

Epoxy Polymers. III. Factors Affecting the Cure

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Synopsis

The rate of cure of epoxy polymers appears to be diffusion-controlled, and after gelation is dependent upon the capillary dimensions in a floccular matrix. The floccule dimensions and packing determine the size of the interfloccular capillaries and are inversely related to the cure temperature. The degree of cure is inversely related to the pregelation cure temperature (thermal history, including preheat) and directly related to the total cure time.

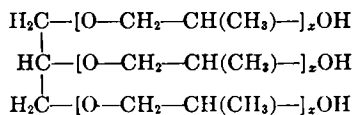
INTRODUCTION

Thermosetting epoxy polymers have been shown to be two-phase systems (roughly spherical floccules in a liquid resembling the uncured starting materials).¹ The formation of the harder, more dense floccules is probably a colloidal process. The size and number of floccules in a given region of the polymer appear to be governed primarily by the rate of cure, i.e., early thermal history. Rapid curing schedules (at high oven temperatures) produce small floccules in large numbers. The total floccule surface area and the volume of low molecular weight interstitial material are consequently larger in a given sample volume. The effects of the process variables on the properties of the epoxy polymers are herein reported.

EXPERIMENTAL

Chemicals

Casting compound C 13-009 (in parts A and B), a polyol-modified anhydride-cured epichlorhydrinbisphenol A epoxy resin, was obtained from the Hysol Corporation, Olean, New York. The polyol structure is



The average value of x is 3.6. The curing agents used were hexahydrophthalic anhydride and benzyldimethylamine. After parts A and B were heated to 54°C., they were mixed in equal quantities by weight and placed in an evacuated chamber, to remove air bubbles. The curing conditions

TABLE I
Polyol-Modified Epoxy Materials

Material	Part A, wt.-%	Part B, wt.-%
Bisphenol-epichlorhydrin resin	82	—
Hexahydrophthalic anhydride	—	62.3
Polyol (P-1180)	18	36.1
Benzyl dimethylamine	—	1.6

were varied, to obtain different properties. Table I shows the composition of the polyol-modified epoxy starting materials.

Epichlorhydrin-bisphenol A (Epon 828), obtained from the Shell Chemical Company, was cured with diethanolamine (DEA), obtained from Fisher Scientific Company. These chemicals were used as obtained without further purification.

Phase Transition Temperatures

Two methods, differential thermal analysis and linear thermal expansion, were used to obtain the phase-transition temperature data. The instruments were locally constructed and are described elsewhere.² The precision of the measurements was about $\pm 1^\circ\text{C}$. for locating the middle of the transition range.

Viscosity Measurements

The viscosities of the polymer starting materials and of the interstitial fluid extracted from the polyol-modified epoxy were determined by the falling-sphere method.^{3a} The precision obtained by this method was $\pm 2.7\%$ of the mean value.

Density Measurements

The density of polymer samples was measured with a precision of ± 0.2 mg./cm.³ by the buoyancy method with a Chainomatic balance. The samples were weighed in air and in distilled water at a constant temperature.^{3b}

Shrinkage and Gel Time Measurements

The shrinkage during polymer cure was obtained as a function of time by measuring the decrease in height of the meniscus in a graduated cylinder filled to about 100 ml. with the liquid starting materials. The height measurements were made with a cathetometer with a precision of ± 0.005 mm. The gel time was taken as the point at which a radical discontinuity in the slope of the height-time curve occurred. The polymer was observed to pull away from the walls of the container at the gel time and was obviously solidified after this point.

RESULTS

The epoxy materials are characterized by at least two phase-transition temperatures. Figure 1 shows typical data obtained by linear thermal expansion measurements for the polymers. The two breaks in the curve were designated as upper and lower transition temperatures, respectively.

Figure 2 shows the upper phase-transition temperature obtained for the polyol-modified epoxy as a function of the initial oven temperature during the cure. The oven temperature was constant but is termed "initial" to distinguish it from a postcure. All the samples of the polyol-modified epoxy were postcured at 160°F. for 24 hr.

Similar data are shown in Figure 3 for the diethanolamine-cured 828 Epoxy. The phase-transition temperatures are presented as a function of the number of thermal expansion cycles. This is thought to be approximately equivalent to extending the time of the postcure at the median temperature (160°F.). The initial oven curing temperatures are noted on the graph for each curve. As for the polyol-modified epoxy (Fig. 2), a high initial curing temperature results in a low phase-transition temperature.

The relative viscosities and the phase-transition temperatures of various mixtures of the starting materials are shown in Figure 4 for the polyol-modi-

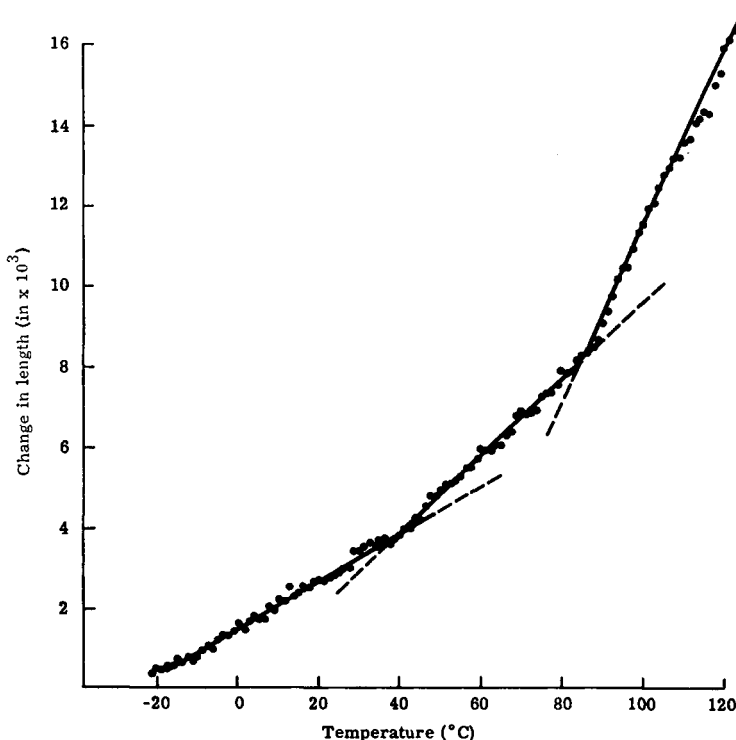


Fig. 1. Linear thermal expansion measurements for the DEA-828 epoxy showing the two phase transitions.

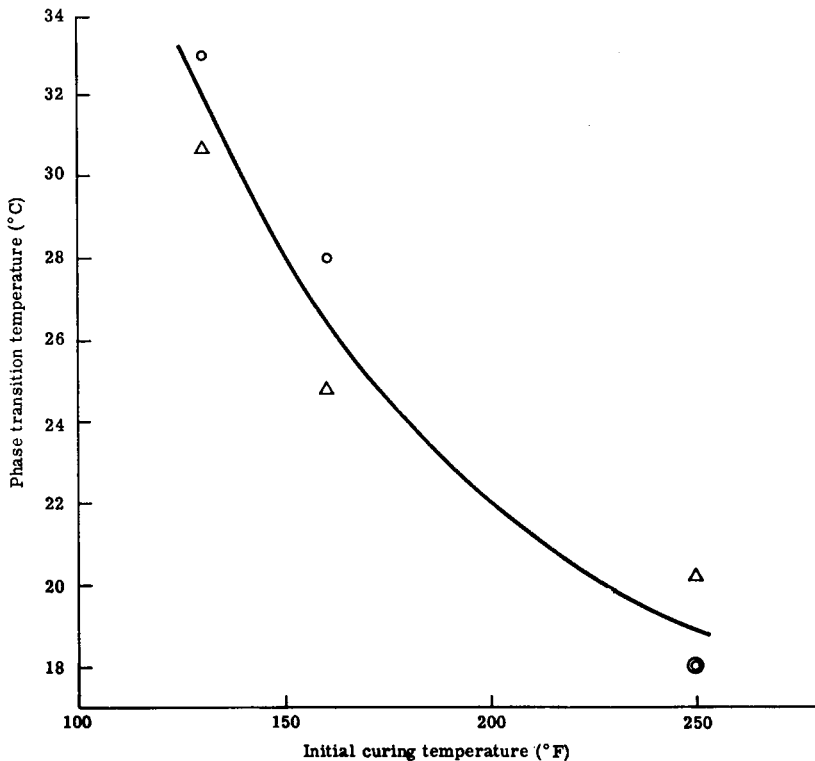


Fig. 2. Upper phase transition temperature as a function of initial curing temperature for polyol-modified epoxy. Postcure temperature maintained constant at 160°F. Measurements obtained by (O) differential thermal analysis, (Δ) linear thermal expansion.

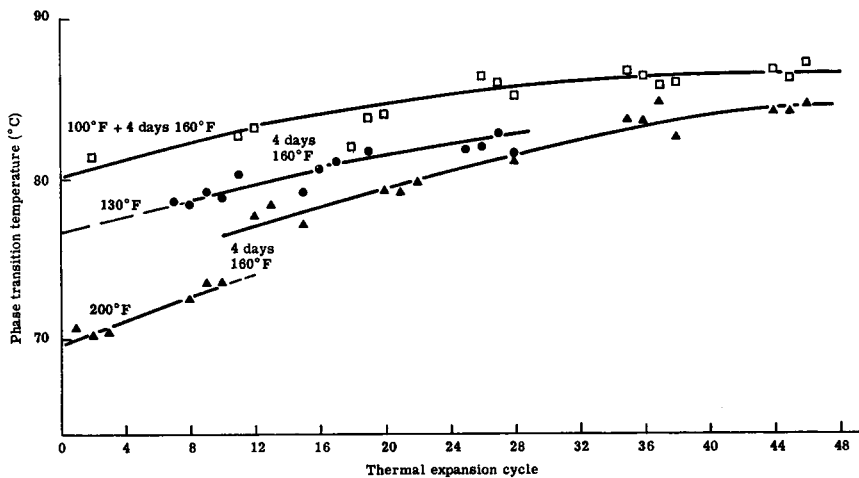


Fig. 3. Upper phase transition temperature for DEA-828 epoxy as a function of number of thermal expansion cycles (postcure).

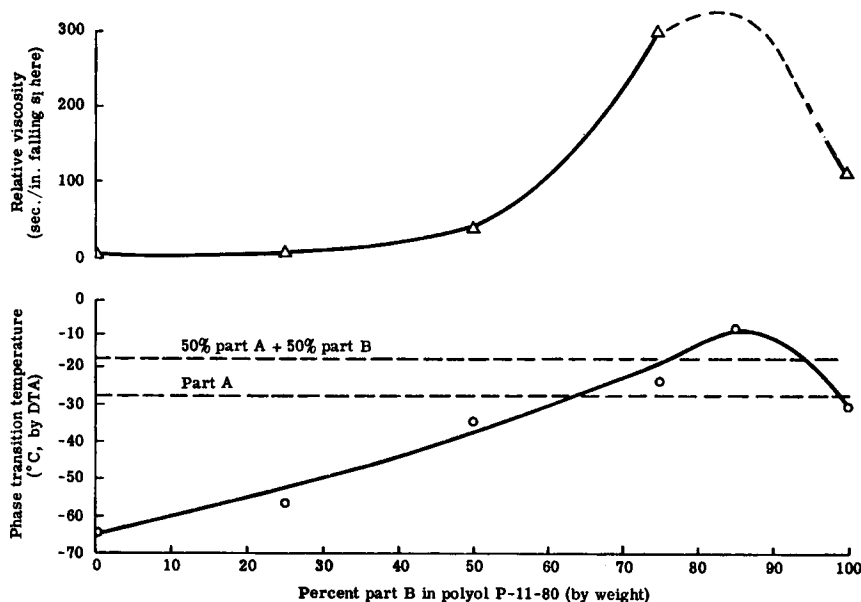


Fig. 4. Phase transition temperatures and relative viscosities for various mixtures of polyol-modified epoxy starting materials and for interstitial fluid extracted from cured polymer.

fied epoxy. A liquid fraction was obtained by extracting the cured polymer with ethanol. This material is thought to be representative of the second phase, the interstitial fluid, in the cured polymer. The properties of these materials are shown in Figure 4 and in Table II.

Figure 5 shows the variation of the polymer density with the floccule size. The experiments describing the determination of floccule dimensions are reported elsewhere.^{1,4} Large floccules were found in the polymer cured at low temperature; the converse, at high temperature. There is some variation in floccule size in a given sample that is not reflected in the

TABLE II
Properties of Polyol-Modified Epoxy and Its Components

Material	Mol. wt. ^a	Viscy., cp.	Dens., g./cm. ³	Refrac. index	Dielec. const., ^b (at 10 khz)
Part A	324	3,993	1.1390	1.5483	7.4
Part B	650	25,449	1.1466	1.4810	14.9
Polyol	660	—	1.0290	1.4533	9.9
A + B (uncured)	—	—	1.1512	1.5151	—
Interstitial fluid	2,655	40,107	1.0724	1.5001	34.7
A + B (cured)	—	—	1.1840	1.5346	3.3

^a Determined by osmometry and freezing-point depression.

^b Private communication, J. L. Wentz, Sandia Corporation.

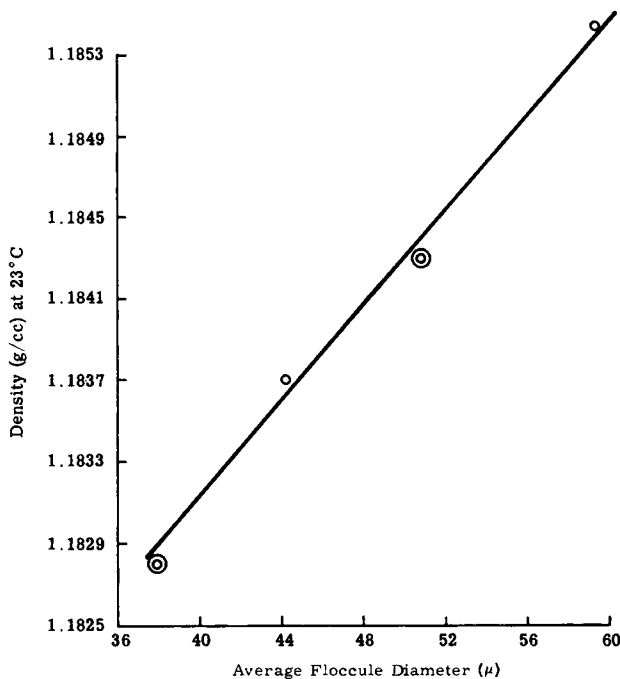


Fig. 5. Density of polyol-modified epoxy polymer as a function of average floccule size.

average values shown in Figure 5. The most precise determinations were made with a micropenetrometer specially constructed for this purpose.

Some properties of the cured polyol-modified polymer are shown in Table III.

A typical volume-time curve for the cure shrinkage in the polyol-modified epoxy is shown in Figure 6. The initial expansion is thought to be a result of the reaction exotherm and the thermal expansion of the liquid mixture, as it approaches the oven temperature. The mixture increases in density

TABLE III
Effect of Initial Curing Temperature on Floccule Size

Curing temp., °F., and time ^a	Average floccule diameter, μ	Properties
130, 7 days	48	Hard, high density, high phase-transition temperature, low electric strength; difficult to etch
130, 16 hr.	44	
160, 16 hr.	35	
200, 16 hr.	28	Soft, low density, low phase-transition temperature, high electric strength; easy to etch

^a All samples were postcured at 160°F. for 24 hr.

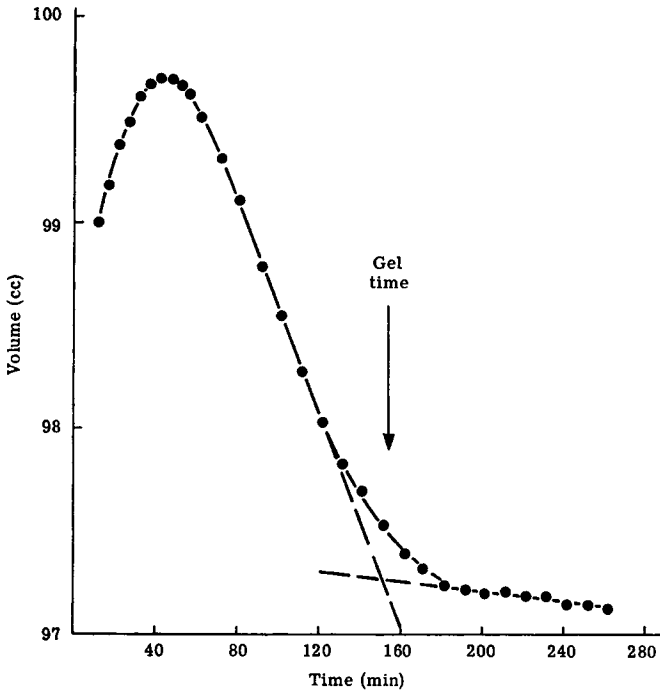


Fig. 6. Volume of polyol-modified epoxy polymer at 160°F. as a function of initial curing time.

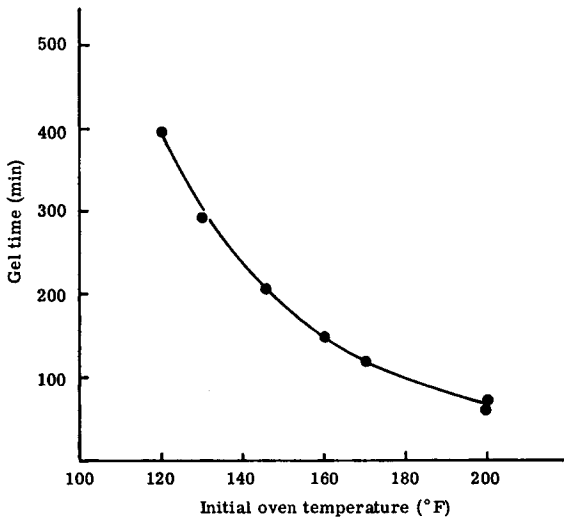


Fig. 7. Gelation time as a function of initial curing temperature for polyol-modified epoxy.

as the reaction proceeds and shrinks as a liquid prior to gelation. The gel time is taken as that corresponding to the radical change in slope of the curve (visual evidence of solidification was obtained shortly after the break in the curve).

Figure 7 shows the temperature dependence of the gel time in the polyol-modified epoxy, and Figure 8 shows the linear relationship obtained

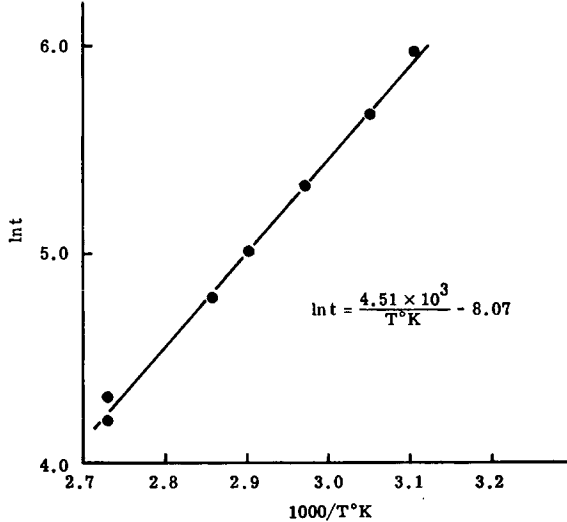


Fig. 8. Logarithm of gelation time as a function of absolute temperature for polyol-modified epoxy.

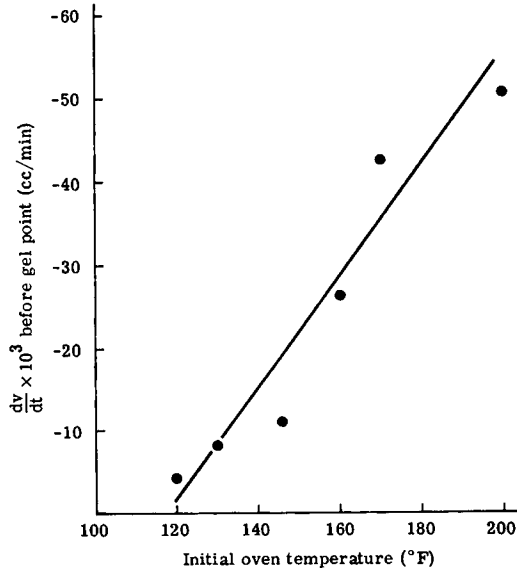


Fig. 9. Slope of volume-time curve prior to gelation as a function of initial curing temperature for the polyol-modified epoxy.

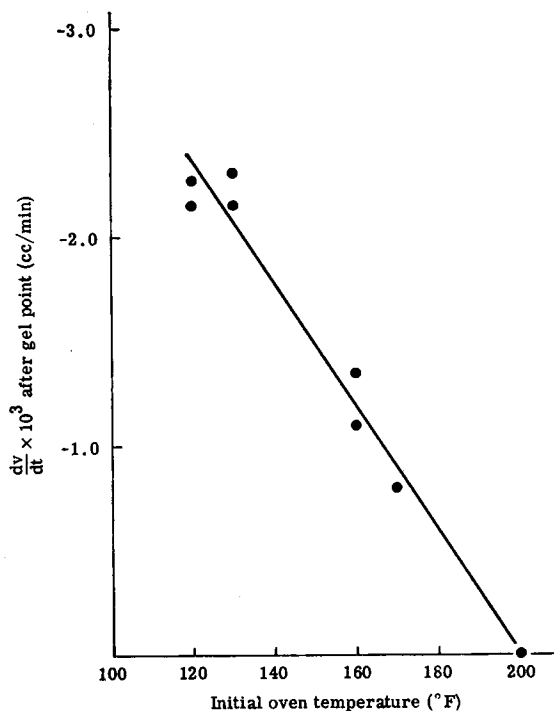


Fig. 10. Slope of volume-time curve after gelation as a function of initial curing temperature for polyol-modified epoxy.

when the data are plotted in an Arrhenius form (a form convenient for extrapolation). Figures 9 and 10 show the slopes obtained from the volume-time curves before and after the gel time, respectively.

DISCUSSION

When an epoxy sample is cured, the liquid starting materials are converted to a solid. The physical properties change from low to high density and from low to high phase transition temperature. Because of the change in density there is a decrease in volume (shrinkage). There is a considerable amount of evidence that the polymerization process is incomplete and that a two-phase system results.^{1,2}

In comparisons of the epoxy samples the relative degree of cure was assessed by physical measurements. A sample exhibiting greater hardness and density and a glass transition at higher temperature than those of other samples is assumed to be polymerized to a greater extent. Figures 2 and 3 show an inverse correlation between the glass transition temperature and the oven temperature during cure and a direct correlation between the glass transition temperature and the cure time. Figure 5 shows a correlation between the floccule size and the polymer density. An inverse correlation between floccule size and oven temperature during cure was

previously obtained.² These data may be qualitatively summarized as follows. A higher oven temperature results in a lower degree of cure, as indicated by the density, hardness, and glass transition temperature (the converse is true of samples cured at lower temperatures). The results of further investigations offer some clues in understanding how this comes about.

The theory of absolute reaction rates is expressed in terms of the kinetics of moving bodies. Collisions are requisite for reaction. This motion can be expressed in terms of diffusion theory, when the reaction medium is not homogeneous (as is probably the case in high-viscosity two-part epoxy polymerization). The motions of molecules, ions, or molecular aggregates (colloidal particles) are caused by a force which, in its result, is the same whether it arises from an externally applied electric field (as in electroosmosis, electrophoresis, and electrolytic conduction), an externally applied mechanical force (as in streaming potentials), or an internally generated electric field caused by differences in chemical potential associated with concentration gradients.

The Eyring theory of transport phenomena is instrumental in obtaining relationships among various macroscopic quantities.⁵ It is found that the viscosity depends on the temperature in the following way:

$$\eta = nh \exp \{3.8T_b/T\} \quad (1)$$

where T_b is the boiling temperature at one atmosphere, T is the absolute temperature, η is the coefficient of viscosity, n is the number of moles per cubic centimeter, and h is Planck's constant. The theory also predicts the following relation between the coefficients of viscosity and self-diffusion, D (similar relationships, differing only by a numerical factor, have been derived by means of the "hydrodynamic theory" of diffusion, the Stokes-Einstein equation for diffusion of large molecules in a solvent and the Sutherland-Einstein equation for self-diffusion in liquids):⁶

$$\eta D = n^{1/3} k T \quad (2)$$

where k is the Boltzmann constant.

Equation (2) may be divided by eq. (1) to give

$$D = AT / (\exp \{3.8T_b/T\}) \quad (3)$$

where the factor A is obtained by combining the various constants in eqs. (1) and (2).

The rate of shrinkage in the epoxy polymerization is assumed to be exactly related to the rate of polymerization (though the mathematical formulation may remain unspecified). If the rate of cure is dependent upon the rate of diffusion of reactants in the liquid mixture, then the change in shrinkage rate with temperature should be related to the change in diffusion coefficients. The shrinkage rates for the liquids prior to gelation are shown as a function of cure temperature in Figure 9. The volume rates of change (dV/dt) were corrected for thermal expansion

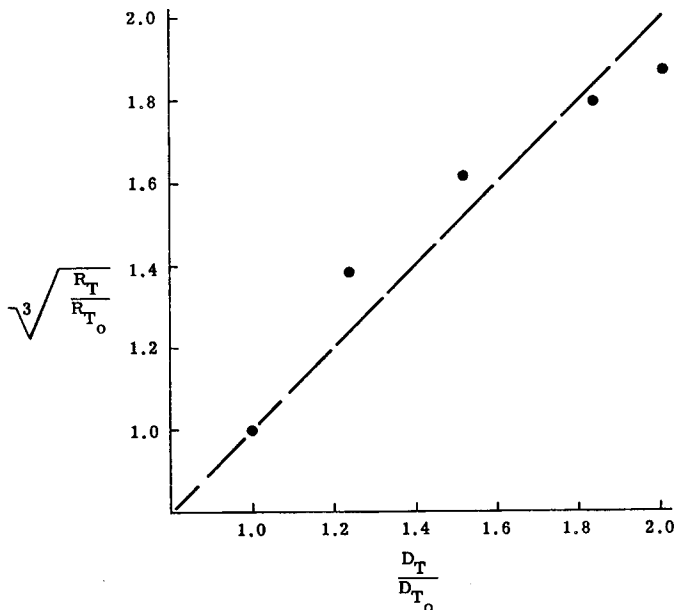


Fig. 11. Correlation chart for shrinkage rates and diffusion coefficients. Dashed line represents a one-to-one correlation.

by multiplying them by the factor V_{23}/V_T where V_{23} and V_T are the sample volumes at room temperature (23°C.) and temperature T , respectively. Because the absolute diffusion coefficients are not yet available, only a relative rate comparison may be made. The ratios R_T/R_{T_0} were obtained by dividing $(dV/dt)_T$ by $(dV/dt)_{T_0}$ where $T_0 = 327.6^\circ\text{K}$. A spherical element of volume was assumed and, since diffusion is a linear, unidimensional measurement, $(R_T/R_{T_0})^{1/3}$ was assumed to be the proper formulation for comparison. The physical model is that of a reaction rate dependent upon the rate of diffusion of reactants along the radii of a spherical microscopic sample element. The diffusion coefficient ratios D_T/D_{T_0} were obtained by reformulating eq. (3) as follows:

$$D_T/D_{T_0} = (T/T_0) \exp \{3.8T_B(1/T_0 - 1/T)\} \quad (4)$$

The one-to-one correlation shown in Figure 11 is the best fit of the data obtained when $T_B = 573^\circ\text{K}$. (300°C.). The results are not appreciably different for boiling points of 200 and or 400°C. Parts A and B were heated separately and boiled vigorously at $300 \pm 50^\circ\text{C}$.

Rates of chemical reactions can, in general, vary over many orders of magnitude, whereas diffusion coefficients are subject to relatively small variations. The one-to-one correlation between shrinkage rates and diffusion coefficients is thought to suggest strongly a diffusion-controlled mechanism in the polymerization of the epoxy resins. The data may be examined with this in mind.

The inverse relationships between shrinkage rate prior to and after gelation (with respect to oven temperature, Figs. 9 and 10) may be explained as follows. Rapid curing systems (high oven temperatures in the early stages of the cure) result in many small floccules.^{1,2} The converse is true of the same epoxy cured at low temperatures. An analogy may be drawn from the characteristics of other materials. Small grain sizes are obtained when melts of metallic alloys are quenched. Small spherulites are obtained when a polyethylene sample is frozen rapidly. The direct reaction rate-temperature dependence prior to gelation may be correlated with diffusion rates in a liquid, open structure. The inverse reaction rate-temperature dependence obtained after gelation may be correlated with diffusion rates that could be postulated for a liquid confined in a network of capillaries. For the higher temperature cures the interfloccular capillaries would be smaller (dependent upon the smaller floccule dimensions), and the shrinkage or cure rate would be very low. A higher rate of cure could be postulated in the larger interfloccular capillaries associated with the lower temperature cures (a similar result was obtained for the rate of change of volume resistivity during cure by R. W. Warfield and M. C. Petree, *SPE Trans.* 1, p. 4, Jan. 1961). Because gelation occurs early in the curing process, the greater postgelation reaction rate associated with the lower temperatures could, at the end of the cure schedule, result in a greater degree of cure than could be obtained at the higher temperatures; thus the inverse relationship between the oven temperature and the density, glass transition temperature, the hardness, and the ease of chemical etching. This relationship may not hold for epoxy systems⁷ characterized by very high exotherm temperatures and very early gelation (the floccule size may be more closely related to the temperature reached during exotherm than to the oven temperature).

These interpretations are consistent with the following observations. The epoxy polymers studied are, at best, incompletely polymerized. The liquid phase in the polyol-modified epoxy is similar to the starting materials and is thought to be a mixture of low molecular weight polymerization products, starting materials, and impurities. Table I shows that the interstitial fluid has a somewhat higher molecular weight and viscosity than any of the starting materials and is very similar in refractive index to the uncured mixture of parts A and B. The density of this fluid is lower than any of the starting materials with the exception of the polyol (this result is predicted by theoretical approximations involving a closely packed floccule model).¹ The dielectric constant of the interstitial fluid is higher than that of any of the starting materials, which is consistent with the replacement of alcohol groups by carboxyl groups on polymerization (in an anhydride-cured system). (There may have been some ethanol contamination in the sample, in which case the measured dielectric constant would be higher than for the uncontaminated liquid.) The solid polymer exhibits two-phase transition temperatures (one at about -34°C . and one at about $+30^{\circ}\text{C}$. for the polyol-modified epoxy). These transitions were

arbitrarily assigned to the two phases: the low-temperature transition to the interstitial fluid and the high-temperature transition to the floccular material. There is some justification for making this assignment in that the interstitial liquid leached from the cured polymer exhibited only the low-temperature transition, while both transitions were found in the solid residue (indicating that all of the solid was removed from the liquid, but some liquid remained with the solid phase). The -34°C . transition for the interstitial fluid is in the temperature range expected (between -10 and -65°C .) on the basis of an assumed similarity to the starting materials (Fig. 4).

CONCLUSIONS

Two-phase transitions were found in the two-phase epoxy systems studied. The low-temperature transition in the cured polymer (polyol-modified epoxy) and the phase transition found in the interstitial fluid extracted from the polymer both occur at the same temperature (-34°C .). The high-temperature phase transition is absent in the liquid extract, is present in the solid residue, and is thought to be associated with the floccule phase.

The degree of cure, as indicated by the density, hardness, ease of etching, and the phase transition temperature,² was found inversely related to the sample temperature in the early stages of the curing period. A diffusion-controlled curing process in a capillary network is postulated to explain this unexpected relationship. The change in shrinkage rate with temperature prior to gelation was correlated with the theoretically predicted change in diffusion coefficients with temperature. Though different chemical reactions may occur, the rate of diffusion in capillaries is thought to be rate-determining in the polymerization after gelation.

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