# Rubber-Modified Epoxies. I. Transitions and Morphology

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## Synopsis

A variety of different morphologies, and therefore mechanical properties, can be obtained from a single rubber-modified epoxy formulation. The volume fraction, domain size, and the number of particles of phase-separated rubber are determined by the competing effects of incompatibility, rate of nucleation and domain growth, and the quenching of morphological development by gelation. These factors can be varied by the butadiene/acrylonitrile ratio of the reactive rubber, the temperature of cure, and the gelation time. These ideas have been exploited to control the development of morphology of these amorphous systems. Phase separation was investigated by electron microscopy, viscometry, and dynamic mechanical analysis.

## INTRODUCTION

Low levels of carboxyl-terminated reactive liquid rubber copolymers of butadiene and acrylonitrile (CTBN) can improve the toughness and impact properties of cured epoxy resins.[1,2] *In situ* phase separation occurs during the cure of the epoxy matrix. The dispersed rubbery phase can introduce energy dissipation mechanisms.

Gelation and vitrification are the two most important macroscopic phenomena that occur during the isothermal cure of crosslinking systems. The theoretical gel point is the critical conversion at which branched molecules of mathematically infinite molecular weight are first formed. Below this conversion all of the molecules are finite. Gelation is accompanied by a large increase in viscosity. In principle, the conversion needed to gel can be calculated from the functionality of the starting material.[3] Vitrification is the formation of a glassy solid from low-molecular-weight liquid or from the rubbery state through a change of temperature, molecular weight, or crosslinking. A specific chemical conversion is needed to vitrify at a fixed temperature.

A mixture of low-molecular-weight bisphenol-A type epoxy resin, 10 parts per hundred parts resin (phr) of CTBN, and 5 phr piperidine is homogeneous at the start of cure if the cure temperature is above some critical solubility temperature (which is designated $T_{s_0}$). In the presence of piperidine there is a rapid reaction of the carboxyl end groups of the CTBN with the epoxide ring.[4] The large excess of bis epoxy resin results in the rubber being capped at both ends by one unit of epoxy. Further reaction of this rubber-containing diepoxide occurs with the unreacted epoxy. There is a simultaneous increase in molecular weight and

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viscosity coincident with the development of the network structure. The rubber and epoxy become less compatible with cure, and a phase separation point is reached where rubber-rich domains precipitate in the epoxy-rich matrix. Once gelation has occurred, the morphology is fixed.[1,4,5,6] Long gel times promote complete separation.[5] If the material gels quickly, the rubber domains may not have sufficient time to develop and smaller, fewer domains form.[5] If gelation occurs prior to phase separation, the rubber is trapped in the network structure and no domains form.

The compatibility of the rubber and epoxy can be controlled by the acrylonitrile content of the rubber modifier as well as the cure conditions. The CTBN modifiers of higher acrylonitrile content are more compatible with epoxy in terms of solubility parameter, and they precipitate at a later stage of cure.

A variety of different morphologies, and therefore material properties, can be obtained from a single rubber-modified epoxy formulation. The volume fraction, domain size, and number of particles of phase-separated rubber are determined by the competing effects of incompatibility, rate of nucleation and domain growth, and the quenching of morphological development by gelation.

## EXPERIMENTAL

### Materials

The rubber modifiers employed were low-molecular-weight copolymers of butadiene and acrylonitrile manufactured by the B. F. Goodrich Co. under the trade name Hycar CTBN. Three rubbers of varying acrylonitrile content were employed. Chemical and physical properties and the nomenclature of the modifiers are presented in Table I. The table also includes information on a carboxyl-terminated liquid polybutadiene (CTB) which was not examined further after finding that it was not initially compatible with the epoxy resin in the range of temperatures used for cure (i.e., $T_{s0} > T_{cure}$).

A low-molecular-weight liquid diglycidyl ether of bisphenol-A (DGEBA) epoxy resin, Epon 828, Shell Chemical Co., was used. It was cured with piperidine (bp 105°C), a tertiary amine catalyst that is effective in promoting the homopolymerization of epoxy.

Formulations and cure conditions are summarized in Table II. Notation for the formulations is also provided in Table II.

TABLE I
Properties of Reactive Liquid Rubbers[a]

| Hycar | CTBN(1300X13) | CTBN(1300X8) | CTBN(1300X15) | CTB(2000X162) |
|---|---|---|---|---|
| Molecular wt. | 3500 | 3500 | 3500 | 4800 |
| Acrylonitrile Content, wt % | 27 | 17 | 10 | 0 |
| Viscosity Brookfield cp, 27°C | 625,000 | 125,000 | 55,000 | 40,000 |
| Solubility parameter | 9.14 | 8.77 | 8.45 | 8.04 |
| Specific Gravity | 0.960 | 0.948 | 0.924 | 0.907 |
| $T_g$,[b] °C (<1 Hz) | −30 | −45 | −59 | −74 |

[a] Materials and data supplied by B. F. Goodrich Co., Brecksville, OH.

[b] Glass transition temperature determined by TBA in the present work.

TABLE II
Composition and Cure of Model Resins[a]

| Modifier | Cure | | |
|---|---|---|---|
| | 90°C/18 hr | 120°C/14 hr | 150°C/4 hr |
| None | 828/90 | 828/120 | 828/135 |
| CTBN (X13) | 13/90 | 13/120 | 13/150 |
| CTBN (X8) | 8/90 | 8/120 | 8/150 |
| CTBN (X15) | 15/90 | 15/120 | 15/150 |

[a] Basic formulation (phr): 100.0 Epon 828, 10.0 CTBN, 5.0 piperidine.

## Techniques

Dynamic mechanical spectra were obtained using a fully automated Torsional Braid Analyzer (TBA)[7] (Plastics Analysis Instruments, Inc., Princeton, NJ) over a temperature range of −190 to 200°C at 1.5°C/min in a dry helium atmosphere. TBA was used to study the glass transition of the rubber ($_RT_g$) and epoxy ($_ET_g$) phases in the cured systems. Specimen preparation consisted of impregnating a multifilament glass fiber braid with the fluid reactant mixture. No solvent was used. After mounting, the specimens were cured in the instrument.

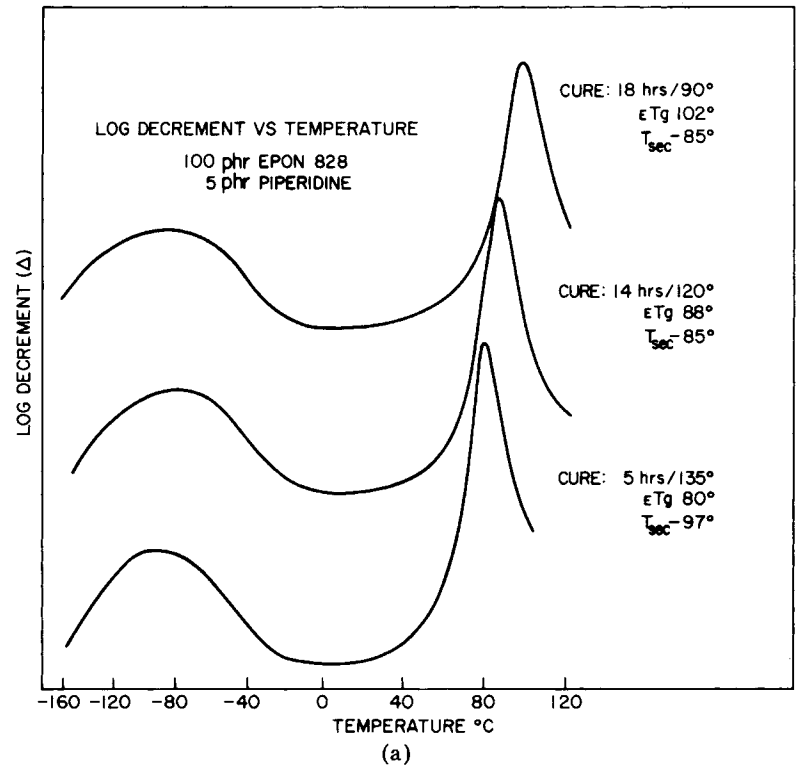
Scanning electron micrographs (SEM) were obtained on fracture surfaces of cured rubber-modified epoxies with an AMR 1000 SEM. Cast specimens (~1/8 in. thick) were fractured in air immediately after being removed from liquid nitrogen. They were coated with a thin layer of gold using a high-vacuum gold sputterer.

Transmission electron micrographs (TEM) were obtained on ultrathin microtomed sections from cast specimens which had been stained with a 1% solution of osmium tetroxide ($OsO_4$/THF).[8]

## RESULTS AND DISCUSSION

The series of rubber-modified epoxies cured with piperidene was used to study the development of morphology. An objective was to develop widely different morphologies from the same proportion of 10 phr of CTBN. A preliminary report has been published.[9] Relationships between morphology and energy dissipation mechanisms for a rubber-modified epoxy system are reported in a subsequent article.[10] Cure temperatures of 90, 120, and 150°C were employed to widen the compatibility range of each rubber. All three temperatures are above the initial solubility temperature, $T_{s_0}$, for each system. The mechanical loss spectrum for each of the modified epoxies is presented in Figure 1. Corresponding SEM micrographs (Fig. 2) indicate that the intensity of the rubber damping peak correlates with the volume fraction of phase-separated rubber. The volume fraction was evaluated from the SEM micrographs using stereology.[11] The morphological results are summarized in Table III. The intensity of the rubber damping peak has been reported to correlate with the volume fraction of phase-separated rubber when specimens are prepared in the same manner and have similar morphologies.[12]

Differences were found in the temperature of the unmodified epoxy glass transition [Fig. 1(a)]. The low temperature cures provide the highest $_ET_g$. This may be the result of different time/temperature paths of cure which result in different network structures. There are, however, complications in the present



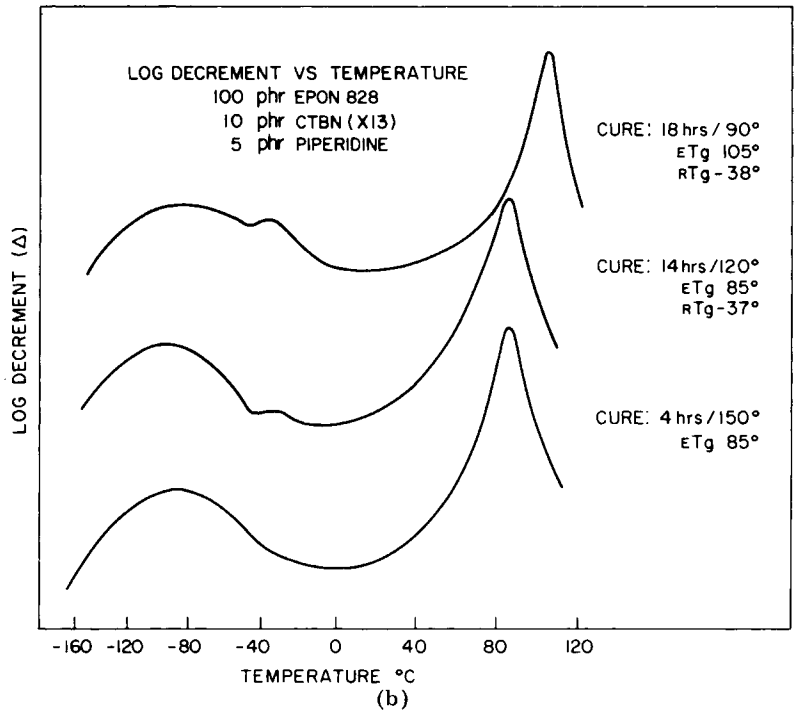
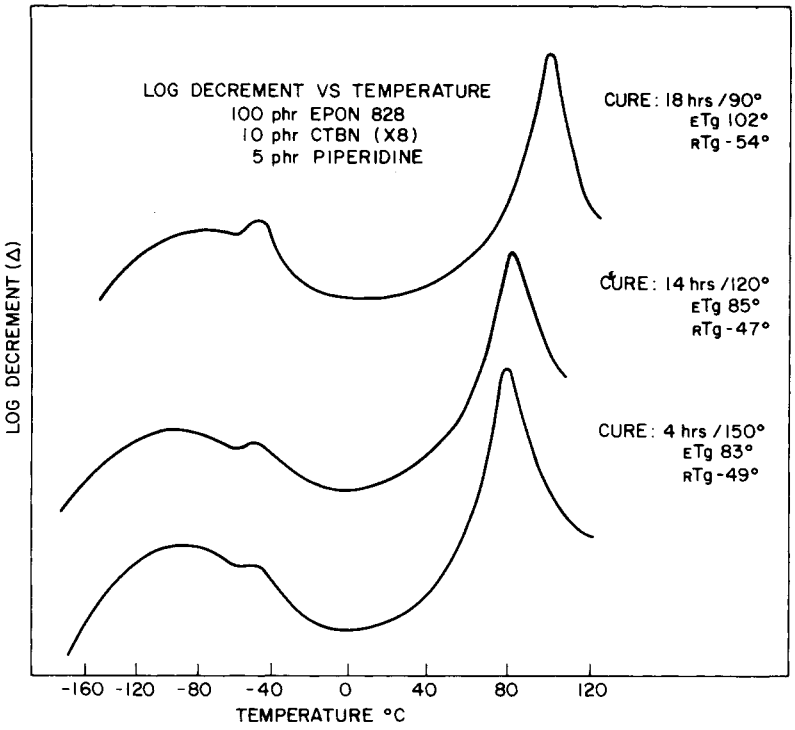
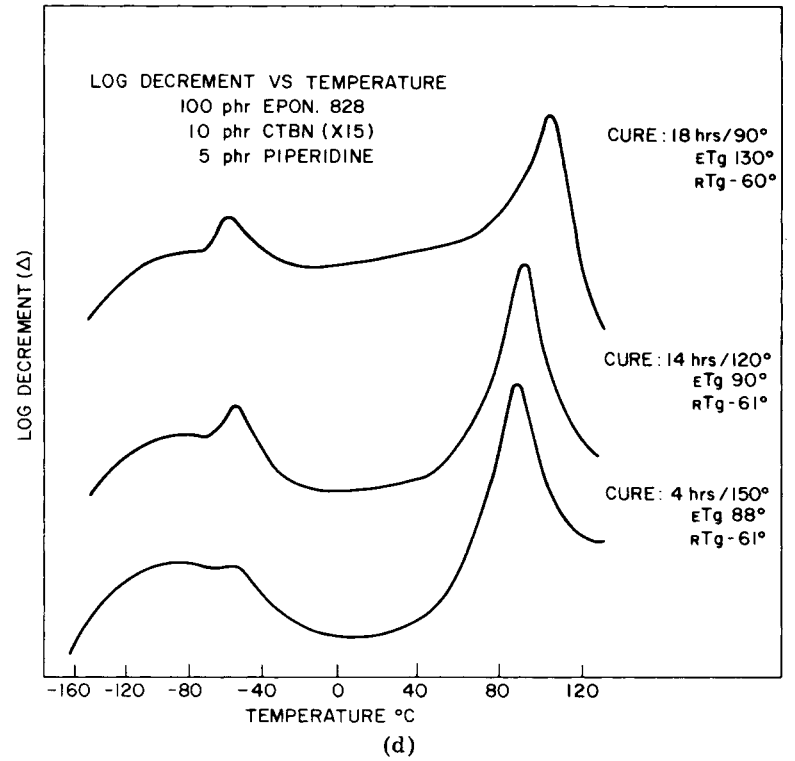




Fig. 1. TBA damping curves for unmodified and modified epoxy resins cured at 150°C (see Table II): (a) 828/90, 828/120, 828/135; (b) 13/90, 13/120, 13/150; (c) 8/90, 8/120, 8/150; (d) 15/90, 15/120, 15/150.

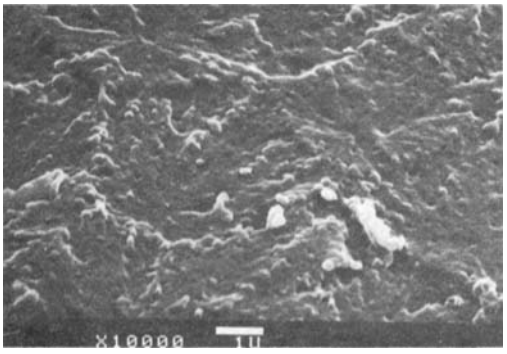



(c)

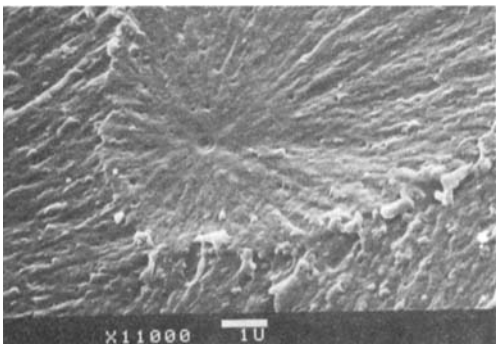



(d)

Fig. 1. (*Continued from previous page.*)




(a)

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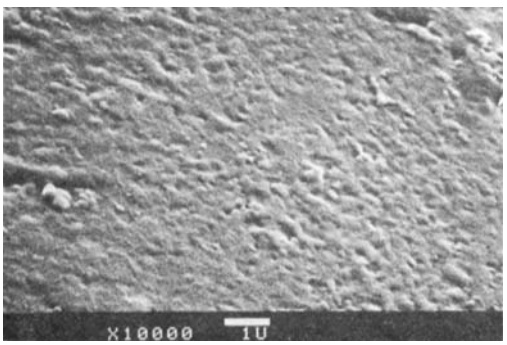
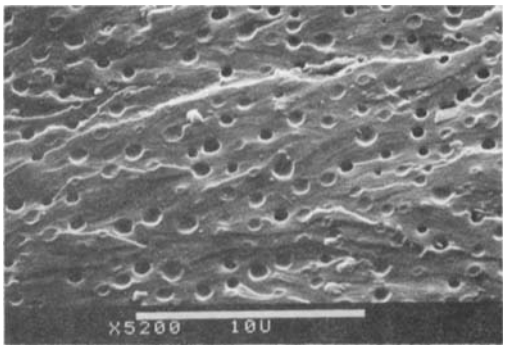



(c)

Fig. 2. SEM micrographs of rubber-modified epoxy cured at 90, 120, and 150°C (see Table II): (a) 13/90; (b) 13/120; (c) 13/150; (d) 8/90; (e) 8/120; (f) 8/150; (g) 15/90; (h) 15/120; (i) 15/150.

system because of volatilization of piperidine. At high cure temperatures the concentration of piperidine could be diminished and again lead to different network structures from those formed at low temperatures.

Rubber that did not phase separate remained dissolved and could plasticize the epoxy glass transition temperature. Because of the complications alluded to, the differences in ${}_{E}T_{g}$ [Figs. 1(b)–1(d)] cannot be attributed to plasticization, but this plasticization phenomenon has been noted in other rubber-modified epoxy formulations.[5,13] Investigation of the anticipated coupling of the tem-

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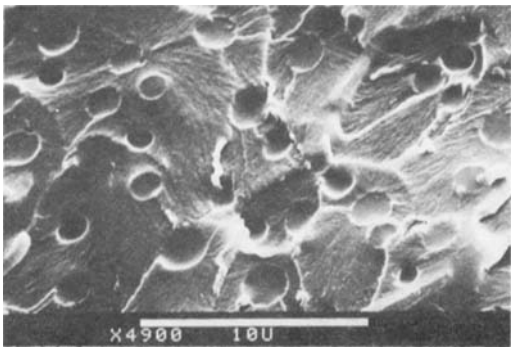


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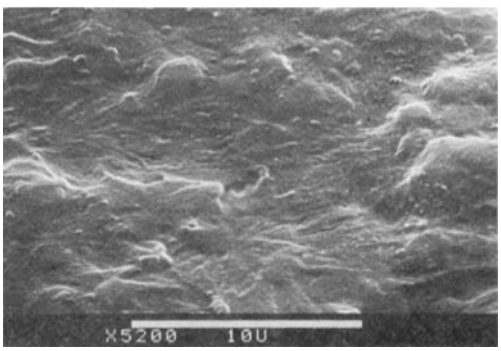
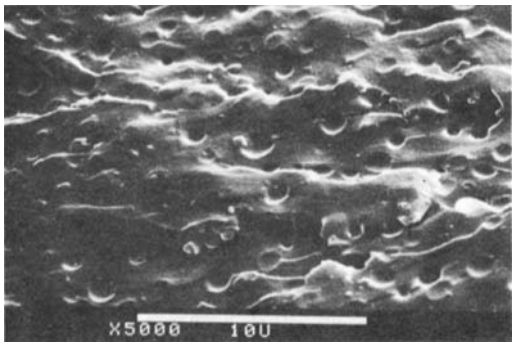



(f)

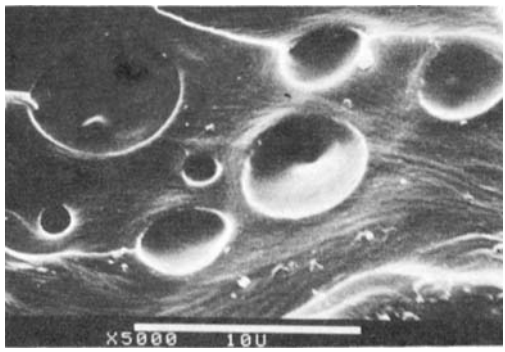
Fig. 2. (*Continued from previous page.*)

perature and intensity of the rubber glass transition with the temperature and intensity of the epoxy glass transition should provide indirect morphological evidence on the extent of phase separation.

However, the rubber damping peak always occurs at or below the $T_g$ of unreacted CTBN even though CTBN is capped with DGEBA (see ref. 5 which also shows that the depression of ${}_RT_g$ *decreases* with increasing amounts of rubber modifier in the formulations). DGEBA and CTBN must be incorporated into the domains since the domain size is much larger than the molecular length of the rubber. For a homogeneous blend, ${}_RT_g$ should be shifted higher than the




(g)

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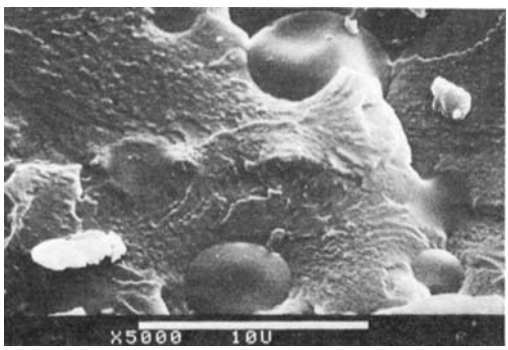



(i)

Fig. 2. (*Continued from previous page.*)

$T_g$ of CTBN, for example according to the Gordon–Taylor copolymer equation.[14] There are several reasons why this shift is not observed. A high magnification transmission electron micrograph of a typical rubber domain (from a dicyandiamide-cured epoxy[10]) is shown in Figure 3. The micrograph of this specimen (stained with $OsO_4$) clearly shows discrete areas of unstained epoxy inside the rubber domain. Phase segregation within the domain may explain why ${}_R T_g$ is not shifted to higher temperature because of blending of rubber and epoxy. (It is noted in Fig. 3 that the rubber appears to be concentrated in the outer annulus of the larger domains.)

TABLE III
Morphology: Summary

| Resin | $D$[a] | $\Phi_2$[b] | $N$[c] |
|---|---|---|---|
| 13/90 | 0.10 | 0.01 | 90 |
| 13/120 | 0.10 | 0.01 | 90 |
| 13/150 | — | 0.00 | 0 |
| 8/90 | 0.7 | 0.14 | 35 |
| 8/120 | 1.4 | 0.12 | 11 |
| 8/150 | 1.3 | 0.05 | 5 |
| 15/90 | 0.8 | 0.10 | 25 |
| 15/120 | 4.1 | 0.17 | 1.4 |
| 15/150 | 3.2 | 0.07 | 0.8 |

[a] Average domain diameter in $\mu$.
[b] Volume fraction of phase-separated rubber.
[c] Number of domains/100 $\mu^2$.

A second consideration is the effect of thermal shrinkage stresses. Triaxial thermal shrinkage stress[15] develops in the dispersed domain phase on cooling through the epoxy glass transition temperature since the coefficient of thermal expansion of the rubbery state is larger than that of the glassy state. The domains are thereby constrained by the glassy epoxy matrix. The glass transition of the rubber in the domain phase is depressed, and therefore ${}_R T_g$ can be below the $T_g$ of pure CTBN.

A third consideration arises from the apparent shift of the ${}_R T_g$ loss peak[5] because of the addition of the intensity of the rubber damping peak to that of the low temperature secondary relaxation of the epoxy (${}_E T_{\text{sec}} < {}_R T_g$).

The extent of phase separation depended on a number of factors. Formulation 13/150 contained the most compatible rubber [CTBN (X13)] and formed a clear

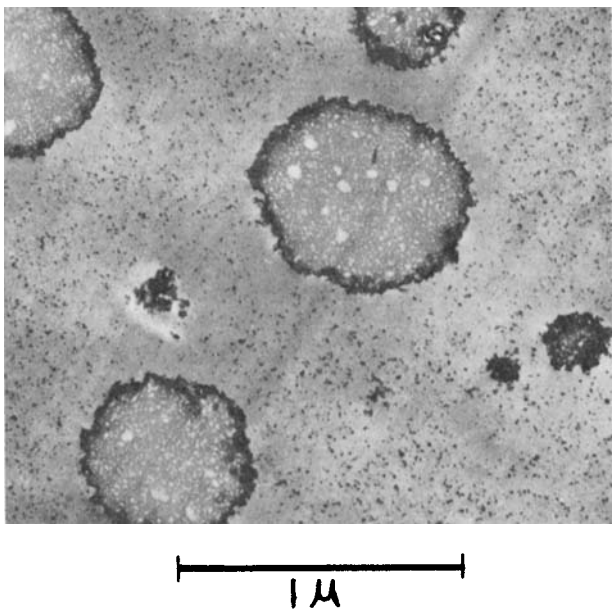



Fig. 3. TEM micrograph of rubber-modified epoxy resin (see text).

single-phase material when cured at 150°C; visibly, all the rubber remained in solution. Cured 13/120 and 13/90 were both two-phase systems with low levels of phase-separated rubber and very small domains. The three cured resins which contain CTBN(X8) showed a maximum in the average domain size at the intermediate cure temperature and a slight maximum in volume fraction of phase-separated rubber at the lowest cure temperature. The resins containing the least compatible of the three rubbers [CTBN(X15)] showed maxima in both domain size and volume fraction at the intermediate cure temperature. The presence of these maxima at intermediate conditions suggests the influence of competing effects. A proposed generalized representation of morphology as a function of cure temperature is presented in Figure 4. It shows the volume fraction of phase-separated rubber at a maximum at intermediate temperatures and an unchanging morphology after gelation.

A complementary study was undertaken to determine how domain formation was influenced by the viscosity of the curing medium. The CTBN(X15)-modified resin was used because it showed maxima in domain size and volume fraction at the intermediate temperature (120°C). Cure was conducted at both 90 and 150°C. Aliquots were removed intermittently and their viscosities at the cure temperature were determined using a Haake Rotovisco cone and plate viscometer equipped for high-temperature measurements. The resin cured at 90°C had a higher initial viscosity than the resin cured at 150°C. The time to gel should follow Arrhenius behavior causing the gel time at 150°C to be much shorter than the gel time at 90°C and a crossover in viscosity versus time (gelation being measured as an isoviscous event[7]). Presumably, because of the loss of piperidine owing to volatilization, the gel time at 150°C was only slightly shorter than that at 90°C. Visual observation of a cloud point in the curing resin indicated that phase separation in both resins occurred prior to this crossover point and before gelation [Figs. 5(a) and 5(b)]. The domains formed at 90°C had precipitated in a more viscous medium than those formed at 150°C.

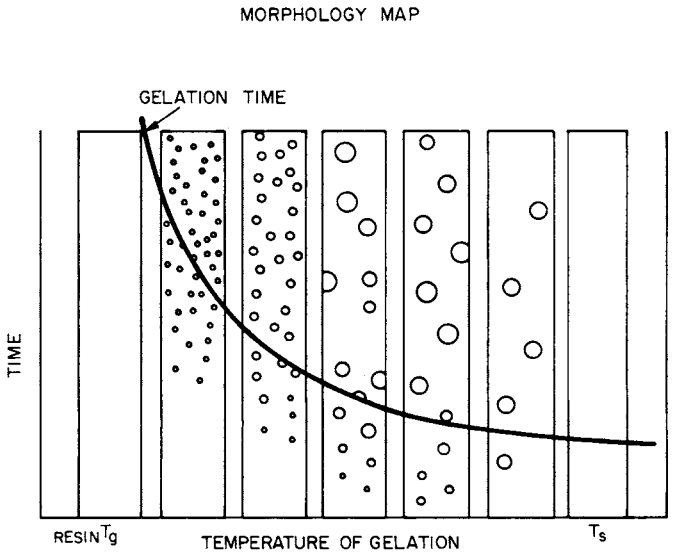



Fig. 4. Morphology map (schematic).

For the sake of discussion, the diffusivity of rubber (A) in epoxy solvent (B) is considered to be proportional to the temperature/viscosity ratio through the Stokes–Einstein relation[16]

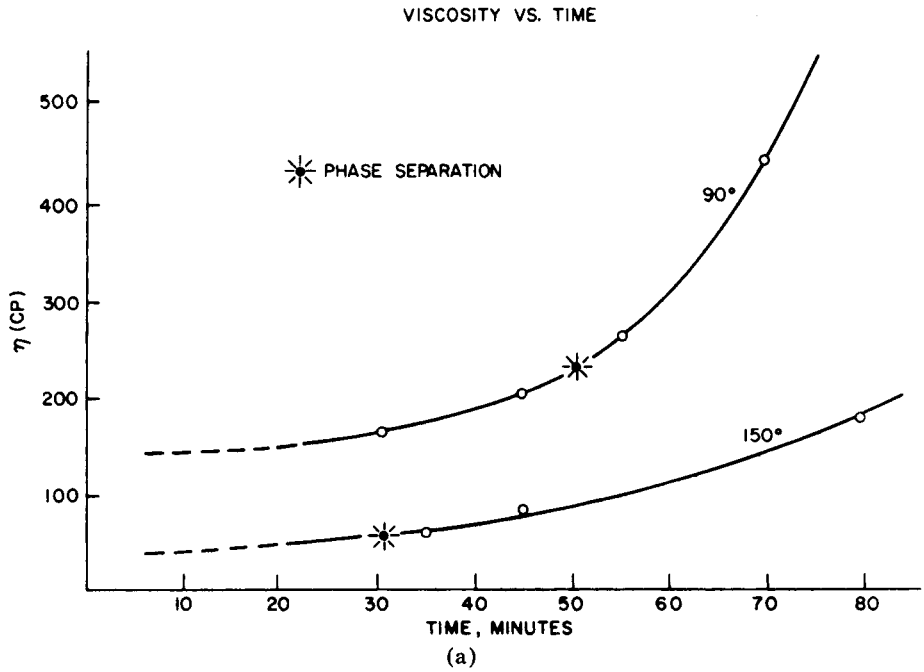
$$D_{AB} = kT/6\pi R_A \eta_B \tag{1}$$

where $k$ is the Boltzmann constant, $R_A$ is the radius of rubber adduct molecules which can be estimated from the molar volume of the rubber adduct, $T$ is the absolute temperature, and $\eta_B$ is the viscosity of epoxy. From the viscosity data [Fig. 5(a)] and eq. (1), a sevenfold increase in diffusivity occurs over the temperature range of cure investigated (90–150°C). Diffusivity is the controlling factor for phase separation if the time required for diffusion ($t_{diff}$) is longer than the time available for phase separation ($t_{ps}$). The characteristic time scale of diffusion in two dimensions is[16]:

$$t_{diff} = \frac{L^2}{2D_{AB}} \tag{2}$$

A length scale ($L$) can be assigned from the average two-dimensional distance between domain centers obtained from micrographs of the cured specimens ($L = 10\ \mu$). It is difficult to assign a representative diffusivity since the diffusivity, like the viscosity, is time dependent. A minimum diffusion time can be obtained by evaluating the diffusivity at the onset of phase separation. Both epoxy and rubber adduct are of low molecular weight at this time, so the Stokes–Einstein expression can probably be applied. A range in diffusion time of ~3 min at 90°C to ~1/2 min at 150°C was calculated from eq. (2).

The nominal time available for phase separation is also difficult to assign be-




(a)

Fig. 5. Steady shear viscosity of curing epoxy resin plotted against the elapsed time of cure: (a) data for times near phase separation; (b) data up to gelation.

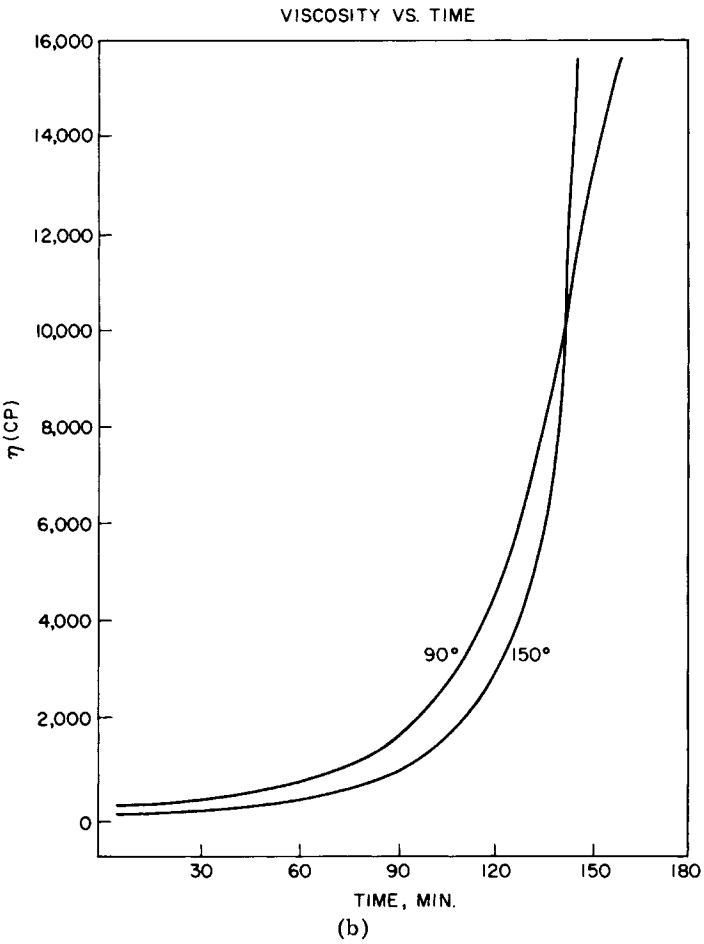



Fig. 5. (*Continued from previous page.*)

cause the rate of phase separation is not uniform. The time difference between the cloud point and the gel time may be used as the maximum phase separation time:

$$t_{ps} = t_{gel} - t_{cl} \tag{3}$$

This time is about 110 min at both 90 and 150°C. Comparison of the time for phase separation with the diffusion time indicates that the minimum diffusion time is considerably shorter than the time for phase separation. No constraint of morphology development would be expected under these conditions for these two temperatures. It is important to note, however, that the diffusivity will decrease continually during cure, whereas the driving function for phase separation increases with increasing molecular weight during cure. The effective diffusion time is therefore longer than the value based on the viscosity at phase separation, whereas the effective phase separation time is shorter than the time between the cloud point and gelation.

Experimental evidence to support this contention has been obtained. Earlier results[17] have shown that domain development in a series of similar resins cured

with different catalyst levels at 170°C was constrained by gelation when the gel time was 5 min or less. The diffusion time for that system at 170°C is therefore about 5 min. In the present case, kinetic effects on the morphology were found at 90°C. There is a tenfold decrease in diffusivity between the cures at 170 and 90°C. The effective time scale for diffusion at 90°C in that earlier system was therefore about 50 min. Assuming that the two systems are similar, the time scales for diffusion and phase separation are not too different for cure at 90°C, and it is therefore feasible to expect kinetic constraint under these conditions.

Comparison of the minimum time of diffusion obtained from the conditions at phase separation with the nominal phase separation time is important because in many commercial applications the resins are viscous materials with gel times of only a few minutes. These resins are highly susceptible to morphological constraint, and this constraint can often be predicted by comparing the diffusion with phase separation time scales.

The kinetic and thermodynamic factors involved in phase separation parallel those that control crystallization of linear polymers. The overall rate of crystallization passes through a maximum between two temperature limits. The glass transition temperature serves as the lower bound below which crystal growth cannot occur because of kinetic limitations of transporting polymer to the crystal surface. The melting point ($T_m$) provides the upper temperature limit. The presence of kinetic and thermodynamic competing effects results in a maximum in the overall rate of crystallization at some intermediate temperature.

In rubber-modified thermosetting materials, there is an upper isothermal temperature limit, the solubility temperature ($T_s$), above which rubber and epoxy are sufficiently compatible that phase separation does not occur prior to gelation. Short gel times inhibit morphological development and lower the $T_s$ temperature. $T_{s_0}$ is the upper temperature limit for phase separation of the unreacted resin and may be above or below the glass transition temperature of the initial reactant mixture ($_{\text{resin}}T_g$). If $T_{s_0} < T_g$, then $_{\text{resin}}T_g$ is the lower temperature limit in practice for phase separation from a homogeneous reactive solution since phase separation does not occur in a vitrified matrix (see Fig. 5). A proposal for general

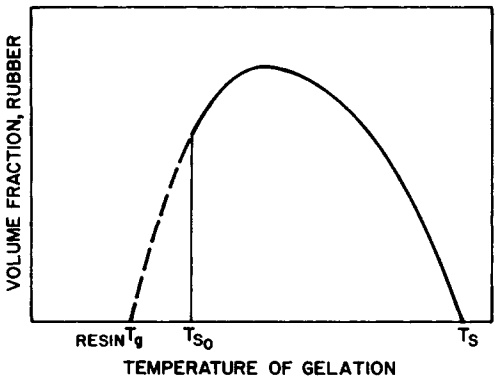



Fig. 6. Schematic plot of volume fraction of phase-separated rubber formed after long times above $T_{s_0}$ from homogeneous solution vs. the isothermal cure temperature. $T_s$ is the minimum temperature at which phase separation occurs prior to gelation. $T_{s_0}$ is the minimum temperature at which the initial reactants are mutually soluble. $_{\text{resin}}T_g$ is the glass transition temperature of the homogeneous reactants. $T_{s_0}$ can be above (as indicated) or below $_{\text{resin}}T_g$ (see text and Fig. 4).

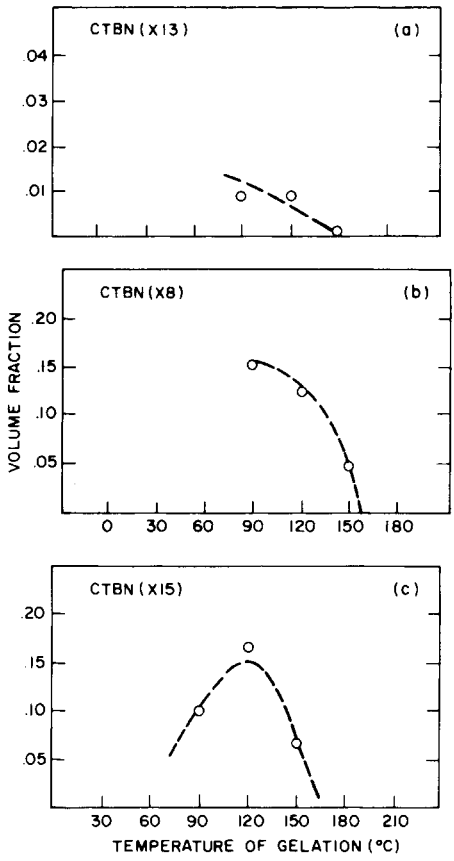



Fig. 7. Volume fraction of phase-separated rubber versus the temperature of gelation: (a) CTBN(X13); (b) CTBN(X8), (c) CTBN(X15).

behavior is illustrated in Figure 6, which shows the volume fraction of phase-separated rubber formed above $T_{s0}$ after long times from homogeneous solution versus the isothermal temperature.

Differences in the compatibility of the CTBN rubber modifiers with epoxy resin cause the cured formulations to fit onto different portions of the curves presented in Figure 6.

CTBN(X13), the most compatible rubber, results in $T_s$ being below 150°C, since resin 13/150 is a clear single-phase material after cure. The plot of volume fraction of phase-separated rubber versus the temperature of cure indicates that formulations with this rubber span only a small portion near $T_s$ of the entire curve [see Fig. 7(a)].

$T_s$ increases as the compatibility of rubber and epoxy decreases. $T_s$ is greater than 150°C for formulations with CTBN(X8) since cured 8/150 is a two-phase material. The data for CTBN(X8) systems still fall on the upper thermodynamically dominated side of the plot of volume fraction of rubber versus temperature of cure, but they are approaching the maximum as the small differences in volume fraction between cured 8/120 and 8/90 indicate [see Fig. 7(b)].

Formulations containing CTBN(X15), the least compatible resin, are shifted sufficiently from their $T_s$ that after cure the volume fraction of phase-separated

rubber straddles a maximum at 120°C [Fig. 7(c)]. CTBN(X15) and Epon 828 did not provide a homogeneous starting material much below 90°C (i.e., $T_{s_0} <$ 90°C).

The systems were not cured above 150°C because of loss of piperidine.

## CONCLUSIONS

The thermomechanical transitions and the extent of phase separation in rubber-modified epoxies have been studied as a function of the acrylonitrile content of the modifier and the temperature of cure. The intensity of the low-temperature damping peak associated with the glass transition of the material in the segregated rubbery phase, ${}_RT_g$, was found to correlate with the volume fraction of phase separated rubber. The ${}_RT_g$ transition is found at or below the value for the pure rubber. The effect of triaxial thermal shrinkage stresses on the domains makes it difficult to obtain any firm conclusions from the location of ${}_RT_g$.

The varying extents of phase separation were attributed to the competing effects of thermodynamic compatibility and transport of the rubber in a poly-

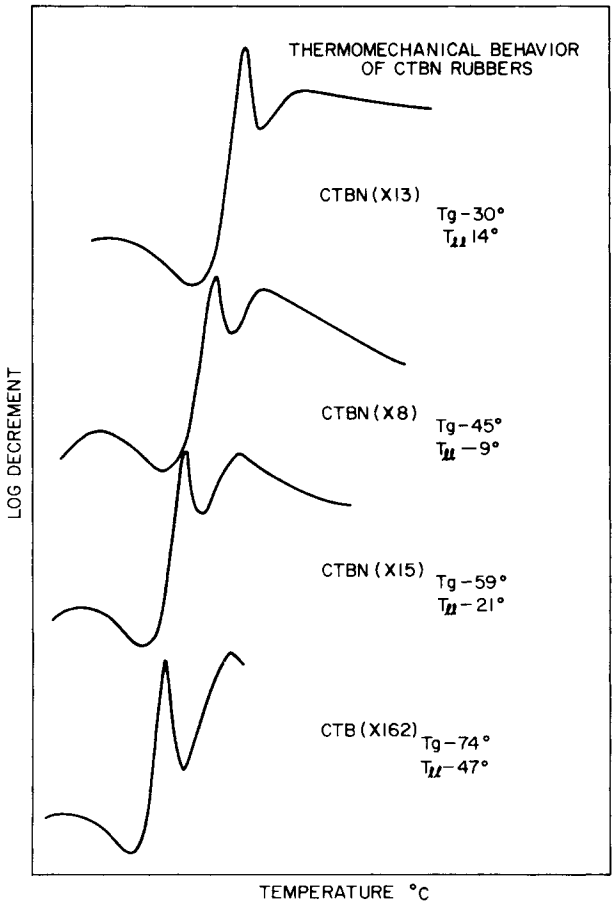



Fig. 8. Thermomechanical spectra (TBA) for CTBN rubbers.

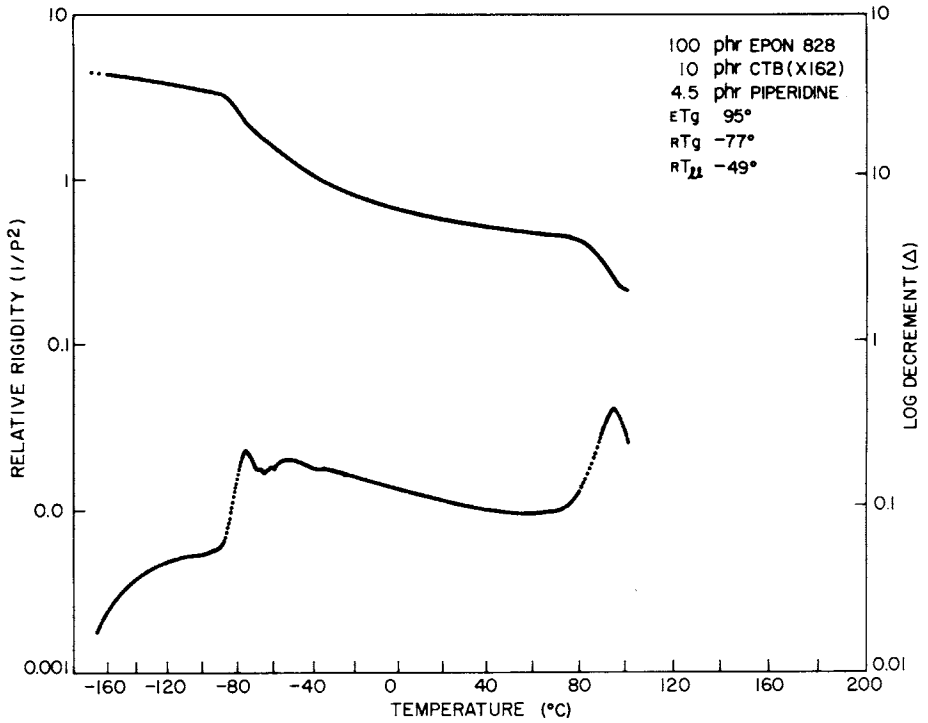



Fig. 9. Thermomechanical spectrum (TBA) for rubber-modified epoxy which displays the $T_{ll}$ relaxation of the rubbery phase.

merizing system in which morphological development is eventually quenched by gelation. This phenomenon is analogous to crystallization kinetics in linear polymers where a maximum in overall crystallization growth rate is obtained at an intermediate temperature between $T_g$ and $T_m$. Domain formation (nucleation) and growth in a thermosetting system are further complicated by polymerization and gelation. There is a finite time required for rubber to separate into the rubber-rich domains. This time is increasing continually during cure because of the increase in viscosity caused by the increase in molecular weight. Actual phase separation may lag the thermodynamic force for phase separation. Gelation halts phase separation and seals the morphology; the temperature of gelation therefore determines the morphology.

## ADDENDUM

In the course of this work, the thermomechanical properties of the components were obtained using TBA. Thermomechanical spectra for the unreacted CTBN and CTB rubbers are presented in Figure 8. A glass transition temperature and a distinct $T > T_g$ relaxation were identified in each spectrum. The ratio of $(T > T_g)/T_g$ $K$ was 1.17, indicating that this event is the $T_{ll}$ phenomenon identified by Boyer and co-workers.[18] The intensity of the $T_{ll}$ relaxation relative to its $T_g$ relaxation decreased with increasing acrylonitrile content of the copolymer.

In most cases curing of a rubber-modified epoxy resin eliminates the $T_{ll}$ relaxation of the rubber. One noted exception is when there is complete phase

separation of CTB(2000X162). (This rubber in the absence of epoxy has the most intense $T_{ll}$.) The thermomechanical spectrum of this two-phase system (Fig. 9) exhibits an epoxy $T_g$, a rubber $T_g$, and a damping maximum above and one (a shoulder) below the glass transition of the rubber. The ${}_RT_g$ and the $T > {}_RT_g$ peaks correspond to the $T_g$ and $T_{ll}$ relaxations for CTB(2000X162).

This approach suggests a technique for characterizing the fluid state of polymers above $T_g$. The material can be encapsulated as a dispersed second phase in a rigid matrix. Thermomechanical properties of the composite can then be obtained by conventional dynamic mechanical methods.

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