

Phase Separation Behavior of Rubber-Modified Epoxies

T. T. WANG and H. M. ZUPKO, *Bell Laboratories, Murray Hill, New Jersey 07974*

Synopsis

The compatibility and phase separation behavior of mixtures of the diglycidyl ether of bisphenol A and carboxyl-terminated butadiene-acrylonitrile copolymers were studied by means of light transmission, viscosity measurements, and optical microscopy. Cloud point measurements of the blends prior to curing showed a strong influence of acrylonitrile on the miscibility behavior, especially near the critical composition of the system. In addition, the cloud point curves showed a highly skewed shape which turned out to be particularly favorable to the formation of a rigid but tough two-phase structure. Blends subjected to isothermal cure at 120°C were found to begin phase separation at a progressively shorter time with increase in the copolymer content. Furthermore, while the phase domains tended to cease growing at the time of gelation, the composition within the sample continued to change well beyond the gel point.

INTRODUCTION

Carboxyl-terminated butadiene-acrylonitrile elastomers are increasingly being used in many areas of epoxy application as a means of improving the fracture toughness of epoxy resins.¹⁻⁵ This improvement is accomplished by utilizing the partially miscible nature of the two components which allows the morphology of the mixture to be manipulated by controlling the composition and curing conditions. For example, McGarry and his co-workers^{6,7} have found a marked improvement in the fracture toughness when the mixture containing a small fraction (~10% by weight) of the elastomer is allowed to phase separate into a rubber-rich phase finely dispersed in an epoxy-rich matrix upon curing at an elevated temperature. Subsequently, it has been found^{1-4,7} that the degree of improvement depends critically on the size of the rubber-rich phase domains and reaches a maximum when the size distribution ranges 1-5 μm . Since the morphology of the cured system depends on the competing effects between phase separation and polymerization during the curing treatment, the various factors which influence the kinetics of both processes need to be understood in order to achieve an optimum heterogeneous structure. In this article we report the results of a study made on the miscibility and phase separation behavior of the blends prior to and during the curing treatment. While the subject has been dealt with in several publications,¹⁻⁸ to our best knowledge no systematic study has been carried out previously.

EXPERIMENTAL

The epoxy resin used in this study was a diglycidyl ether of bisphenol A (DGEBA) made by Shell Chemical Company (Epon 828). The two rubber modifiers were liquid copolymers of carboxyl-terminated butadiene-acrylonitrile

(CTBN) containing 10 and 17 wt % bound acrylonitrile, both of which are available from B. F. Goodrich under the trade name of Hycar. For simplicity, they will be referred to as CTBN(10) and CTBN(17) in the subsequent discussion. Some of the pertinent properties supplied by the manufacturer are listed in Table I. The curing agent, piperidine (Fisher Scientific Company), was used as received.

To study the phase separation behavior prior to the addition of curing agent, blends of DGEBA and CTBN were prepared by stir-mixing the two liquid resins in desired volume proportions for about 10 min at temperatures between 60 and 80°C (in a silicone oil bath) for the system containing CTBN(17) and between 130 and 150°C for the system containing CTBN(10). These temperatures were chosen so as to ensure thorough mixing in the compatible state (as judged by the transparency of the mixture) and at sufficiently low viscosity. After the mixing, the blend was degassed in a vacuum chamber (maintained at ca. 1 torr) for about 3 min, and then, while still warm, a drop was quickly placed inside a 0.25-mm-deep, 8-mm-diameter cavity on a glass slide created by bonding a perforated sheet of lead to the glass slide with an epoxy adhesive. The filled cavity was then covered with a cover glass and pressed with a 90-g weight for about 3 min to allow the liquid resin to spread evenly in the cavity. This assembly was then transferred to a hot stage (Mettler FP52) mounted on a Reichert Zetopan microscope and conditioned at temperatures similar to those used in mixing to bring the sample to a compatible state. The microscope was equipped with a long working distance lens with its iris diaphragm opening set at maximum to facilitate observation of morphological development and the light transmission study.

The cloud point was determined by measuring the change in the intensity of light transmitted through the sample while the sample was being cooled or heated at a rate of 0.2°C/min. The intensity of the transmitted light was monitored with a photocell placed inside one of the eyepiece sockets on the microscope and recorded as an output voltage on a chart recorder. The temperature at which the voltage output began to drop in the cooling run is defined as the cloud point. The sample temperature was regulated with a Mettler FP5 unit connected to the hot stage. Calibration of the hot stage temperature was accomplished by means of the triplet points of naphthalene ($80.24 \pm 0.05^\circ$) prepared in specimens matching the present sample geometry.

Measurements of the phase separation behavior during the isothermal curing reaction were performed on blends of DGEBA and CTBN(17). Samples used in these measurements were prepared by stir-mixing the two liquid resins in desired proportions at 120°C for about 10 min, at which point piperidine was added to the mixtures (at 5% weight fraction of the epoxy component in each sample), which were further mixed for 1 min and degassed in a vacuum chamber

TABLE I
Properties of Epoxy and CTBN

	Epoxy (Epon 828)	CN 1300 × 15	CTBN 1300 × 8
Molecular weight \bar{M}_n	380	3,500	3,500
Density at 20°C	1.168	0.924	0.948
Acrylonitrile content, wt %	0	10	17
T_g , °C ^b	-9°	-59°	-45°

(ca. 1 torr) for 3 min. (The loss of piperidine during degassing was less than 2% of the total amount added to the mixtures.) Upon degassing, glass slides of the samples were prepared in the same manner as described earlier and transferred to a hot stage maintained at the cure temperature for observation of changes in morphology and the light transmission behavior. Concurrent with this measurement, a portion (ca. 15 g) of each degassed sample was placed in a Haake Rotovisco RV3 equipped with a pair of concentric cylinders (SV II) for simultaneous monitoring of changes in shear viscosity at the same cure temperature. To minimize the length of time during which the samples were sheared, rotation of cylinder was interrupted between the intervals of viscosity measurements, except during the final stage of cure when the viscosity rose rapidly. The cure time was counted from the moment the curing agent was added to the mixture.

RESULTS AND DISCUSSION

Phase Separation Behavior of the Systems Prior to Addition of Curing Agent

Figure 1 is a plot of cloud point curves for the two systems DGEBA-CTBN(10) and DBEGA-CTBN(17), with the copolymer content ϕ (in volume fraction) ranging from 0.03 to 0.38. Data at greater copolymer contents were not obtained because of the extremely slow changes in the transmitted light intensity at low temperatures. Several features are evident in Figure 1. Firstly, there is a large spread in the temperature between the two curves, especially around the maximum temperatures (which correspond approximately to the upper critical solution temperatures, UCSTs, of the systems⁹), indicating that the mixing behavior is highly sensitive to the acrylonitrile content in the copolymer. Sultan and McGarry⁷ and Manzione, Gillham, and McPherson⁸ have noted a tendency for the copolymer with a higher acrylonitrile content to mix more readily with epoxy and attributed this to closer matching of solubility parameters between epoxy and acrylonitrile.

Secondly, the miscibility gaps (i.e., the regions under the cloud point curves) for both systems are skewed appreciably toward the left (epoxy) axis, with the apparent UCST located at a ϕ of about 0.07. (This composition will be referred to as ϕ_{cr} subsequently.) This is apparently caused by the large difference in the molecular weight between the two mixing components and can be understood in terms of the combinational entropy of mixing in the theory of polymer solution.^{9,10}

While the choice of these resin molecular weights has been based on empirical deductions,^{3,6} it can be seen from Figure 1 that the resulting skewness in the miscibility gap is particularly favorable to the formation of a two-phase structure in which one phase consists almost entirely of epoxy while the other contains both epoxy and the copolymer in a more balanced proportion. Furthermore, while the composition of the first phase always remains nearly constant, the composition of the second phase changes widely depending on the copolymer content in the mixture and the temperature at which phase separation takes place. (Note that the presence of a proper fraction of epoxy in the second phase is essential for reaction with the copolymer to form a rubbery network.⁴⁻⁷) Obviously, this

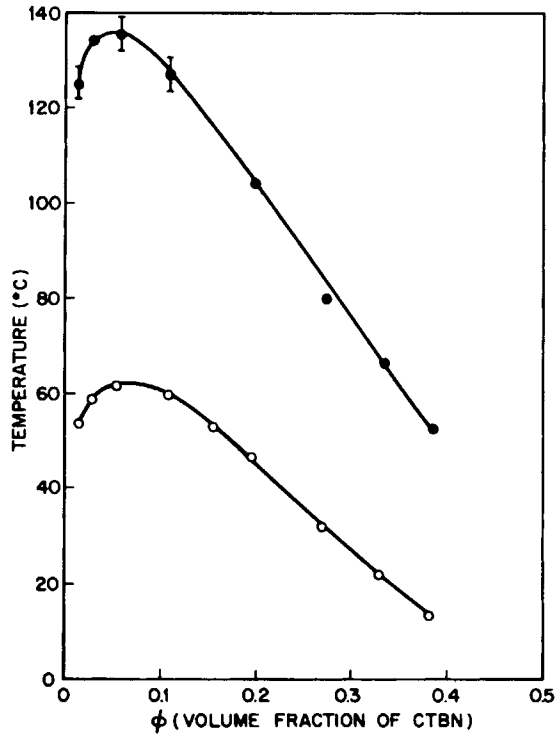


Fig. 1. Plots of cloud point curves for systems DGEBA-CTBN(10), (●), and DBEGA-CTBN(17), (○).

observation is valid only for the mixtures prior to the addition of curing agent. Nevertheless, it indicates the possibility of changing the composition of the second phase in the cured polymer (and hence its property) over a wide range by controlling the elastomer content in the blends and the rate of polymerization (e.g., by changing the cure temperature or by the use of different type of curing agent).

In addition to the cloud point curve data, the light transmission measurements revealed that the changes of the transmitted light intensity, I , in the cooling and heating cycle followed two distinct patterns in different ranges of composition depending upon the resin systems. Typical results for mixtures of DGEBA and CNBN(17) are shown in Figures 2 and 3. For $\phi \leq 0.25$ (Fig. 2), the light transmission behavior is nearly identical on cooling and on heating, while for $\phi > 0.25$ (Fig. 3), the change in I is rather abrupt and rapid on cooling but gradual and steady on heating. The latter behavior has also been observed in the system polystyrene-poly(vinyl methyl ether) near its ϕ_{cr} ¹¹ and is thought to be associated with spinodal decomposition of the mixture. While this anomalous behavior was observed in our system at compositions much greater than the ϕ_{cr} determined from the cloud point curve, it is quite possible that the true critical point, which is the point where the spinodal meets the binodal, is located at a higher composition than the cloud point because of the high polydispersity of CTBN(17).¹²

The DGEBA-CTBN(10) system also exhibited two light transmission modes similar to those observed in the DGEBA-CTBN(17) system; however, the transition between the two modes was found to occur at a much smaller com-

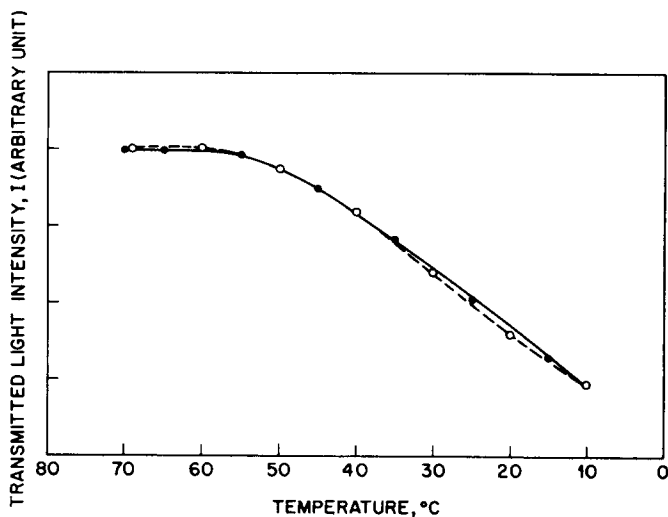


Fig. 2. Plots of transmitted light intensity as a function of temperature for the mixture DBEGA/CTBN(17) = 94/6. O, heating; ●, cooling.

position ($\phi \sim 0.03$). In addition, mixtures with high concentrations of the copolymer showed a residual turbidity upon completion of the cooling and heating cycle. One possible reason for this may be found in the tendency for the mixture to stratify upon phase separation, apparently because of the difference in density between the two phases. An example is shown in Figure 4 for the mixture DGEBA/CTBN(10) = 73/27 (by volume), which was cooled down slowly ($2^\circ\text{C}/\text{min}$) after mixing thoroughly at 135°C . Since, according to the phase diagram (Fig. 1), the composition of the epoxy-rich phase remains nearly constant, any addition of the copolymer to the mixture tends to be incorporated into the

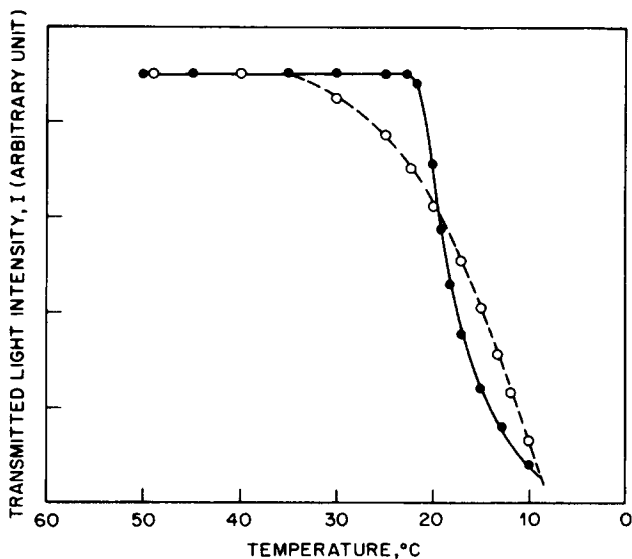


Fig. 3. Plots of transmitted light intensity for the mixture DGEBA/CTBN(17) = 67/33. O, heating; ●, cooling.

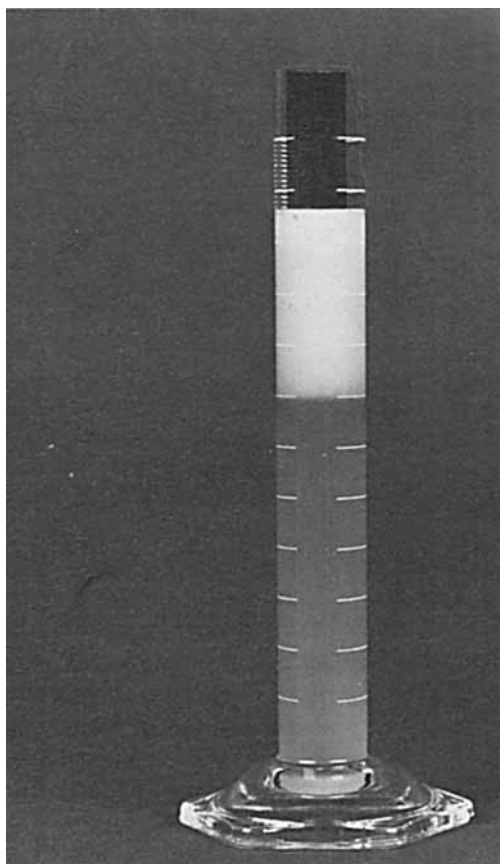


Fig. 4. Photograph of the mixture DGEBA/CTBN(10) = 73/27 upon phase stratification. The upper (light-shaded) layer is the rubber-rich phase, and the bottom layer is the epoxy-rich phase.

second phase. Consequently, as the copolymer is much lighter than epoxy (cf. Table I), the density of the second phase should decrease rapidly with the increase in ϕ , while the density of the first phase remains nearly constant. Once stratified, remixing of phases becomes more difficult in the subsequent heating cycle.

While mixtures of DGEBA and CTBN(17) also tended to stratify upon phase separation, the process was much slower and its effect was not detected in the light transmission measurements, in part, because the phase separation occurred at low temperatures where the viscosity effect became significant and also because CTBN(17) had a somewhat higher density than CTBN(10).

Phase Separation Behavior During Isothermal Curing

The phase separation behavior during the crosslink reaction was studied under isothermal conditions since changing the temperature during the curing treatment affects not only the compatibility of the blend directly but also the rate of polymerization, which in turn influences the phase separation behavior of the blend. Results of the light transmission and viscosity measurements performed

on blends containing 3 to 38 vol % of CTBN(17) at 120°C are shown in Figures 5 and 6. (The viscosity measurements on samples with 33 and 38 vol % of CTBN were terminated prematurely because of fracture resulting from the shearing action.) As noted earlier in the experimental section, the two types of measurements were conducted simultaneously on the same blend to allow a close tracking of the phase separation process at different stages of polymerization.

It is seen from the plots that both the light transmission and viscosity characteristics depend strongly on the composition of the blend. In addition, comparison of the light intensity data with the corresponding viscosity data for the same composition shows that even after the viscosity has risen sharply, the light intensity continues to drop at a steady rate and does not level off until long after

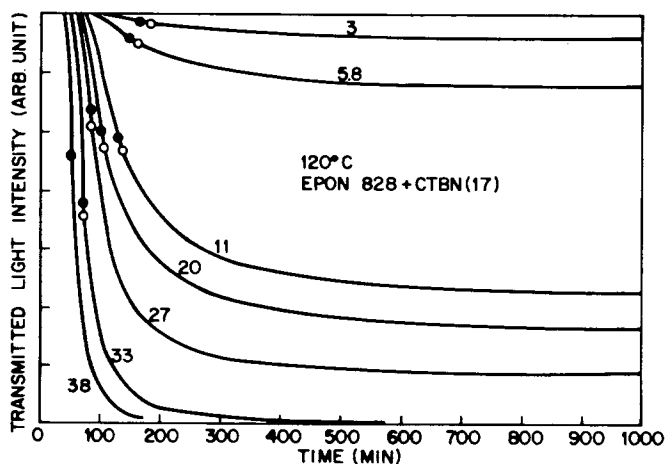


Fig. 5. Changes in the transmitted light intensity as function of cure time for the blends of epoxy and CTBN(17). Filled and open circles mark the times at which the viscosities reach 200 and 1000 poises, respectively.

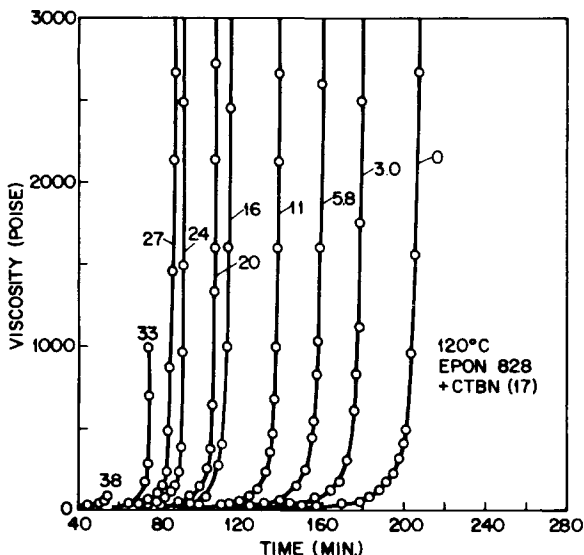


Fig. 6. Changes in the viscosity as function of cure time for the blends of epoxy and CTBN(17).

the sample has gelled. (The solid and open circles on the light intensity curves mark the time at which the samples reach the viscosities of 200 and 1000 poises, respectively.)

This result is particularly interesting since microscopic examination of the samples during the crosslink reaction revealed that the growth of phase domains ceased approximately at the time the viscosity began to rise rapidly. A typical result is given in Figure 7, which displays the domain structure of a sample, DGEBA/CTBN(17) = 89/11, at different stages of cure. At the first indication of phase separation, marked by a sudden drop in the transmitted light intensity, the domains grew very rapidly for a few minutes, and then the rate of growth fell sharply to a very low level until the viscosity reached a value of about 200 poises (ca. 130 min) beyond which no further change in the domain size was detected. This observation, which has also been reported earlier by Gillham, Glandt, and McPherson¹³ in a similar system cured with different catalysts, indicates that the decrease in the transmitted light during the postgelation period was not caused by changes in the overall domain patterns.¹⁴

Visconti and Marchessault¹⁵ have studied the phase separation behavior of an epoxy-CTBN system by means of small-angle light scattering and detected a further increase in the scattered light after the sample has been cured (isothermally) beyond its gel point. They ascribe this to an artifact due to the evolution of small gas bubbles in the sample cell at the glass-solid interface. However, results obtained from our light transmission study showed that the decrease in the transmitted light was not only reproducible but was also consistently observed for all compositions except the pure components (epoxy and CTBN), which did not exhibit any change in the transmitted light when mixed with 5 wt % piperidine and heated at 120°C.

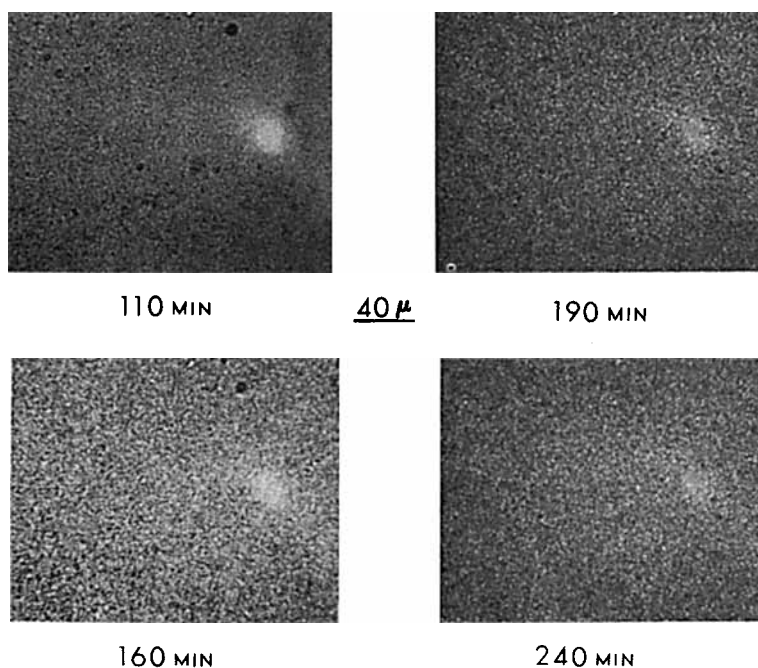


Fig. 7. Photomicrographs of a sample DGEBA/CTBN(17) = 89/11 undergoing isothermal cure at 120°C. The times denote the cure times at which the pictures were taken.

These observations, together with the consideration that even after gelation there should be sufficient mobility in the network for the molecular segments to migrate in a limited range, suggest that the postgelation light transmission behavior might be associated with relatively localized changes in composition with the sample. Such local compositional changes could result in formation of more well-defined domain boundaries (cf. Fig. 7) and further precipitation of finely dispersed phase domains within the supersaturated domains formed prior to gelation.^{1,8,16}

Sultan and McGarry⁷ and Riew, Rowe, and Siebert⁴ have studied the chemistry of rubber-toughened epoxy systems and reported that polymerization takes place primarily by a chain extension reaction between epoxy and CTBN followed by a crosslink reaction among the epoxy molecules and between the chain-extended molecules and the remaining epoxy groups. Since these reactions precede phase separation, the increased viscosity could be expected to significantly retard the long-range migration of molecules in the subsequent phase separation. Indeed, evidence in support of the protracted phase separation has been reported by Mogensen, Jacobsen, and Pethrick.¹⁷

Another point of interest, as already noted earlier, is the compositional dependence of the light transmission and viscosity behavior. This dependence can be put in more proper perspective by plotting the phase separation time (or isothermal cloud point) and the time to reach 200 poises (isoviscous time) as functions of composition, Figure 8. The progressive shortening of these two time parameters with the increase in CTBN concentration cannot be accounted for by the initial compatibility of the mixtures prior to cure (which shows minimum compatibility at $\phi \sim 0.07$ according to Fig. 1) and indicates the intervention of other factors brought on by the polymerization.

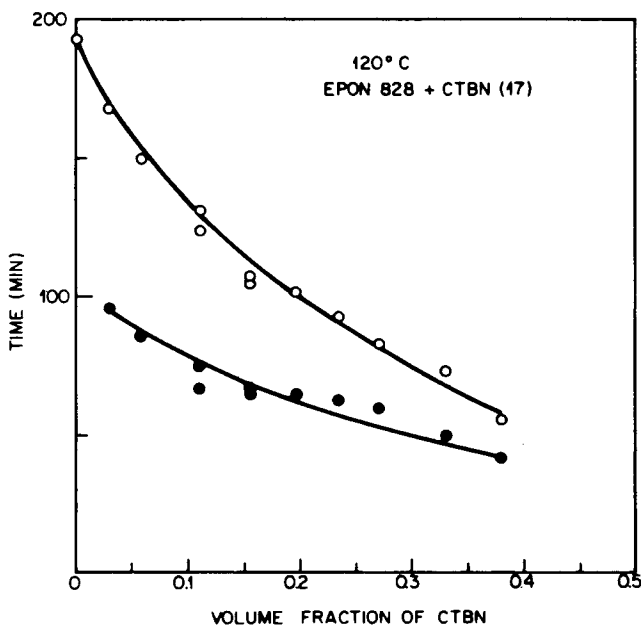


Fig. 8. Plots of isothermal cloud point, ●, and isoviscous time (200 poise), O, as functions of CTBN(17) concentration.

In the reaction mechanisms suggested by Riew, Rowe, and Siebert,⁴ the chain extension reaction between epoxy and CTBN leads to the formation of extended-chain molecules with pendent hydroxyl groups which promote crosslink reaction with the remaining epoxy molecules. Since the chain extension reaction occurs more rapidly than the crosslink reaction,^{4,7,18} addition of CTBN should enhance the rate of polymerization and hasten the onset of phase separation in the blends (cf. the lower curve in Fig. 8). Once the phase separation commences, the ensuing migration of molecules should further increase the reaction rate, resulting in still faster rise in the sample viscosity. This diffusion effect, which is felt only after the blend begins to phase separate, might have been responsible for the steeper fall in the isoviscous curve than in the isothermal cloud point curve.

Results for the blends undergoing isothermal cure at other temperatures (60, 75, 80, 100, and 140°C) have also shown similar dependence of the light transmission and viscosity behavior on composition. However, detailed comparison of these results was complicated by the volatilization of piperidine which occurred at different rates depending on the temperature of cure.

CONCLUSIONS

Several features were noted from the light transmission measurements of the blends prior to the addition of curing agent. The cloud point curves exhibited a UCST behavior with the critical composition located near the epoxy axis. The miscibility gap was much broader for the DGEBA-CTBN(10) system than for the DGEBA-CTBN(17) system, indicating a strong influence of acrylonitrile on the compatibility between the two resins. This influence was especially prominent around the critical composition (ϕ_{cr}). The light transmission behavior under a cooling and heating cycle varied widely depending on the acrylonitrile content in the copolymer as well as the concentration of the copolymer in the blend. The anomalies have been attributed to the difference in the density of the two phases which causes the lighter phase to rise above the other.

Light transmission and viscosity measurements of the blends undergoing isothermal cure showed that both the phase separation behavior and the rate of polymerization depended strongly on composition. Specifically, the isothermal cloud point and the isoviscous time were found to decrease progressively with the increase in the concentration of the copolymer. The phase domains developed rapidly upon phase separation but their overall appearance tended to cease changing as the polymerization approached the gel point. However, the light transmission data indicated that the compositional change within the sample did not cease at the time of gelation but continued to take place well beyond the gel point.

The authors are grateful to Drs. L. T. Manzione and E. B. Davidson for helpful discussions and to Dr. H. D. Keith for kindly reviewing our manuscript.

References

1. F. J. McGarry, *Proc. Roy. Soc. London*, **A319**, 59 (1970).
2. J. N. Sultan and F. J. McGarry, *Polym. Eng. Sci.*, **13**, 29 (1973).
3. E. H. Rowe, A. R. Siebert, and R. S. Drake, *Mod. Plast.*, 417, 110 (1970).

4. C. K. Riew, E. H. Rowe, and A. R. Siebert, in *ACS Advances in Chemistry Series, No. 154*, R. D. Deanin and A. M. Crygnola, Eds., 1976.
5. J. K. Gillham, C. A. Glandt, and C. A. McPherson, *ACS Prepr. Div. Org. Coat. Plast. Chem.*, **37** (1), 195 (1977).
6. F. J. McGarry and A. Willner, Research Report R68-6, School of Engineering, Massachusetts Institute of Technology, 1968.
7. J. N. Sultan and F. J. McGarry, Research Report R68-8, School of Engineering, Massachusetts Institute of Technology, 1968.
8. L. T. Manzione, J. K. Gillham, and C. A. McPherson, *ACS Prepr., Div. Org. Coat. Plast. Chem.*, **41**, 364 (1979).
9. R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).
10. L. P. McMaster, *Macromolecules*, **6**, 760 (1973).
11. T. Nishi, T. T. Wang, and T. K. Kwei, *Macromolecules*, **8**, 227 (1975).
12. R. Koningsveld and A. J. Staverman, *J. Polym. Sci., A-2*, **6**, 349 (1968).
13. J. K. Gillham, C. A. Glandt, and C. A. McPherson, in *Chemistry and Properties of Crosslinked Polymers*, S. S. Labana, Ed., Academic, New York, 1977, p. 491.
14. R. S. Stein, in *Polymer Blends*, Vol. 1, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Chap. 9.
15. S. Visconti and R. H. Marchessault, *Macromolecules*, **7**, 913 (1974).
16. S. Visconti and R. H. Marchessault, *ACS Polym. Prepr.*, **15** (2), 66 (1974).
17. O. E. Mogensen, F. Jacobsen, and R. A. Pethrick, *Polymer*, **20**, 1034 (1979).
18. F. B. Alvey, *J. Polym. Sci., A-1*, **7**, 2117 (1969).

Received October 30, 1980

Accepted January 16, 1981