

Influence of Cure Conditions on Glass Transition Temperature and Density of an Epoxy Resin

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Synopsis

The glass transition temperature T_g and density of a TGDDM-DDS epoxy resin system were studied as a function of cure times at various cure temperatures. Both T_g and density asymptotically increased toward a maximum value with increasing cure time. The T_g and density measurements were related to the extent of cure, and the relationship in both cases was found to be independent of cure temperature.

INTRODUCTION

The chemical kinetics and mechanisms of the cure reactions in tetraglycidyl-diaminodiphenylmethane-diaminodiphenylsulfone (TGDDM-DDS) resin system has been continuously studied in our laboratories for the last few years. We have reported continuing series of papers on the subject in which we attempted to derive an overall mechanistic picture for this system as a function of cure temperature and time.¹⁻³ It is well known that the cure reactions directly control the composite processing and the final epoxy network structure.^{4,5} The latter directly influences many of the physical and mechanical properties of the system. The effectiveness of such a network manifests itself by the change in the glass transition temperature T_g and density, both of which change with a change in the degree of cross-linking.⁶⁻⁹

In this paper, we report on the changes in the glass transition temperature and density of TGDDM-DDS resin system as a function of cure times at various cure temperatures. The T_g and density measurements are related to the extent of cure in terms of the theory of gelatin, such as functionalities of the reactants and the molecular distribution. A model explaining this relationship has been proposed.

EXPERIMENTAL

Materials

The formulation used in this study was composed of Ciba-Geigy's MY720 epoxy resin, which contains basically the tetraglycidyl-diamino-

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diphenylmethane molecules (TGDDM), and diaminodiphenylsulfone (DDS) hardener. Both of the ingredients were used as received. The mixtures of MY720 and DDS, containing 28 phr DDS by weight, were prepared by first heating the resin to 120°C under high purity N₂ gas. Then the curing agent, DDS, was added slowly with continuous stirring by hand, under N₂ gas, until a clean mixture was obtained. The total mixing time was approximately 15 min. The mixture was then immediately poured into several aluminum weighing dishes and cured isothermally at a given temperature in an electrically heated oven under a positive pressure of N₂ gas. Curing was carried out at four different temperatures, 140, 153, 177, and 201°C. The oven temperature was controlled by a thermocouple placed inside a metal plate on which the sample dishes containing the resin mixture were placed. At each cure temperature, samples were withdrawn at time intervals ranging from 15 to 360 min (6 h).

DETERMINATION OF EXTENT OF CURING

The extent of curing was determined by differential scanning calorimetry. The instrument used was a duPont 1090 thermal analyzer coupled with a duPont 910 DSC. The residual heat of cure H_R was determined on partially cured samples in closed aluminum pans in DSC by scanning them in a dynamic mode at a rate of 10°C/min. Sample size was kept at approximately 15 mg. The total heat of cure H_T was obtained in a similar way by using uncured sample (freshly prepared resin mixture). The extent of cure α was then calculated as $\alpha = (H_T - H_R)/H_T$.

GLASS TRANSITION TEMPERATURE MEASUREMENTS

A duPont 943 thermomechanical analyzer (TMA) was used to measure the glass transition temperature of the epoxy resin as a function of state of cure. An expansion probe with a contact diameter of 2.54 mm was used. Tests were made on small samples with a thickness of about 2 mm, and the width, which is the same as the diameter, of the probe tip resting on the sample. The load on the probe was 1 g, and the heating rate was 10°C/min. The glass transition temperature was taken as the temperature where the two tangent lines to the thermal expansion curves intersect.

DENSITY MEASUREMENTS

Density measurements were carried out in a density gradient column prepared according to ASTM D1505-68. The liquid used was potassium carbonate solution whose density ranged from 1.21 to 1.30 g/mL over the length of a 80-cm column. This gives the sensitivity of 0.0017 g/mL per cm of column length. Three specimens were measured for each condition, and the reported data here are the average of the three specimens. The specimens were immersed in the low-density liquid before being dropped into the column. This was done to ensure perfect wetting and to prevent the formation of air bubbles around the specimens.

THEORETICAL ANALYSIS

Gel Point

As seen in Table I, the resin system, as formulated, is epoxy rich; hence its gelation behavior is of interest. Applying the standard gelation theory by Flory,¹⁰ we can write the following equations describing the extent of reaction at the gel point:

$$P_{E(g)} = \left(\frac{m_A f_A}{m_E f_E (f_A - 1)(f_E - 1)} \right)^{1/2} \quad (1)$$

and

$$P_{A(g)} = \left(\frac{m_E f_E}{m_A f_A (f_A - 1)(f_E - 1)} \right)^{1/2} \quad (2)$$

where $P_{E(g)}$ is the fraction of epoxy group that has reacted at the gel point, m_E is the number of moles of epoxy component, and f_E is the functionality of the epoxy component present. The subscript A refers to the analogous quantities for the amine component, and the subscript g refers to the quantities evaluated at the gel point. As shown in Table I, the value of m_A is 0.113 and of m_E is 0.237.

A display of eqs. (1) and (2) is shown in Fig. 1. The conditions for gel formation are plotted in terms of the functionality of the epoxy f_E and the functionality of the amine f_A . Gel formation is only possible when the values of the (f_E, f_A) pair fall within the area bounded by the heavy lines. We have assumed that both f_E and f_A have maximum values of 4. Within this area the curves as depicted by the dotted lines represent the contours of constant extent of reaction of the amine P_A and the curves as depicted by the dashed lines represent the contours of constant extent of reaction of the epoxy groups P_E .

The information contained in Fig. 1 can be used in several ways. One can estimate the extent of reaction in terms of either of the components at the gel point if the functionalities of the components are known. For example, at point E in Fig. 1, $f_E = 3.32$, $f_A = 2.5$, $P_{E(g)} = 0.32$, and $P_{A(g)} = 0.90$. What this means is that 32% of the epoxy groups and 90% of the amine groups would have reacted when the gel point E is reached.

TABLE I
Composition of TGDDM-DDS Resin System

Ingredient	Weight (g)	Molecular weight (g/mol)	No. moles	Equivalent ^a
MY720	100	422	0.237	$0.237f_E$
DDS	28	248	0.113	$0.113f_A$

^a Where f_E = functionality of epoxy and f_A = functionality of amine.

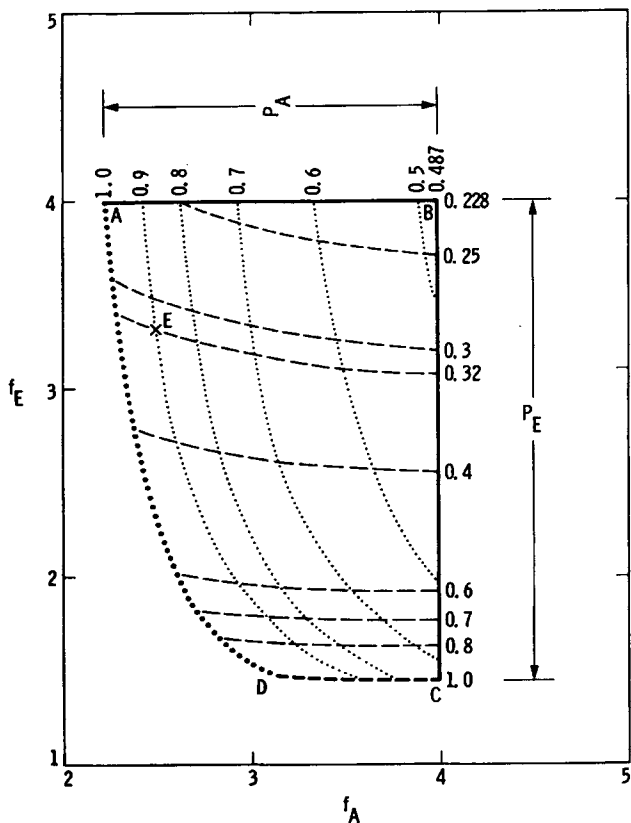


Fig. 1. Conditions for gel formation as a function of functionalities of epoxy f_E and the amine f_A . Gel formation is only possible for points following on or within the heavy boundaries. The curves within the area represent contours of the extent of reaction at the gel point of epoxy group $P_{E(g)}$ (dashed lines) and of amine $P_{A(g)}$ (dotted lines).

MOLECULAR WEIGHT

In the pregel region, that is, at P_A or P_E less than that required for gel formation, it is possible to calculate both the weight-average and the number-average molecular weight of the system. Stockmayer¹¹ derived a general expression for the weight-average molecular weight of condensation polymers. For M_w of the present system corresponding to the stoichiometric amounts shown in Table I, the Stockmayer's equation becomes

$$M_w(P_A) = 384.93 + \left\{ \frac{182.39f_A P_A + [155.18f_E(f_A - 1) + 25.101f_A(f_E - 1)](f_A/f_E)P_A^2}{1 - 0.468(f_A - 1)(f_E - 1)(f_A/f_E)P_A^2} \right\} \quad (3)$$

or

$$\frac{M_w(P_A)}{M_w(0)} = 1 + \left\{ \frac{0.4738f_A P_A + [0.403f_E(f_A - 1) + 0.065f_A(f_E - 1)](f_A/f_E)P_A^2}{1 - 0.468(f_A - 1)(f_E - 1)(f_A/f_E)P_A^2} \right\} \quad (4)$$

Since

$$P_A = \frac{f_E}{0.468f_A} P_E \quad (5)$$

Equation (4) can be expressed in terms of P_E as

$$\frac{M_w(P_E)}{M_w(0)} = 1 + \left\{ \frac{1.012f_E P_E + [1.8383f_E(f_A - 1) + 0.2973f_A(f_E - 1)]f_E/f_A P_E^2}{1 - 2.1356(f_A - 1)(f_E - 1)f_E/f_A P_E^2} \right\} \quad (6)$$

where $M_w(0)$ is the weight-average molecular weight of the unreacted mixture, that is, when $P_E = 0$. Thus the eq. (6) provides the $M_w(P)$ as a function of the extent of reaction of the epoxy component and of the functionality of the epoxy and amine components. $M_w(P)$ approaches infinity when the system reaches the gel point.

The corresponding number-average molecular weight M_n is given by the equation

$$M_n(P_E) = \frac{M_n(0)}{1 - \left(\frac{m_E}{m_E + m_A} \right) P_E f_E} \quad (7)$$

where $M_n(0)$ is the number-average molecular weight of unreacted mixture, which was calculated to be 287.35 g/mol for the formulation shown in Table I. Since $m_E = 0.237$ and $m_A = 0.113$, eq. (7) reduces to

$$M_n(P_E) = \frac{M_n(0)}{1 - 0.681f_E P_E} \quad (8)$$

$M_n(P_E)$ approaches infinity when the denominator $(1 - 0.681f_E P_E)$ approaches zero. The value of the extent of reaction P_E at that point is greater than the value calculated from eq. (1); hence eq. (8) is invalid for extents of reaction beyond the gel point. The weight-average molecular weight at the gel point is infinite because it is sensitive to the higher molecular weight

species. However, the number-average molecular weight remains finite through the gel point; in fact, it has a relative value.

It is of interest to examine the behavior of both $M_w(P_E)$ and $M_n(P_E)$ as calculated from eqs. (6) and (8), respectively. These values are listed in Tables II and III for the two different pairs of values of f_A and f_E . For example, Table II lists the values calculated assuming $f_A = 4$ and $f_E = 3.32$. The first column in the table lists the values of P_E —fraction of epoxy group that has reacted—which ranges from zero (no reaction) to 0.285, the value characteristic of the gel point. The third column lists the values of the ratio $M_w(P_E)/M_w(0)$ calculated from eq. (6). For small values of P_E , the ratio increases only relatively slowly; however, as P_E approaches the characteristic value at the gel point, the ratio increases very rapidly, becoming infinite at the gel point.

The values of the ratio of the number-average molecular weight, $M_n(P_E)/M_n(0)$ are shown in the last column. In contrast to the rapid increase

TABLE II
Calculated Values of $M_w(P_E)/M_w(0)$ and $M_n(P_E)/M_n(0)$ for $f_E = 3.32$, $f_A = 4^a$

P_E	P_A	$M_w(P_E)/M_w(0)$	$M_n(P_E)/M_n(0)$
0	0	1	1
0.056	0.1	1.26	1.15
0.113	0.2	1.71	1.34
0.17	0.3	2.65	1.62
0.226	0.4	5.42	2.04
0.254	0.45	10.61	2.34
0.265	0.47	16.85	2.50
0.276	0.49	40.0	2.66
0.282	0.50	120.35	2.76
0.284	0.503	306.70	2.78
0.285	0.5043	∞	2.80

^a $M_w(0) = 384.93$ g/mol; $M_n(0) = 287.35$ g/mol.

TABLE III
Calculated Values of $M_w(P_E)/M_w(0)$ and $M_n(P_E)/M_n(0)$ for $f_E = 3.32$ and $f_A = 3^a$

P_E	P_A	$M_w(P_E)/M_w(0)$	$M_n(P_E)/M_n(0)$
0	0	1	1
0.042	0.1	1.17	1.11
0.085	0.2	1.43	1.24
0.127	0.3	1.83	1.40
0.170	0.4	2.49	1.62
0.21	0.5	3.77	1.92
0.25	0.6	7.35	2.34
0.275	0.65	13.36	2.64
0.287	0.68	25.1	2.86
0.296	0.70	61.7	3.02
0.3011	0.712	221.5	3.13
0.3015	0.713	787.1	3.14
0.3016	0.7132	∞	3.15

^a $M_w(0) = 384.93$ g/mol; $M_n(0) = 287.35$ g/mol.

of the weight-average molecular weight as P_E approaches the value at the gel point, the number-average molecular weight ratio increases slowly. At the gel point, the molecule contains only three monomer units and the number-average molecular weight would be only 862 g/mol.

Table III shows the similar calculation for the case where $f_E = 3.32$ and $f_A = 3$.

At the gel point, there is an infinitesimal quantity of material with infinite average molecular weight. Since the quantity of gel is infinitesimal regardless of its weight, the bulk viscosity of the system will be controlled by the viscosity of the sol, which is relatively low. The system would consist of very small gel particles immersed in a relatively low-molecular-weight substrate. As the reaction proceeds beyond the gel point, the fraction of material in the gel phase increases, and the fraction of the material in the sol phase decreases. The number-average weight of the sol fraction decreases as the extent of reaction increases beyond the value characteristic of the gel point.

RESULTS AND DISCUSSION

Glass Transition Temperature

The glass transition temperature T_g of the epoxy system was determined as a function of cure time and cure temperature as a means of monitoring the relative degree of cross-linking in the system. These data are shown in Fig. 2. As seen from the figure, for the three highest temperatures the T_g asymptotically approaches a common value for longest cure time. Figure 3 shows the same data in terms of cure temperature for the different cure times. The figure clearly shows that the reaction rate increased with tem-

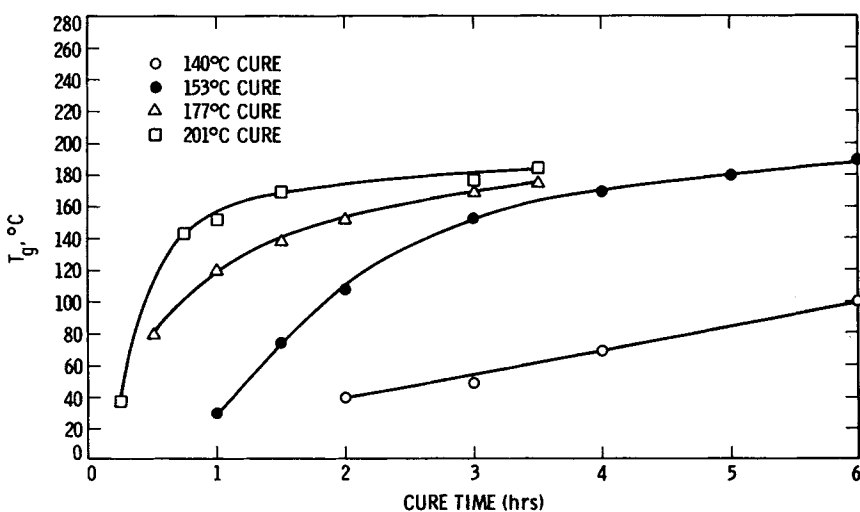


Fig. 2. Glass transition temperatures of epoxy as a function of cure temperature and cure time.

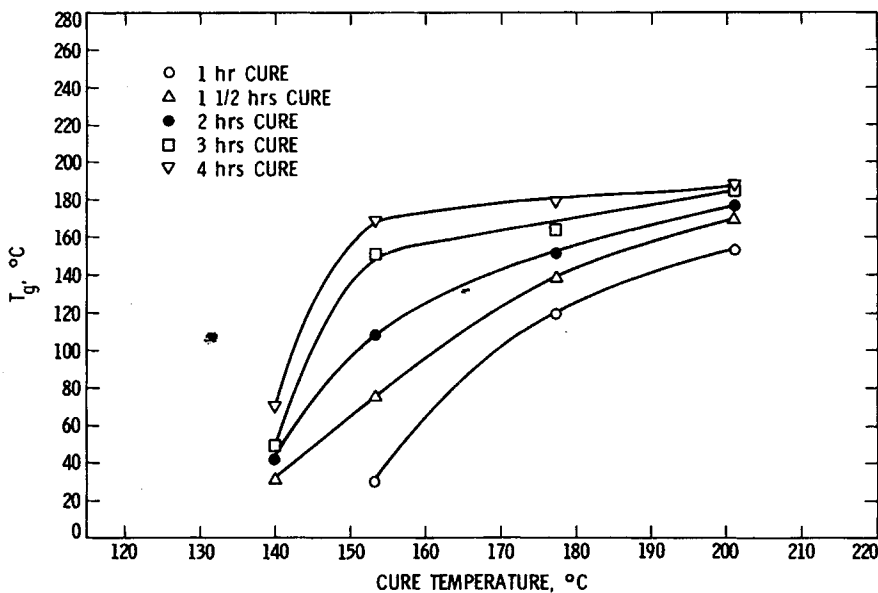


Fig. 3. Glass transition temperatures as a function of cure temperature, each at several cure times.

perature, and at higher cure temperatures ($>177^{\circ}\text{C}$), T_g converges to a similar value with lessened effect of time.

As the extent of reaction increases, the average molecular weight of the polymer chains also increases, and therefore the T_g is also expected to increase. Beyond the gel point, an additional factor that leads to an increase in T_g is the introduction of increasing numbers of cross-links within the system. Both the increase in molecular weight prior to the gel point and the introduction of cross-links beyond the gel point produce corresponding increases in T_g .

Fox and Loshaek¹² have shown that the glass transition temperature can be expressed in terms of molecular weight and cross-link concentration by means of the equation

$$T_g = T_g^{(\infty)} - \frac{K}{M_n} + K_x X \quad (9)$$

where $T_g^{(\infty)}$ is the glass transition temperature of the uncross-linked polymer of infinite molecular weight; that is, as $M \rightarrow \infty$, $X = 0$, X is the concentration of cross-links (moles per gram), and K and K_x are the constant parameters specific for each polymer type.

In the pregel region where $X = 0$, it was shown earlier that M_n is related to the extent of reaction by means of eq. (8). Hence, eq. (9) can be expressed as

$$T_g = T_g^{(\infty)} - \frac{K(1 - 0.681P_E)}{M_n(0)} \quad (10)$$

Since $X = 0$, eq. (10) can be rewritten as

$$T_g = T_{g(0)} + \frac{0.681K}{M_n(0)} P_E \quad (11)$$

where $T_{g(0)} = T_g(\infty) - K/M_n(0)$ represents the glass transition temperature of the system when the extent of reaction is zero. Hence, according to eq. (11), the plot of T_g versus extent of reaction should be linear with slope equal to $0.681K/M_n(0)$, which is independent of cure temperature.

Beyond the gel point, the previously homogeneous system becomes heterogeneous; the sol fraction and the gel fraction. The sol fraction is comprised of those molecules that are not yet a part of the gel. The maximum number-average molecular weight of the sol occurs at the gel point. As the reaction proceeds, both the quantity of sol fraction and its number-average molecular weight decrease, and in the limit of complete reaction the sol fraction becomes zero. For the gel fraction, there is a simultaneous increase in both the quantity and its complexity. The major process occurring in the gel itself, as reaction proceeds, is to increase the degree of cross-linking. It has been shown by Fox and Loshaek¹² that T_g increases linearly with increasing degree of cross-linking. Hence for cross-linked polymers, T_g can be expressed as

$$T_g = T_{g(0)} + \frac{0.681K}{M_n(0)} P_E + XK_x P_E \quad (12)$$

or more simply as

$$T_g = T_{g(0)} + K' P_E + K_x P_E \quad \text{when } P_E > P_{E(g)} \quad (13)$$

where $K' = 0.681 K/M_n(0)$ and $K_x = XK_x$.

In eqs. (12) and (13) we have assumed that the concentration of cross-links X is directly proportional to the extent of reaction.

Figure 4 shows the data of Fig. 2 plotted as T_g versus extent of reaction. As may be seen, the data can be reasonably represented by two linear segments with a transition between the two centered about the presumed gel point. Linear extrapolation indicates a gel point occurring at an extent of reaction of about 70%. It was expected that the relationship between T_g and conversion should be independent of cure temperature. This is true for the lowest, 140°C, and the two highest cure temperatures, 177 and 201°C. The data for the intermediate temperature (153°C) diverge significantly, although the experiments at this temperature were repeated twice to check the data and the results were the same. At present, we have no simple explanation for this.

The slope of the initial linear portion of Fig. 4 is 130°C, but the slope of the final linear portion is about three times as large and equal to 430°C. The composition listed in Table I contains 6.17×10^{-3} equivalence of epoxy group per gram of mixture, and thus the slope of Fig. 4 in the $P_E > P_{E(g)}$ region becomes 7×10^4 g/eq °C in these units, assuming that all of the

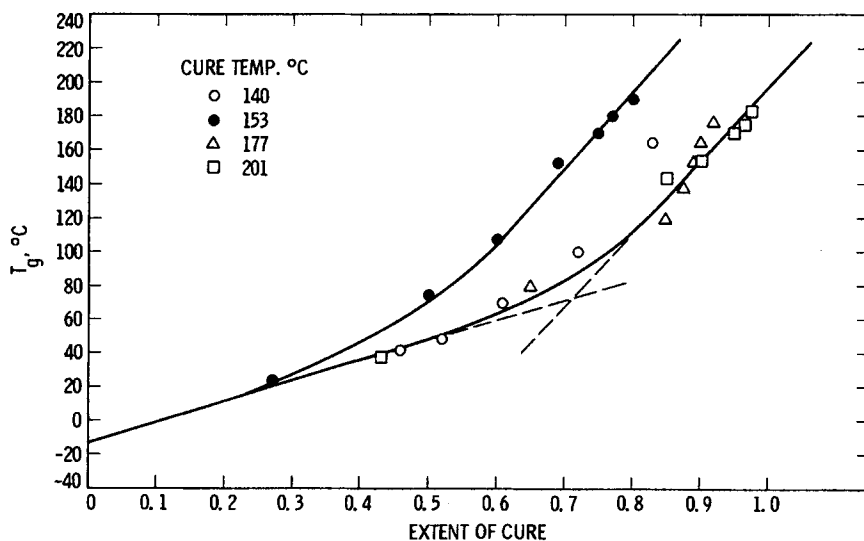


Fig. 4. Glass transition temperatures of TGDDM-DDS system as a function of extent of cure.

epoxy groups are involved in cross-link formation. From Mason's data¹³ for peroxide vulcanized natural rubber, it can be shown that the slope of the T_g versus cross-linked unit concentration is about 2×10^4 g/mol °C, which is similar in magnitude to the value for the epoxy system studied. Actually, the correspondence between the two systems is closer than this because only a fraction of the epoxy groups serves as cross-links and the rest serves to form the linear chain between cross-links. This serves to decrease the quantity 7×10^4 g/eq °C to a lower value. For example, if only half of the epoxy groups are involved in cross-linking, the slope for the epoxy system would be 3.5×10^4 g/eq °C.

DENSITY MEASUREMENT

The change of density as a function of cure time for the four cure temperatures is shown in Fig. 5. As may be seen from the figure that, at a given cure time, the density of the resin increases with an increase in cure temperature. When density data are plotted against the conversion (extent of curing), a linear relationship independent of cure temperature was obtained, as shown in Fig. 6. The increase of density with conversion suggests that the free volume in the resin system is reduced by cross-linking. This is probably because the molecular segments are tied up by cross-linking points.

A correlation of these data can be obtained on the assumption of additivity of volumes; that is, it is assumed that the total volume is the sum of the individual volumes, and no volume change occurs as a result of interaction between individual components. If we assume the following two reactions

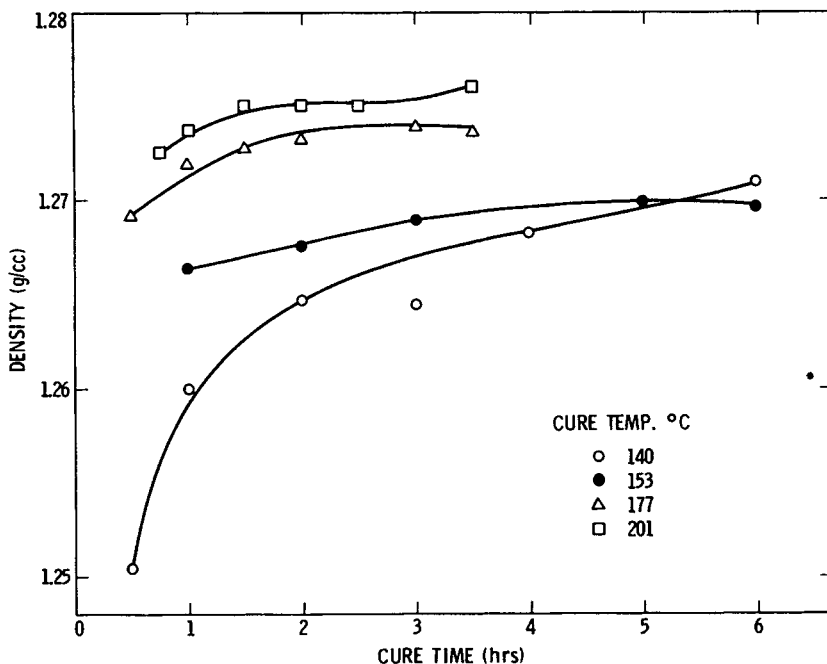
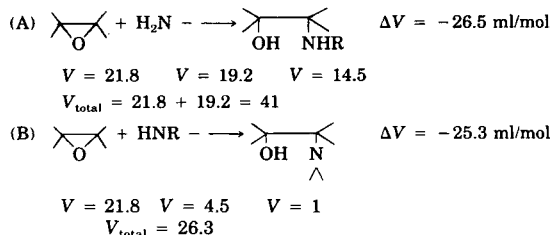


Fig. 5. Densities of TGDDM-DDS resin system as measured at room temperature as a function of cure times at four cure temperatures.

to be the main reactions in the epoxy system, the volume changes ΔV (mL/mol) as a result of these reactions can be shown as



In reaction A, the epoxy group reacts with the primary amine to produce an hydroxyl group and a secondary amine. In reaction B, an epoxy group reacts with a secondary amine to form an hydroxyl group and a tertiary amine. By using volume increments from Ref. 14, one can show that reaction A would lead to a molar volume contraction of 26.5 mL/mol of amine reacted, and reaction B would lead to a molar volume contraction of 25.3 mL/mol of amine reacted, which is essentially the same value given by reaction A. We use the average of the two in order to represent the overall molar volume change, which is a decrease of 25.9 mL/mol.

The volume of the system initially at a fixed temperature, such as 25°C, can be written as

$$V_0 = m_E f_E V_E + m_A f_A V_A + \Sigma V_R \quad (14)$$

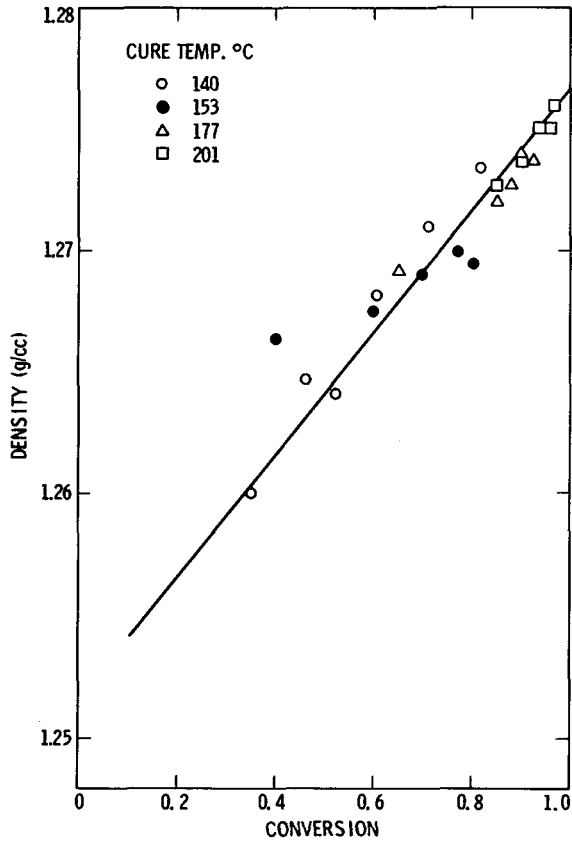


Fig. 6. Densities as a function of conversion (extent of curing) at four cure temperatures.

where V_E and V_A are the volumes occupied by an epoxy and amine group, respectively, and ΣV_R is the volume contributed by all groups other than epoxy and amine. At any extent of reaction P_E , the volume can be written as

$$V = V_0 + m_E f_E [(V_H + V_{A'} - (V_A + V_E)] P_E \quad (15)$$

where V_H and $V_{A'}$ are the volumes of the hydroxyl group and the product amine group, respectively. From the early discussion, the term in square brackets can be taken to have the value of -25.9 mL/mol. Furthermore, by dividing the total volume by the total weight of the mixture, which is 128 g (from Table I) we obtain the specific volume. Thus eq. (15) becomes

$$\nu = \nu_0 - 0.202(m_E f_E P_E) \quad (16)$$

if we take the functionality of epoxy f_E to be 3.32 and $m_E = 0.237$ from Table I, then eq. (16) becomes

$$\nu = \nu_0 - 0.16P_E \quad (17)$$

According to eq. (17), a plot of the specific volume (reciprocal of density) against conversion should be linear with a negative slope, and the response should be independent of temperature. Figure 6 shows the density data plotted in this fashion. As seen, the response is linear and independent of cure temperature. The slope has a value of -0.025 , whereas the slope from eq. (17) is predicted (based on the additive group volume contribution) to be -0.16 . The discrepancy between the predicted and experimental results can be attributed to the following: (1) the approximate nature of the value of volume increments used as shown in reactions A and B; (2) it was assumed in the derivation of equations that the epoxy groups are completely depleted at the end of the reaction, that is, stoichiometric amount (this is in fact not the case for the TGDDM-DDS system studied in this work, because the system studied is epoxy rich—ratio of epoxy to amine is 2—and the epoxy groups are never completely used up at the end of the curing reactions); and (3) the presence of porosity or void formed during cure.

CONCLUSIONS

A study of the glass transition temperature and density of a tetraglycidyl-diaminodiphenylmethane epoxy resin cured with a diaminodiphenylsulfone curing agent has been carried out as a function of cure times and temperatures. The following conclusions were reached from this study.

At a given cure temperature, T_g asymptotically increases toward a maximum value with an increase in cure time. At a given cure time, T_g increases with increasing cure temperature.

The T_g were related to the extent of reaction (or conversion), and the relationship between T_g and conversion was found to be independent of cure temperature. The experimental data were in qualitative agreement with expressions for T_g in terms of average molecular weight and the extent of reaction.

At a given cure time, the density of the system increases with an increase in cure temperature. A linear relationship between the density and the extent of reaction was obtained. This relationship was also found to be independent of cure temperature.

The conditions for gel formation were analyzed in terms of functionalities of the epoxy and amine groups.

Equations were derived to calculate both the number-average and weight-average molecular weight corresponding to the percentage amounts of ingredients used in this study. It was shown that, as the reaction proceeds toward the gel point, weight-average molecular weight increases rapidly and becomes infinite at the gel point, whereas the number-average molecular weight increases slowly, and at the gel point it becomes finite; for example, the molecule contains only three monomer units.

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References

1. M. Cizmecioglu and A. Gupta, *SAMPE Quart.*, **13**(3), 16, (April 1982).
2. A. Gupta, M. Cizmecioglu, D. Coulter, R. H. Liang, A. Yavrouian, F. D. Tsay, and J. Moacanin, *J. Appl. Polym. Sci.*, **28**, 1011 (1983).
3. J. Moacanin, M. Cizmecioglu, S. D. Hong, and A. Gupta, *ACS Symp. Ser.*, (227), C. A. May, Ed., p. 83 (1983).
4. R. J. Morgan and J. E. O'Neal, *Polym. Plast. Technol. Eng.*, **10**(1), 49 (1978).
5. R. J. Morgan, C. M. Walkup, and T. Hoheisel, *J. Appl. Polym. Sci.*, **30**, 289 (1985).
6. N. D. Danieleley and E. R. Long, *J. Polym. Sci., Chem. Ed.*, **19**, 2443 (1981).
7. W. Fisch, W. Hofmann, and R. Schmid, *J. Appl. Polym. Sci.*, **13**, 295 (1969).
8. Akio Shimazaki, *J. Polym. Sci., Part C*, **23**, 555 (1968).
9. L. E. Nielsen, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C3**(1), 69 (1969).
10. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 347.
11. W. H. Stockmayer, *J. Polym. Sci.*, **9**(1), 69 (1952).
12. T. G. Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).
13. P. Mason, *Polymer*, **5**, 20 (1964).
14. R. F. Fedors, *Polym. Eng. Sci.*, **14**, 152 (1974).

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