temperature changes from 100 to 160°C, i.e., the ratio of the rate constants for the reaction of epoxide with secondary amine and
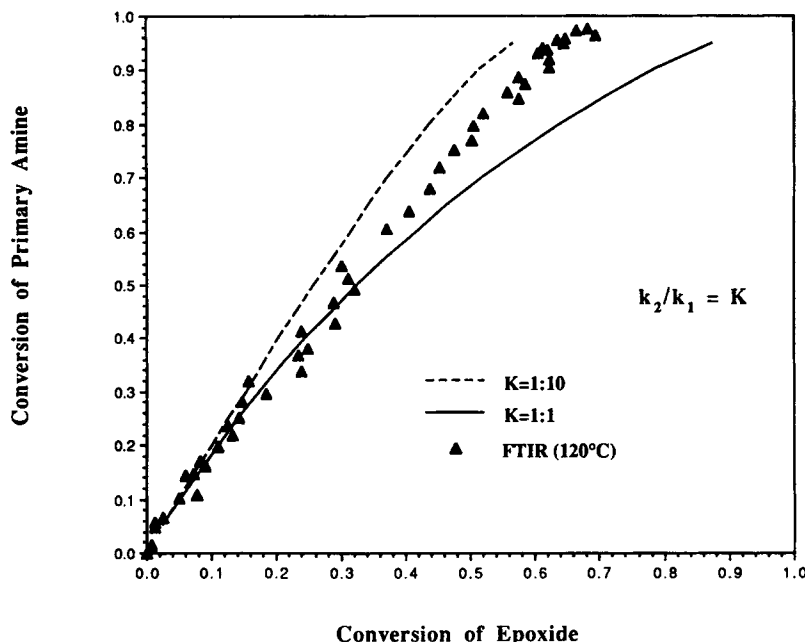
Figure 10   Conversion of primary amine vs. epoxide as determined by FTIR (120°C) compared with theoretical curves from eqs. (9) and (10). The lower the conversion of epoxide, the more insensitive the effect of the kinetic ratio (k_2/k_1).

primary amine increases as the curing temperature increases. The difference between the activation energies $(E_2 - E_1)$ can be expressed by the Arrhenius expression

$$K = \frac{A_2}{A_1} \cdot \exp\left(-\frac{E_2 - E_1}{RT}\right) \qquad (11)$$

where A_2/A_1 is a constant. Taking the logarithm of eq. (11) gives

$$\ln(K) = \ln\left(\frac{A_2}{A_1}\right) - \frac{E_2 - E_1}{RT} \qquad (12)$$

Figure 13 shows that the experimental data from Table III fit a straight line with $(E_2 - E_1)$ equal to about 3.7 kcal/mol. These results are relevant to the controversies concerning the ratio k_2/k_1 found in the literature, since the ratio is influenced by the cure temperature.

In contrast, other researchers have considered the activation energies for the reactions of epoxy with the amino hydrogens to be the same. The ratio $k_2/k_1 \neq 0.5$ has been suggested to be the result of the frequency factor A[3,7,8,15] rather than due to differences in activation energies. However, according to Eyring's theory, the frequency factor for a reaction is

$$A = \frac{k_B T}{h} \cdot \beta \cdot \exp\left(\frac{\Delta S^*}{R}\right) \qquad (13)$$

where k_B = Boltzmann's constant, h = Planck's constant, β = reaction complex coefficient parameter, and ΔS^* = entropy of activation. β and ΔS^* are functions of the structure of the reaction complex (which differs from that of two reactants) and are independent of the reaction temperature. Therefore, the frequency factor A is a linear function of temperature, and the ratio k_2/k_1, derived from eq. (13), will be independent of cure temperature, which contradicts the present experimental data.

TTT Diagram vs. k_2/k_1 Ratio

When the conversion of a curing system increases, the average molecular weight and crosslinking density increase, thereby, increasing T_g. For the system TMAB/DGEBA, it has been shown that there is a one to one relationship between T_g and conversion.[3] It is apparent from Figure 14 that T_g relates to conversion in a nonlinear fashion with T_g rising more sharply with small increases in conversion at high conversion. This characteristic is considered to arise from the dependence of T_g on the crosslinking density,[2-6,27-31] which is considered to be made up of tricrosslinking units.[29] After gelation, the properties
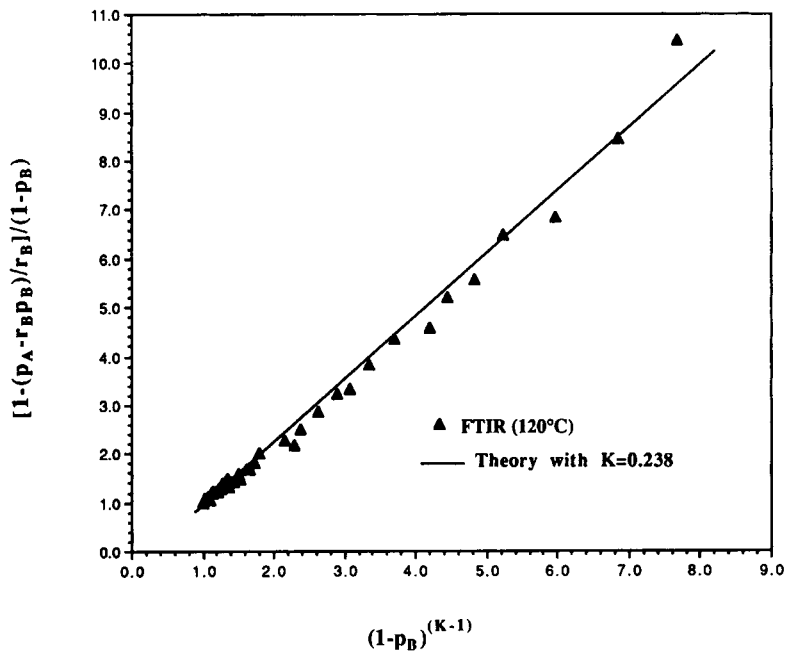
EXPERIMENTAL TEST of THEORY

Figure 11 $[1 - (p_A - r_B p_B)/r_B]/(1 - p_B)$ vs. $(1 - p_B)^{K-1}$ during cure at 120°C. K = 0.238.

of the curing system are determined primarily by the reaction between secondary amine and epoxy groups which increases the crosslinking density. The

concentration of the crosslinking units increasing at high conversion results in T_g rising more sharply at high conversion since a single reaction between
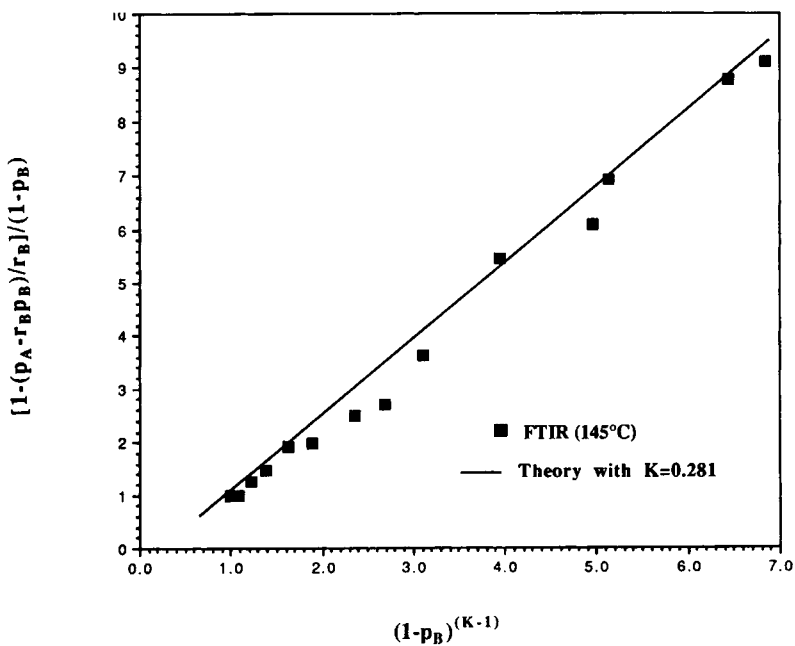

Figure 12 $[1 - (p_A - r_B p_B)/r_B]/(1 - p_B)$ vs. $(1 - p_B)^{K-1}$ during cure at 145°C. K = 0.281.

Table III   Range of Kinetic Constants vs. Temperature

Temperature (°C)	100	120	130	145	160
k_2/k_1	0.158	0.238	0.270	0.281	0.330
Regression range for p_B	0–0.935	0–0.937	0–0.933	0–0.931	0–0.920

amine and epoxy groups produces two trifunctional crosslinking sites.[29]

The transformation occurring in a thermosetting polymerization may lead to two distinct transitions: (1) the change of sol to gel and (2) the change of rubber to glass. A current method for analyzing the phenomena is the TTT diagram.[1] Generally the experimental time to vitrification is determined from the isothermal time–conversion curve (e.g., Figure 8) at the conversion when $T_g = T_{cure}$ [using the conversion-T_g relationship (Fig. 14)]. The analytical time to vitrification can be determined from kinetic equations [e.g., eqs. (3) and (4)] and the conversion-T_g relationship. Vitrification contours calculated for different kinetic ratios are shown in Figure 15. At low temperatures, the vitrification point is relatively insensitive to the ratio (on a log time scale). However, at higher temperatures, the ratio significantly influences the relative times to vitrify. In tetrafunctional diamine-cured difunctional epoxy resin systems, the reaction of secondary amine with epoxy increases the crosslink density, and increases T_g, more than the reaction of primary amine with epoxy. When the ratio K decreases ($K < 1$), which implies that the cure kinetics are controlled mainly by the reaction of secondary amine with epoxide, the time for the curing system to reach the vitrification point increases. When the ratio K increases, the opposite occurs. If the ratio K is larger than 10/1, which implies that the cure kinetics are virtually controlled by the first step, there is almost no dependence of the vitrification contour on the ratio.

CONCLUSIONS

1. The reactivity of the primary amine is found to differ from that of the secondary amine in the cure of the epoxy/amine system for the
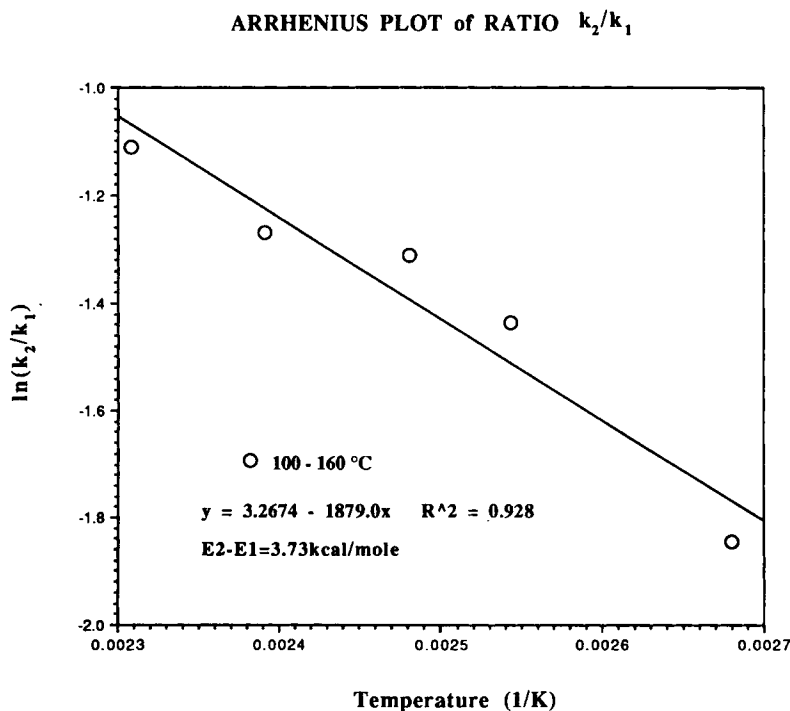
ARRHENIUS PLOT of RATIO k_2/k_1

Figure 13   The reactivity ratio changes with temperature. The difference between the activation energies is 3.7 kcal/mol according to the Arrhenius expression (100–160°C).
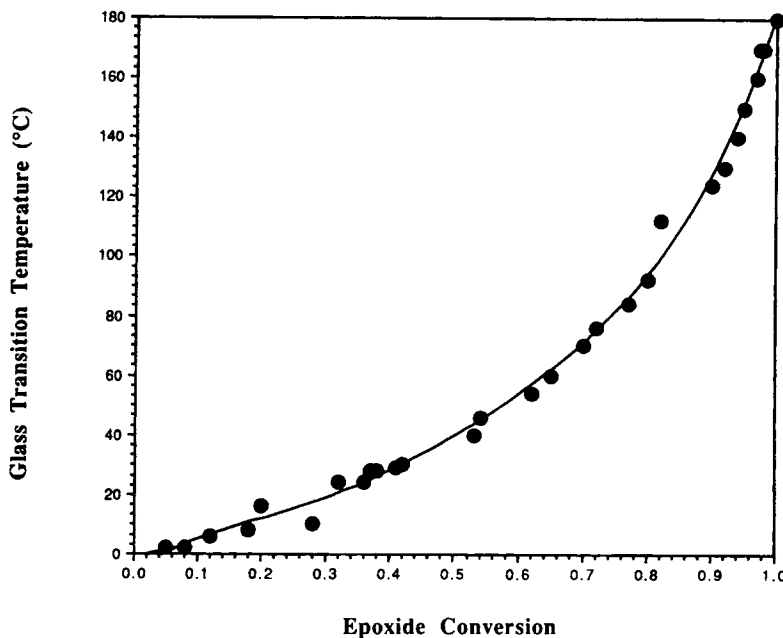
Figure 14 The one-to-one relationship between T_g and conversion by DSC.[3] T_g relates to conversion in a nonlinear fashion, with T_g rising more sharply with conversion at high conversion.

system trimethylene glycol di-p-aminoben-zoate-cured diglycidyl ether of bisphenol A.

2. The ratio of the rate constants for the reaction of epoxide with secondary amine and primary amine, k_2/k_1, increases with cure

temperature, from 0.158 to 0.33 for temperatures from 100 to 160°C (in contrast, earlier work[3] used values of the ratio which were constant with temperature).

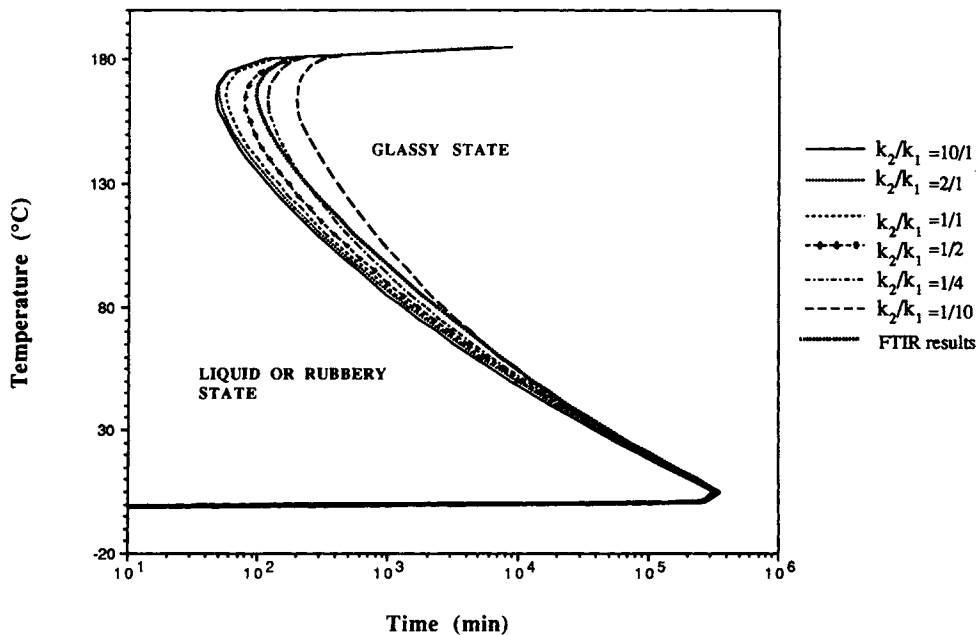3. The reason that the ratio changes with cure

Figure 15 Effect of the reactivity ratio (k_2/k_1) on the vitrification contour in the isothermal TTT diagram. [Results calculated from the kinetic equation and the conversion vs. Tg relationship, with $r_B = 0.5$, $k_1 = 3.5 \times 10^7 \exp(-7.6 \times 10^3/T)$].

temperature is the different activation energies for the reactions between the secondary amine and primary amine with epoxide, rather than the effect of different frequency factors for the reacting groups. The difference of activation energies for the competing reactions is 3.7 kcal/mol.

4. The effect of the ratio k_2/k_1 on the vitrification contour of the TTT diagram is discussed. The results show that the ratio affects the time to vitrify for the curing system, and that the effect is more significant at higher curing temperatures.

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