Kinetic Study of Polymerization/Curing of Filament-Wound Composite Epoxy Resin Systems with Aromatic Diamines

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Synopsis

The kinetics of the polymerization/curing of an 80/20 blend of a diglycidyl ether of bisphenol A (DGEBA) and a diglycidyl ether of 1,4-butanediol (DGEBD) with a commercial mixture of methylene dianiline and *m*-phenylene diamine (Tonox 60/40) was studied, at amine/epoxy ratios ranging from 1.1 to 4.4. Fourier transform infrared (FT-IR) measurements were used to follow the extent of epoxy conversion at 18–122°C, and bulk viscosity measurements were used to define the working range of the resin. For an amine/epoxy ratio of 1.1, the activation energy for the polymerization/curing reaction (based on time to 50% epoxy conversion in the S-shaped conversion-time plots) was 11.9 kcal/mole by FT-IR. This value compared favorably with the corresponding value of 12.7 kcal/mole obtained by Moroni and co-workers in a complementary differential scanning calorimetry (DSC) study of the same system. The FT-IR conversion-time plots were fitted to a kinetic expression that can be accommodated by an autocatalytic mechanism; the expression contains two rate constants with activation energies of 13.7 and 10.0 kcal/mole, respectively. The viscosity of the curing epoxy resin was found to obey the Williams-Landel-Ferry equation, with a Di Benedetto expression for the glass transition temperature.

INTRODUCTION

Despite extensive literature on the polymerization/curing of epoxy resins with diamines,[1] there is a frequent need for detailed kinetic studies on specific epoxy-amine systems for unusual applications. One such application is the current development of a filament-wound case (FWC) for the space shuttle solid rocket motors which, constructed from lightweight graphite fiber-reinforced composite resins instead of steel, has the potential of providing increased payload launch capability for the shuttle. The predominant composite epoxy resin system in the FWC under development comprises an 80/20 blend of a diglycidyl ether of bisphenol A (DGEBA) and a diglycidyl ether of 1,4-butanediol (DGEBD), known as HBRF-55A, plus a commercial mixture of methylene dianiline (MDA) and *m*-phenylene diamine (*m*-PDA), known as Tonox 60/40 and used as a curative.[2] Much difficulty attends the fabrication of flightworthy cases because of problems in trying to scale up the filament winding and cure processes from small thin-walled cylindrical missile rocket motor cases to the rather large thick-walled cases needed for the space shuttle. Such problems may be due in part to the fact that the HBRF-55A:Tonox 60/40 resin system undergoes a slow polymerization/curing, with consequent stresses built up by the prolonged filament-winding process at ambient temperatures, attended by increased viscosity, solidifi-

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cation, and gelation prior to the required elevated temperature cure and postcure processes. To provide a better understanding of both the chemistry of the FWC resin system and the filament-winding process, a kinetic study of the epoxy conversion in HBRF-55A:Tonox 60/40 over a wide temperature range was carried out using Fourier transform infrared spectroscopy (FT-IR), supported by bulk viscosity measurements as a function of degree of cure. The present study complements a differential scanning calorimetry (DSC) study carried out on the same system by Moroni and co-workers.[3]

Several studies have been reported in the literature concerned with the use of FT-IR to follow the disappearance of the epoxy groups,[4-7] or the use of DSC to monitor the heat released,[8] as a function of time and curing conditions. The cure kinetics have been described through n-th order[4-10] or autocatalytic mechanisms.[11-15] Also, several attempts have been made to predict the bulk viscosity of a resin as a function of time and temperature of curing.[16,17]

EXPERIMENTAL

Materials

The epoxy resin used in this work, Hercules HBRF-55A, was an 80/20 blend of Epon 826, a DGEBA ($n = 0$, 87.6%; $n = 1$, 7.4%; $n = 2$, 1.0%; dihydroxy species, 4.0%) and Epirez 5022, a DGEBD ($n = 0$, 51.2%; $n = 1$, 34.3%; $n = 2$, 9.2%; $n \geq 3$, 4.3%; xylene, 0.9%).[3] The curative used, Uniroyal Tonox 60/40, was a mixture of aromatic di- and polyamines (MDA, 42%; m-

DGEBA

DGEBD

MDA m-PDA   BABA
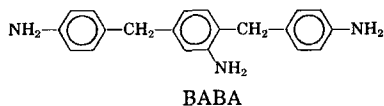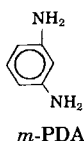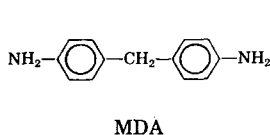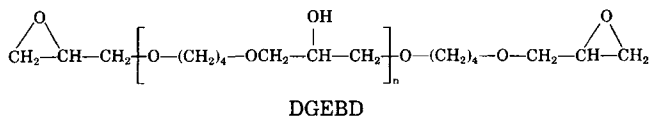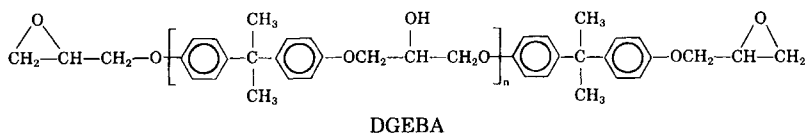
PDA, 42%; 2,4-bis(aminobenzyl)aniline, BABA, and oligomers, 16%). The DGEBA and DGEBD resins had epoxide equivalents of 183 and 131, respectively, while the Tonox 60/40 had an active hydrogen equivalent weight of 37. The stoichiometric ratio of the DGEBA:DGEBD:Tonox 60/40 system for most of the work was 80:20:24, for an amine/epoxy ratio of 1.1. A portion

of the work was also carried out at amine/epoxy ratios of 2.2, 3.3, and 4.4. Because of slow curing at ambient temperature, measurements were commenced on this resin system as soon as the ingredients were mixed and homogeneous solutions obtained.

Infrared Spectroscopy

Aliquots of the HBRF-55A:Tonox 60/40 resin system, hereinafter designated as the H-T system, were sandwiched between pairs of NaCl plates separated by a 0.015-mm thick annular spacer. The salt plates were mounted in a Barnes Spectra-Tech High Temperature Heated Cell and held for different periods of time at temperature >24°C; for curing studies at lower temperatures, the salt plates were placed in a demountable pathlength cell which was held in a constant temperature bath. Infrared spectra before and after various extents of polymerization/curing were obtained with a Nicolet MX-1 FT IR Spectrometer. The cure kinetics were followed using the approach of Enns and Gillham[18] which makes use of the absorbance ratio, A_{915}/A_{1184}, where the 915-cm^{-1} band is characteristic of the epoxide group and the 1184-cm^{-1} peak corresponds to the C—C stretching of the bridge carbon atom between the two p-phenylene groups.

Typical FT-IR spectra of the H-T system (amine/epoxy ratio = 1.1) before and after heating at 23°C for 3170 min are presented in Figure 1. In general, the intensity of the 1184-cm^{-1} band decreases in the early stages of the thermal polymerization/curing process through heat-induced flow and thinning of the FT-IR specimen, but after ca. 20–40% epoxy conversion the intensity reaches a minimum value, thereafter increasing due to secondary processes affecting the background of that band. Thus, in contrast to Enns and Gillham's work which assumes that the 1184-cm^{-1} band is a good internal standard *throughout* the epoxy-amine chemistry, we use this band as a reference up to the point at which it begins to steadily increase; beyond this point, however, the changes in the 915-cm^{-1} band are calculated on the assumption that the thickness remains constant so that an internal standard is no longer required.

Bulk Viscosity Measurements

Bulk viscosity measurements were carried out on the H-T system at 17–54°C using a Brookfield cone and plate viscometer, fitted with a water jacket for maintaining the resin samples at constant temperature.

RESULTS AND DISCUSSION

Consumption of Epoxy Groups

Kinetic curves for the disappearance of epoxy groups in the polymerization/curing of the H-T system (amine/epoxy = 1.1) at various temperatures over the range 18–122°C, measured by FT-IR, are shown in Figures 2(A) and (B). The dashed lines are curves drawn through the experimental points,
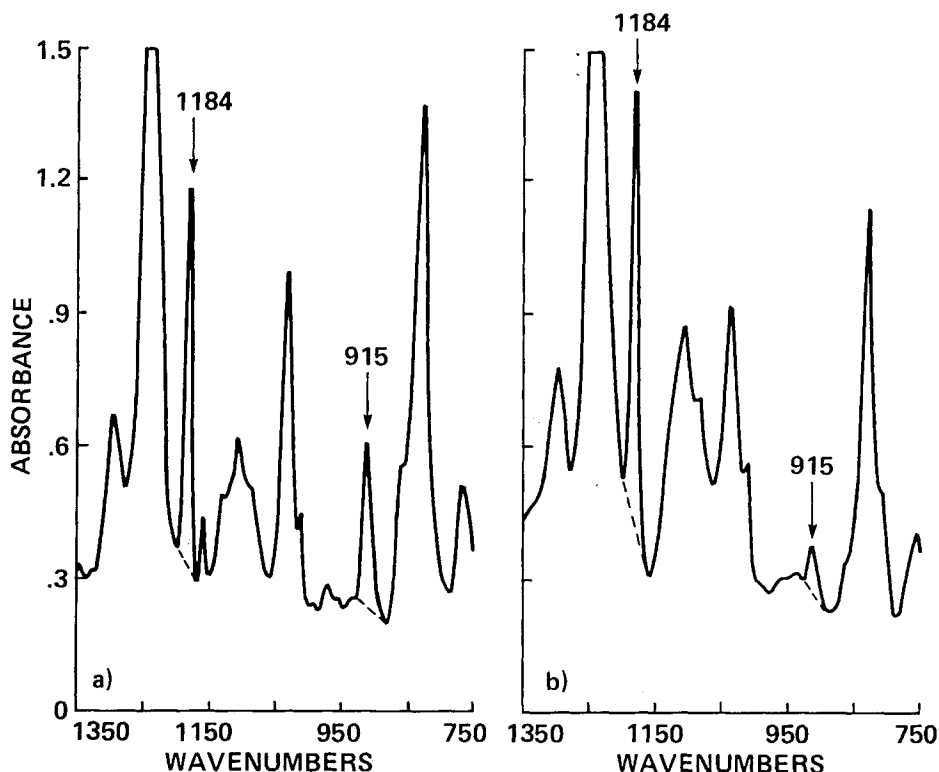
Fig. 1. FT-IR spectra of the H-T system (amine/epoxy = 1.1) (a) before and (b) after heating at 23°C for 3170 min.

while the solid lines correspond to computer fitting of those points through the use of Eq. (1):

$$\alpha = \frac{1 - \exp[-(k_1 + k_2)t]}{1 + (k_2/k_1)\exp[-(k_1 + k_2)t]} \tag{1}$$

which corresponds to the integrated form of the well-established rate law:[11–13,15]

$$\dot{\alpha} = d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{2}$$

with $m = n = 1$, as a special case of the generally accepted relationship, $m + n = 2$. In these equations, $\dot{\alpha}$ and α are the rate and extent of epoxy conversion, respectively; k_1 and k_2 are kinetic rate constants; and $(m + n)$ is the overall reaction order. These equations are applicable only up to the gel point, which corresponds to $\alpha = \sqrt{r/(f - 1)}$, where r is the amine/epoxy ratio, and f is the number of active hydrogens in the amine; for $r = 1.1$, and $f = 4$, as in Figures 2(A) and (B), the limiting α is 0.61, which agrees with the observed α at the gel point. Equation (2) was invoked by Moroni and co-workers[3] to describe integral DSC plots at high temperatures where the
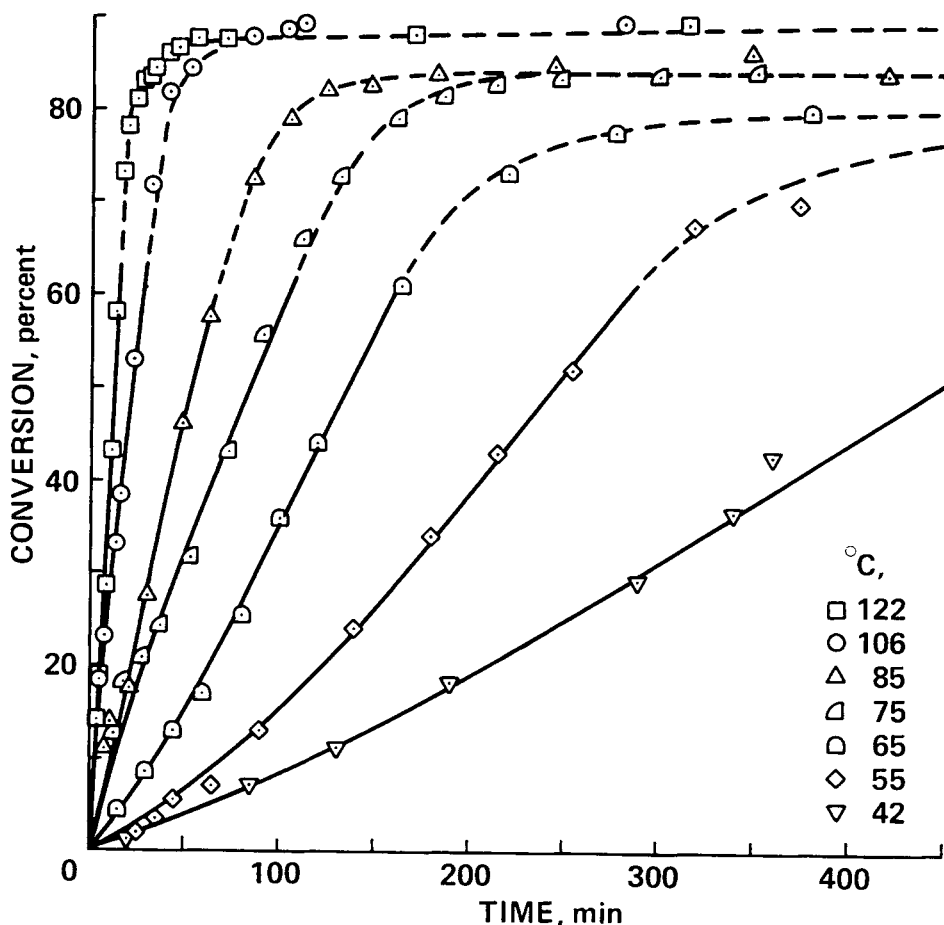
Fig. 2(A). Kinetic curves of epoxy conversion for the H-T system at different temperatures obtained from FT-IR data. The solid lines are plots of Eq. (1) to a conversion of 61% (see text), while the dashed lines are curves drawn through the experimental points.

conversion is carried to virtual completion, or $\alpha = 1$. As a first approach and for comparison with the results of other workers, we took the time to 50% epoxy conversion as a measure of the rate of reaction; this permitted construction of the Arrhenius plot of Figure 3. From the slope of this plot (through the closed squares), the activation energy for the polymerization/ curing of DGEBA/DGEBD with the mainly aromatic diamines, MDA and m-PDA of the Tonox curative, was calculated to be 11.9 kcal/mole. This value, besides being close to the literature values[5,18] of 12.8 and 12.6 kcal/ mole, respectively, for analogous processes involving DGEBA with two different aliphatic diamines, is also close to the value of 12.7 kcal/mole obtained by Moroni and co-workers[3] for the same H-T system (amine/epoxy = 1.1), based on time to 50% epoxy conversion in S-shaped integral DSC plots. Although Chiao and co-workers[2] did not report the activation energy for the curing of their H-T system, they did provide times to 50% epoxide conversion at various temperatures. These data, superposed on Figure 3 as open
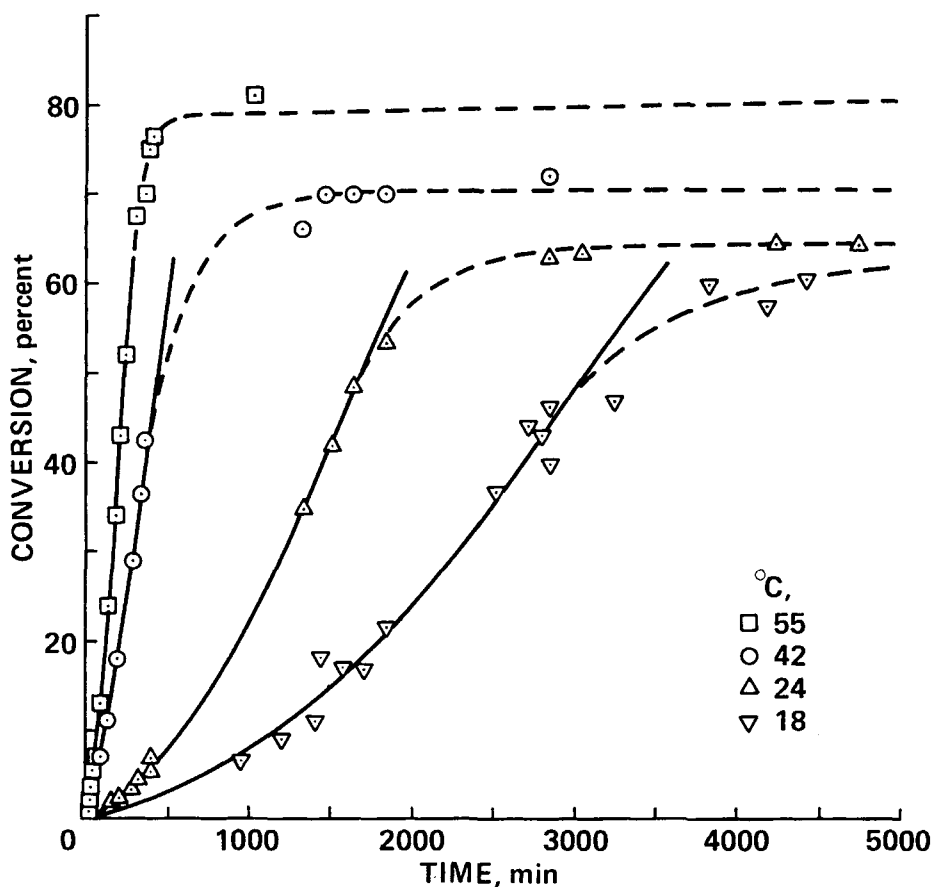
Fig. 2(B). Continuation of Figure 2(A).

squares, agree very well with the data obtained in this study and lead to the same activation energy as that indicated above.

According to Moroni and co-workers,[3] the sigmoidal shapes of the integral DSC plots (and presumably also the FT-IR conversion plots) suggest auto-catalytic curing kinetics for the H-T system.

The inability of the epoxy conversion to reach completion [Figs. 2(A) and (B)] is attributable to a combination of solidification[18] and gelation. At low temperatures ($\leq 18°$), solidification causes immobilization of the epoxy and amine reactants, and hence incomplete conversion. At higher temperatures, on the other hand, gelation is observed, but the reaction may proceed beyond the gel point. The maximum extent of epoxy conversion increases with temperature up to a limiting value at ca. 100°C, and stays constant there-after. Presumably, this limiting conversion occurs at a cross-link density sufficiently high that the remaining unreacted epoxy groups are effectively immobilized.

The rate constants k_1 and k_2 in Eq. (1), derived by fitting that equation to the experimental points of Figures 2(A) and (B), were used to construct the Arrhenius plots shown in Figure 4. The kinetic data at the higher
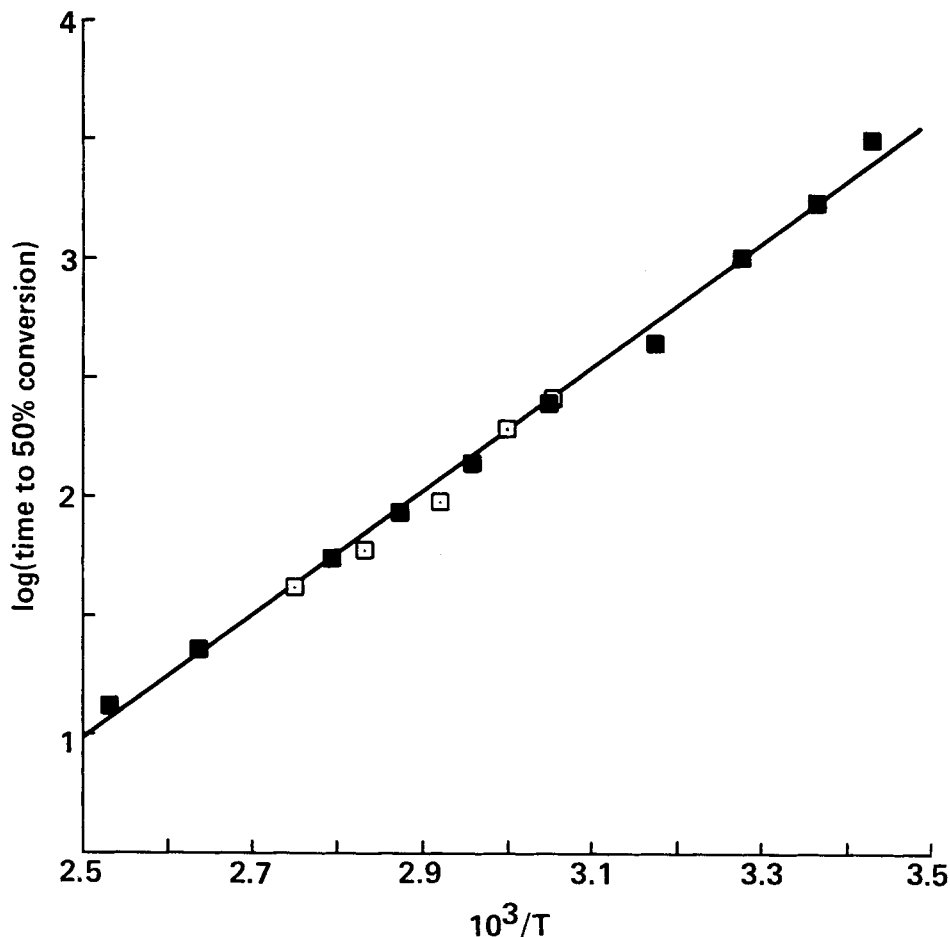
Fig. 3. Arrhenius plot for the polymerization/curing of the H-T system, based on time to 50% conversion: (■) This report; (□) Data from Chiao and co-workers.[2]

temperatures are less accurate than those at the lower temperatures because of thermal lag and the difficulty of obtaining many experimental points before gelation sets in, in the former case. Included in Figure 4 are k_1 and k_2 data obtained from viscosity measurements, to be discussed below. Interestingly, the activation energies for the separate kinetic processes represented by k_1 and k_2 were the same whether determined by the FT-IR method for following epoxy conversion, or the viscosity method for following extent of cure. The activation energies were found to be 13.7 and 10.0 kcal/mole, respectively, which bracket the "composite" activation energy of 11.9 kcal/mole obtained by the use of time to 50% conversion.

Analysis by Moroni and co-workers[3] of the temperature-dependence of k_1 and k_2 derived from isothermal DSC data yielded an activation energy of ≈13.5 kcal/mole for k_1 (a primary reaction, assumed to involve catalytic ring-opening by the amino groups through a ternary transition state of an amine, an epoxide and a hydrogen donor present in the reaction medium), and an activation energy of ≈12.0 kcal/mole for k_2 (a secondary reaction,
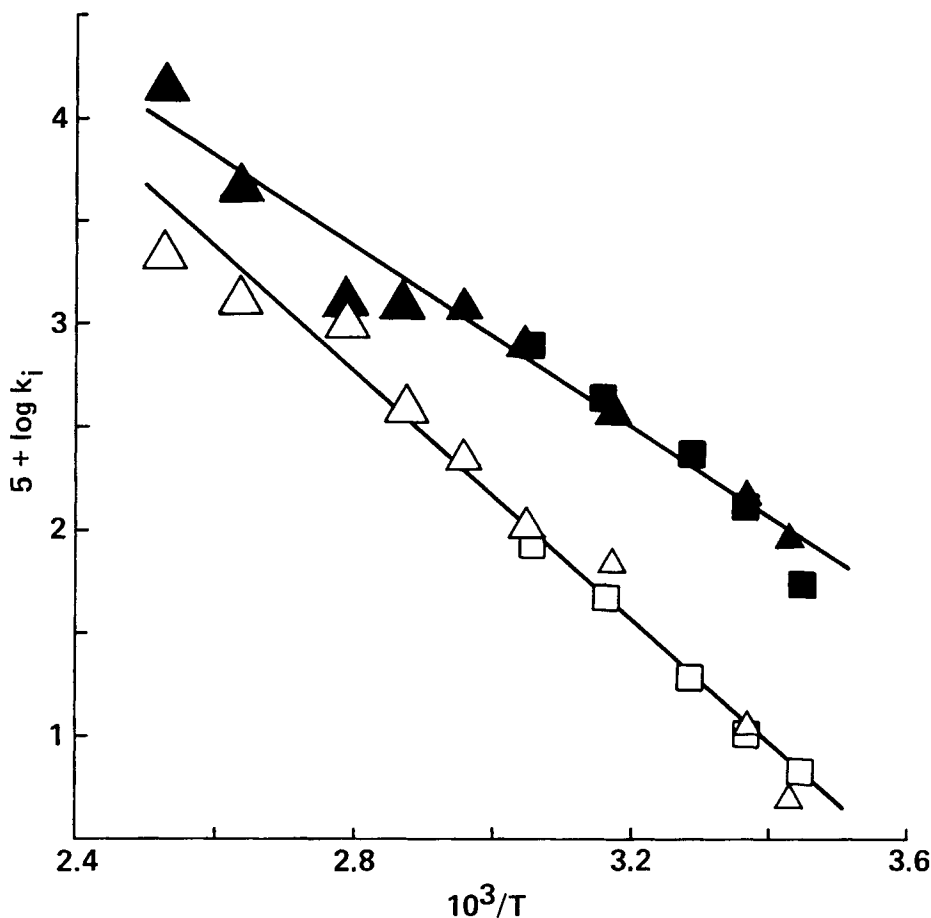
Fig. 4. Arrhenius plots of rate constants, k_1 and k_2, used to fit Eq. (1) to experimental data for amine/epoxy ratio = 1.1. FT-IR points: ($\triangle$) k_1; ($\blacktriangle$) k_2. Viscosity points: ($\square$) k_1; ($\blacksquare$) k_2.

assumed to involve an autocatalytic ring opening involving an amine, an epoxide, and a hydroxyl group formed by the opening of the first epoxy ring). These activation energies for k_1 and k_2 based on DSC are reasonably close to the corresponding values obtained here based on FT-IR studies.

Viscosity of the Curing Epoxy Resin

For many simple polymerization reactions, the logarithm of the polymer bulk viscosity when plotted against time of reaction gives a straight line, the slope of which is proportional to the reaction rate. The slope thus follows an Arrhenius relationship with reaction temperature.[16] However, epoxy resins which become highly cross-linked on curing do not exhibit linear relationships between the logarithm of the viscosity and reaction time.

For a wide variety of materials, Williams, Landel, and Ferry[19] found the following relationship to hold between viscosity and glass transition temperature, T_g:

$$\log(\eta_T/\eta_{T_g}) = -17.44(T - T_g)/(51.6 + T - T_g) \qquad (3)$$

where η_T and η_{T_g} are the viscosities at temperatures T and T_g, respectively. For many polymer systems, $\log \eta_{T_g} \approx 13$. A version of Eq. (3) was successfully applied to viscosity data for epoxy resins, but this involved the use of an arbitrary reference temperature.[17] This necessitated finding empirical expressions for both the reference temperature and that viscosity at that temperature as a function of extent of cure. Adabbo and Williams[20] found that, for a variety of epoxy resins based on DGEBA, the glass temperature is related to epoxy conversion, α, through Eq. (4):

$$T_g = T_{g_0}/(1 - s\alpha) \qquad (4)$$

where T_{g_0} is the glass transition temperature at $\alpha = 0$, and s is a constant. Equation (4) is a modification of the expression for T_g developed by Di Benedetto for styrene-divinylbenzene cross-linked systems.[21]

Equations (1), (3), and (4) were used to generate the solid curves through the experimental points in the viscosity-time plots for curing the H-T system (amine/epoxy = 1.1) shown in Figure 5. For this purpose, the following parameter values were used:

$$T_{g_0} = 215.6 \qquad s = 0.4368 \qquad \log(\eta_{T_g}) = 13.72$$

these having been obtained by best computer fit of the viscosity data.

Table I compares values of the maximum epoxy conversion observed for the H-T system at various temperatures with corresponding values calculated by means of Eq. (4), assuming that the glass temperature equals the cure temperature at α_{max}. This table provides an explanation for the fact, noted earlier, that the polymerization/curing does not go to completion at the lower temperatures, namely, the glass transition of the partially cured resin exceeds the reaction temperature. At higher temperatures, on the other hand, the reaction does not go to completion because the resin becomes highly cross-linked, thereby immobilizing unreacted epoxy and amine groups.

Effect of Stoichiometry

To throw light on the curing mechanism, kinetic plots for the disappearance of epoxy groups during polymerization/curing of the H-T system were obtained from FT-IR measurements at several temperatures with different amine/epoxy ratios. Figure 6 shows a typical set of such plots for curing at 42°C, from which it is seen that the rate of epoxy conversion increases as the amine/epoxy ratio is increased from 1.1 to 4.4. As may also be seen in this figure, the epoxy conversion is almost complete for the higher amine/epoxy ratios (97% for ratios of 4.4 and 3.3; 94% for ratio of 2.2). Applying ideas advanced by Flory[22] on the polymerization of nonlinear polymers, we expect that the H-T mixtures with ratios of 4.4 and 3.3 would not gel, while those with ratios of 2.2 and 1.1 would gel at ca. 87% and 61% conversion, respectively. We may, therefore, infer that the formation of a highly cross-
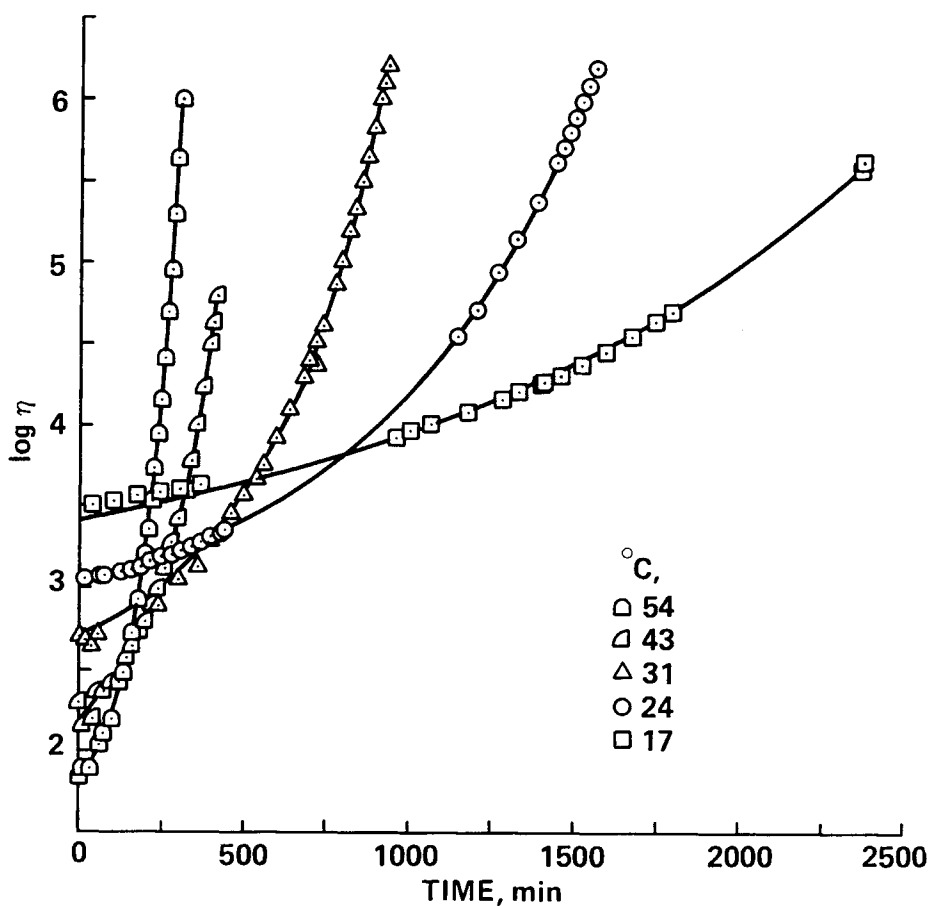
Fig. 5. Viscosity-time plots for curing the H-T system (amine/epoxy = 1.1) at various temperatures. The solid lines represent curves generated through experimental points, using Eqs. (1), (3), and (4).

TABLE I
Comparison of Observed and Predicted
Values for Maximum Epoxy Conversion,
α_{max}

T_{cure}	Observed	Calculated[a]
291	0.61	0.60
297	0.65	0.63
316	0.72	0.73
327	0.80	0.83
338	0.80	0.83
348	0.84	0.87
358	0.86	0.91
379	0.90	0.99

[a] Calculated from expression, $\alpha_{max} = [1 - (T_{g_0}/T_g)]/s$, obtained from Eq. (4), where T_g is identified with T_{cure}.
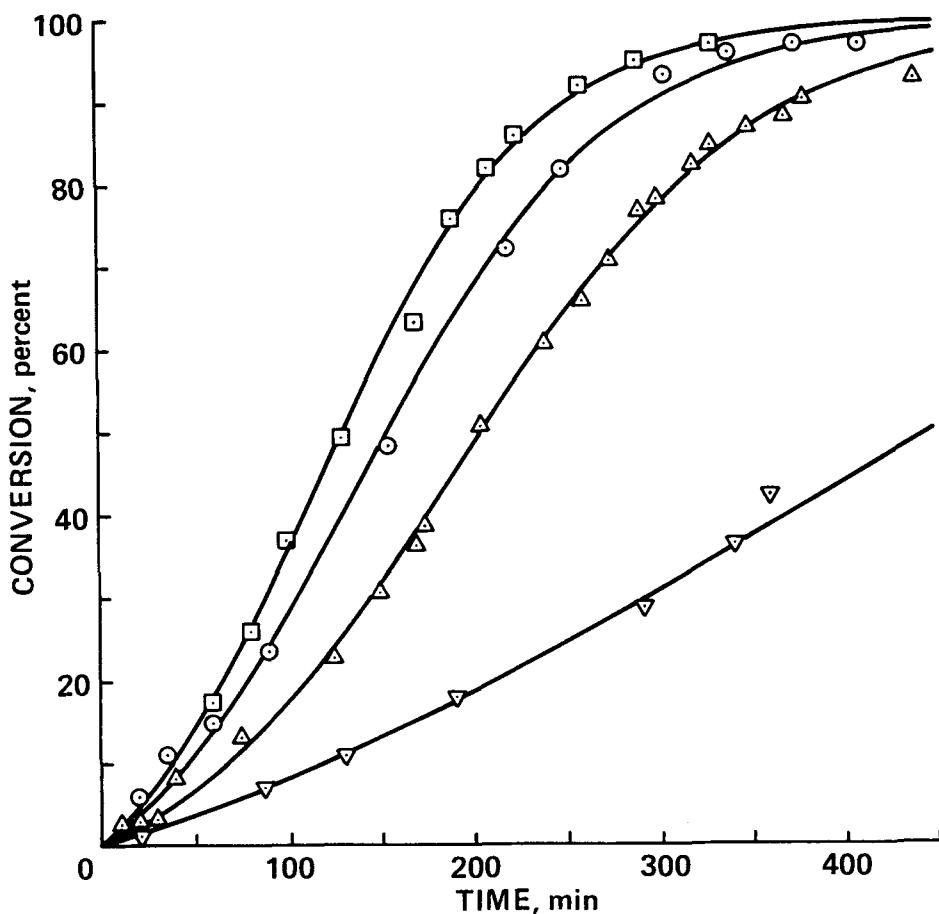
Fig. 6. Kinetic plots of epoxy conversion in the H-T system at 42°C for different stoichiometries, based on FT-IR measurements. Amine/epoxy ratios: (□) 4.4; (○) 3.3; (△) 2.2; and (▽) 1.1.

linked network is in large part responsible for the incomplete conversion (ca. 70%) observed in the mixture with amine/epoxy = 1.1.

The solid lines in Figure 6 were generated using Eq. (1). Similar plots were obtained at 65° and 24°C. The rate constants k_1 and k_2 obtained by fitting Eq. (1) to the data at the three temperatures and the four amine/epoxy ratios are presented in Table II. For purposes of comparison, it is appropriate to regard the mixture with amine/epoxy = 4.4 as being the most accurate kinetically, uncomplicated by gelation effects. Inspection of Table II reveals that the two rate constants decrease with decreasing amine/epoxy ratio, but more specifically are roughly proportional to the amine concentration. A similar first-order dependence on amine content is found in the work of King and Bell,[23] for DGEBA and 1,4-diaminobutane. However, the latter work differs from this work in exhibiting straight-line kinetic plots (zero order in epoxy content) in contrast to the S-shaped plots presented here.

TABLE II
Rate Constants for Epoxy Conversion in the H-T System with Different Amine/Epoxy Ratios

Amine/ epoxy ratio	[A] mEq/g resin	24°C		42°C		65°C	
		$10^3 k_1$	$10^2 k_2$	$10^3 k_1$	$10^2 k_2$	$10^3 k_1$	$10^2 k_2$
4.4	13.24	0.399	0.346	2.024	1.525	10.41	3.02
3.3	11.31	0.305	0.366	1.686	1.306	9.56	2.94
2.2	8.77	0.255	0.273	1.037	1.149	6.19	2.22
1.1	5.23	0.111	0.150	0.713	0.372	2.33	1.22

Figure 7 shows viscosity-time plots for the H-T system (amine/epoxy = 2.2) at several temperatures. The solid lines were obtained using Eqs. (1), (3), and (4) and the following parameter values:

$$T_{g_0} = 223.4 \qquad s = 0.3859 \qquad \log(\eta_{T_g}) = 13.42$$

Again, k_1 and k_2 values were obtained from computer fitting and were normalized with respect to an amine/epoxy ratio of 1.1; these rate constants were also found to fall well on the Arrhenius plots of Figure 4, but for simplicity were not displayed there. However, the bulk viscosity data were consistent with a reaction scheme in which the rate constants are proportional to the amine concentration.

Reaction Scheme for Amine-Epoxy Polymerization/Curing Process

To account for Eq. (2) and the observation just noted that k_1 and k_2 are each proportional to the amine concentration, we propose a modification of the reaction scheme advanced by Horie and co-workers.[11] A hydrogen-bond donor molecule, HX (which may involve trace amounts of water present), reacts with the epoxide, E, to form an activated complex, $E^\ddagger$:

$$HX + E \longrightarrow E^\ddagger \tag{5}$$

Equation (5) is regarded as the rate-controlling step for the amine-epoxy reaction. The activated complex then reacts very rapidly with a primary or a secondary amine to form a secondary or a tertiary amine, respectively, plus a hydroxyl group, while the hydrogen-bond donor molecules are regenerated. The OH group formed in the epoxy–amine reaction is itself a hydrogen-bond donor and may undergo a reaction analogous to Eq. (5):

$$OH + E \longrightarrow E^{\ddagger\ddagger} \tag{5'}$$

$E^{\ddagger\ddagger}$ is assumed to react in a manner similar to that of $E^\ddagger$. The rate of disappearance of epoxide is given by:

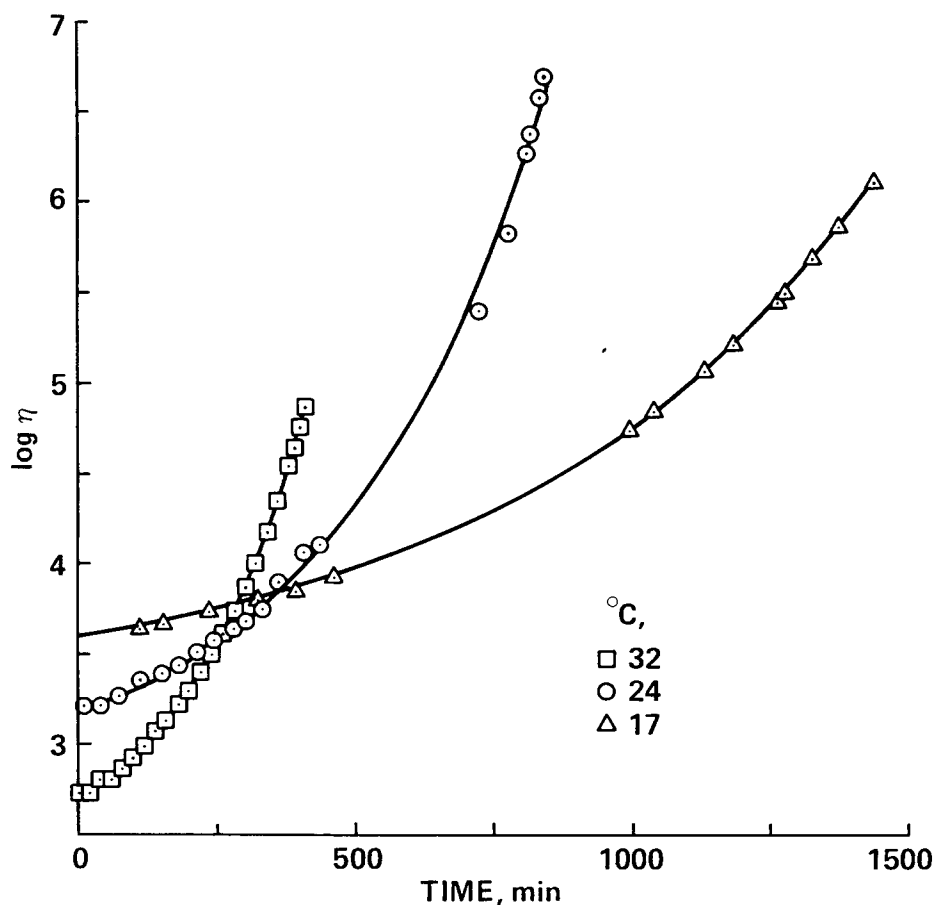$$\frac{-d([E])}{dt} = (k_5[HX] + k_{5'}[OH])[E] \tag{6}$$

Fig. 7. Viscosity-time plots for curing the H-T system (amine/epoxy = 2.2) at several temperatures. The solid lines represent curves generated through experimental points, using Eqs. (1), (3), and (4).

Since an OH group is produced for every epoxy consumed, $[OH] = [E]_0\alpha$, where $[E]_0$ is the initial concentration of epoxide. Also, since the initial uncured epoxy resins DGEBA and DGEBD contain OH groups, we may assume $[HX] = \kappa[E]_0$, where κ is a constant. Inasmuch as $[E] = [E]_0(1 - \alpha)$, $d[E]/dt = -[E]_0 \cdot d\alpha/dt$, and we obtain:

$$d\alpha/dt = (k_5\kappa + k_{5'}\alpha)(1 - \alpha)[E]_0 \qquad (7)$$

Equation (7) is identical to Eq. (2) if we set $k_5\kappa[E]_0 = k_1$, and $k_{5'}[E]_0 = k_2$. Now, $[E]_0$ decreases with increase in amine/epoxy ratio, n, according to the relation:

$$[E]_0 = \frac{c}{(1 + 0.22n)} \qquad (8)$$

Here c is the reciprocal of the molecular weight of the initial epoxy resin. It follows that k_1 and k_2 would be expected to likewise decrease with increase in n or amine/epoxy ratio, but this is contrary to what was observed in this work (see Table II).

King and Bell[23] have proposed a complicated mechanism to account for their observed dependence of epoxy conversion rates on amine/epoxy ratios, and that mechanism, with some modification, presumably could account for our observed dependence of k_1 and k_2 on those ratios. Consider that still another activated complex is formed between *any* amine (primary, secondary or tertiary) and the *unreacted* epoxy group, E:

$$A + E \longrightarrow E'^{\ddagger} \tag{9}$$

and that this complex decomposes principally via a reaction with *any reacted* or *unreacted* epoxy (designated E_0, since this corresponds to the *initially present* epoxy groups):

$$E'^{\ddagger} + E_0 \longrightarrow A + E_0 + E \tag{10}$$
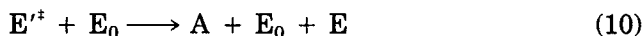
If we assume that reaction (10) is the principal route for disappearance of $E'^{\ddagger}$, we obtain the relation:

$$[E'^{\ddagger}] = \frac{k_9[A][E]}{k_{10}[E_0]} \tag{11}$$

Finally, if it is further assumed that $E'^{\ddagger}$, rather than E, is the reactant in Eqs. (5) and (5'), the rate of epoxy conversion becomes:

$$\frac{d\alpha}{dt} = \left(\frac{k_5 \kappa k_9[A]}{k_{10}} + \frac{k_{5'} k_9[A]\alpha}{k_{10}} \right)(1 - \alpha) \tag{7'}$$

Comparing Eq. (7') with Eq. (2), we see that k_1 is identified with $k_5 \kappa k_9[A]/k_{10}$, and k_2 with $k_{5'} k_9[A]/k_{10}$, and hence these rate constants have the required dependence on amine concentration.

CONCLUSIONS

The kinetics of polymerization/curing of a special filament-wound composite epoxy resin, namely, an 80/20 DGEBA/DGEBD blend (HBRF-55A) + an MDA/m-PDA blend (Tonox 60/40), was investigated at various temperatures by means of FT-IR and bulk viscosity measurements. The activation energy for this reaction, based on time to 50% epoxy conversion, was found to be 11.9 kcal/mole using FT-IR; this value compared well with the corresponding value of 12.7 kcal/mole obtained by Moroni and co-workers[3] in a complementary DSC study. The sigmoidal shapes of the respective FT-IR conversion-time and integral DSC plots suggested an autocatalytic mechanism: for our FT-IR work, kinetic expression (1) contains two rate constants, k_1 and k_2, with activation energies of 13.7 and 10.0 kcal/mole, respectively. The bulk viscosity was found to follow the Williams-Landel-

Ferry equation [Eq. (3)], where the glass transition temperature was related to the conversion through an expression due to Di Benedetto [Eq. (4)]. As in the Moroni work, an autocatalytic mechanism was invoked to account for the observed kinetics of the amine-epoxy polymerization/curing process. However, for that mechanism to be consistent with the observed increase in rate constants with increase in amine/epoxy ratio, it was necessary to postulate the formation of an activated complex from an amine, an epoxide, and a hydrogen-bond donor molecule.

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