

Rubber-Modified Epoxies. I. Influence of Carboxyl-Terminated Butadiene-Acrylonitrile Random Copolymers (CTBN) on the Polymerization and Phase Separation Processes

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Synopsis

A bisphenol-A diglycidylether (DGEBA) based epoxy was cured with a cycloaliphatic diamine (4,4'-diamino-3,3'-dimethyldicyclohexylmethane, 3DCM), in the presence of an epoxy terminated butadiene-acrylonitrile random copolymer (ETBN). Results showed that vitrification is slightly delayed with the rubber addition. With ETBN the auto-catalytic mechanism by $[OH]_0$ is predominant at the beginning of the reaction, and on the contrary dilution is the dominant factor after $x = 0.15$. Phase separation takes place completely, well before gelation and vitrification; the conversion at the onset of phase separation decreases with the rubber amount but does not depend significantly on the temperature. The maximum T_g of the rubber-modified matrix does not depend on the cure temperature but decreases with the initial rubber concentration. This implies that a significant amount of rubber remains in solution in the continuous phase. This explains the delay in vitrification.

INTRODUCTION

The incorporation of low levels of carboxyl or epoxy-terminated butadiene-acrylonitrile random copolymers (CTBN or ETBN) to normally brittle epoxy resins is often used to improve the crack resistance and impact strength of the material. This enhancement in toughness results from the separation during cure of a randomly dispersed rubbery phase.¹⁻⁴

A general description of phase separation was first reported by Visconti and Marchessault.⁵ A CTBN was dissolved in a mixture of a cycloaliphatic epoxy resin with an anhydride hardener, in the presence of catalysts. During an initial polymerization period, the mixture remained homogeneous; at a certain reaction extent an elastomeric phase precipitated and small regions, a few micrometers in size were detected by transmission electron microscopy (TEM). The variation in size and shape of the spherical domains was studied as a function of CTBN content by small-angle light scattering. It was found that phase separation took place well before the gelation point and that beyond a CTBN concentration of 20% by weight there was a phase inversion.

Manziona et al.^{6,7} showed that a variety of different morphologies, and therefore mechanical properties, could be obtained from a single rubber-modified epoxy formulation by varying the cure temperature. This arises from the fact that the volume fraction, domain size, and concentration of particles of phase-separated rubber are determined by the competing effects of nucleation and growth rates, on the one hand, and the polymerization rate, on the other. Recently, Montarnal et al.⁸ discussed similar results for an epoxy-diamine system modified by ETBN. It was shown that the phase separation process was arrested well before gelation or vitrification. Increasing the cure temperature from 27°C to 100°C increased the average diameter of particles from 0.5 μm to 1.1 μm with a nearly constant volume fraction. Mechanical properties were strongly dependent on the separated phase morphology.

A model to predict the fraction, composition, and average radius of the dispersed phase segregated during a thermoset polymerization was reported.⁹ It was based on a thermodynamic description through a Flory-Huggins equation as well as constitutive equations for nucleation, coalescence, and growth rates. The possibility of phase inversion, the arrest of phase separation at the gel point, the presence of epoxy copolymer in the dispersed domains, the increase in the volume fraction and average radius of dispersed phase domains with the initial rubber amount, and the appearance of a maximum in the average radius as a function of cure temperature were predicted. An extension of the model, enabling the calculation of the particle size distribution, and a comparison of model predictions with experimental results, was recently reported.¹⁰

Several papers^{4,7,8,11-16} have been devoted to analyzing the mechanisms involved in the toughening process. It is very difficult, however, to state which is the best quantity of particles and particle size distribution for toughening purposes. As Siebert¹⁷ pointed out, resolving this question is a problem because changing one parameter in these systems, without affecting other parameters, is difficult.

In this context, a cooperation program between our laboratories was started in order to get a deeper understanding of the different factors affecting the phase separation process and the resulting morphologies and mechanical properties. A particular system consisting of a bisphenol-A diglycidylether (DGEBA) based epoxy cured with a cycloaliphatic diamine (4,4'-diamino-3-3'-dimethyl-dicyclohexylmethane, 3DCM), was selected. The importance of cycloaliphatic amines as curing agents for epoxy resins lies on the fact that they are much more reactive than their aromatic counterparts and still can provide a rigid, high T_g epoxy network.¹⁸ Moreover, the relatively long pot-life and low viscosity of epoxy-cycloaliphatic amine formulations makes them suitable for many applications.

The kinetics, gelation, and vitrification of this particular system were carefully studied and results reported elsewhere.¹⁹ After the characterization of the neat matrix (i.e., without CTBN or ETBN) a systematic analysis of rubber-modified networks was carried out. The results will be reported in a series of papers comprising: (i) influence of ETBN on the build-up of the epoxy-diamine network and phase separation process, (ii) analysis of generated morphologies in relation to cure parameters and selected formulations, (iii) analysis of experimental trends in terms of a phase separation model, (iv) mechanical properties in relation to generated morphologies.

The CTBN rubber is usually prereacted with an excess of the diepoxide. The resulting ETBN adduct participates in the polymerization with the diamine, leading to rubber-rich domains covalently bonded to the matrix. The aim of this part of the series is to assess the effect of the ETBN adduct on the formation of the epoxy-diamine network. Both cure temperature and ETBN concentration will be varied.

Few studies have been reported on the effects of adding ETBN adducts on parameters related to the network formation. Chan et al.²⁰ analyzed a particular system consisting of a DGEBA-based epoxy, cured with an aromatic diamine and containing a constant amount of a particular ETBN adduct (15 parts of rubber per hundred parts of DGEBA). The rubber showed no significant effect on the polymerization kinetics as revealed by the constancy in the times to gelation at a particular temperature. However, the vitrification times were delayed. Most of the phase separation took place well before gelation, although some changes were observed afterwards. The maximum glass transition temperature, ${}_E T_{g\infty}$ (i.e., the one of the epoxy-rich phase), appeared to be practically independent of cure temperature. Values were 4–6°C less than the ones for the neat epoxy-diamine network. This means that the extent of phase separation, as measured by the amount of rubber remaining in the continuous phase, was insensitive to cure temperature. No results concerning the influence of CTBN mass fraction were reported.

Montarnal et al.⁸ discussed results for a ETBN-modified DGEBA epoxy cured with -1,8-diamino *p*-menthane (MNDA) (15% of CTBN \times 8). In relation to the influence of ETBN on the cure, it was shown that both gelation and vitrification were delayed in the rubber-modified system. Phase separation occurred well before gelation and vitrification. Values of ${}_E T_{g\infty}$ for the rubber-modified samples were lower than for the neat system by 10–15°C, in a range of cure temperatures between 29°C and 100°C. This is consistent with results reported by Chan et al.,²⁰ in the sense that the extent of phase separation does not depend significantly on the cure temperature.

EXPERIMENTAL

Materials

Figure 1 shows the structural formulae of the epoxy prepolymers, the cycloaliphatic diamine and the CTBN rubber. The DGEBA-based epoxy was DER 332 (DOW), with an equivalent weight of epoxy groups equal to 174.3 g/eq, as determined by acid titration. Its main species is pure DGEBA ($M = 340$ g/mol, $n = 0$). The average ratio of secondary hydroxy to epoxy groups is equal to 0.015. The diamine was 4,4'-diamino-3,3'-dimethyldicyclohexylmethane (3DCM, Laromin C260, BASF). The amino content, determined by a potentiometric titration, agreed with the theoretical value within the experimental error.

The CTBN rubber used was Hycar 1300 \times 8 (GOODRICH). It has a 18% acrylonitrile content and a number average molecular weight close to 3600. ETBN adducts with the epoxy monomer DGEBA $\bar{n} = 0.03$ were prepared following a procedure described previously.²¹ It essentially consists of an almost complete reaction of carboxyl groups with epoxides, using a carboxyl-to-epoxy

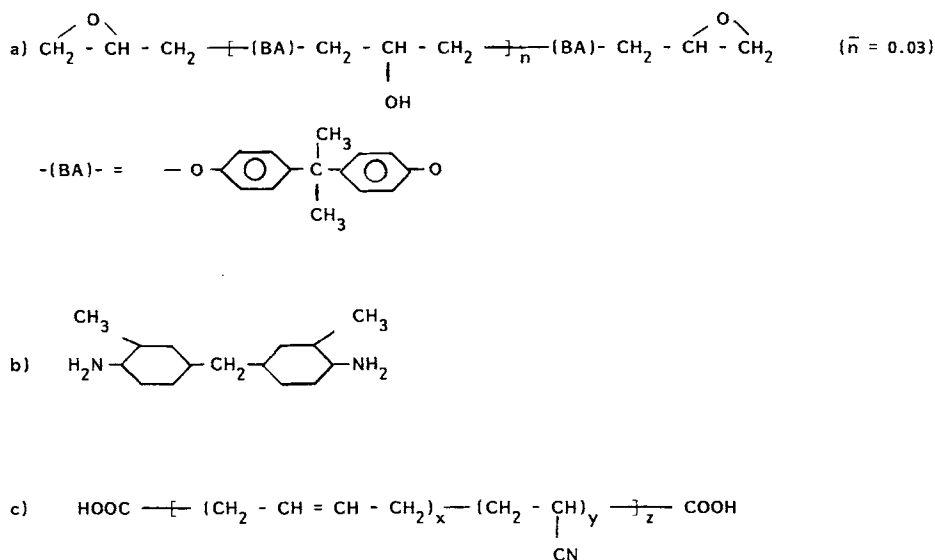
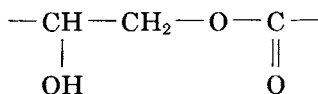


Fig. 1. Structural formulae of (a) epoxy prepolymer, (b) diamine and (c) CTBN rubber.

ratio equal to 0.065, at 85°C, in the presence of 0.18% by weight of triphenylphosphine. Due to the large excess of DGEBA $\bar{n} = 0.03$, chain extension is low,²¹ so the ETBN is at 90% a triblocks copolymer DGEBA/CTBN/DGEBA and DGEBA blocks are linking to CTBN by the segment



resulting from the reaction.

Cure Cycles

The formulations were prepared by incorporating the selected amount of adduct to the epoxy monomer, stirring under vacuum at moderate temperatures, cooling to room temperature and mixing with a stoichiometric proportion of diamine (with respect to the sum of epoxides coming from monomer and adduct). The resulting clear solutions were cured at constant temperatures up to a reaction extent well after gelation (i.e., 400 min at 50°C or 100 min at 75°C), and postcured 14 h at 190°C in order to get the maximum conversion of the epoxy-diamine matrix, without any degradation reactions.¹⁹ Phase separation was completed during the initial heating period.

In what follows, the butadiene-acrylonitrile rubber (R) concentration in the formulations will be expressed as a percentage mass fraction, indicated by % R estimated from the initial CTBN content before any reaction has occurred.

Techniques

The polymerization kinetics up to gelation was followed by size exclusion chromatography (SEC) of the partially reacted samples at a selected temper-

ature. A WATERS apparatus with a refractive index detector and tetrahydrofuran (THF) as elution solvent were used. As discussed elsewhere,¹⁹ the kinetics of the pregel stage may be determined by following the decrease with time in the height of DGEBA peak ($n = 0$) in SEC chromatograms. The overall conversion of epoxides is given by

$$x = 1 - (h/h_0)^{1/2}$$

where h/h_0 is the ratio of the peak height at any time with respect to the initial peak height. Gelation was noticed during sample preparation before injection.

Both a METTLER TA3000 and a DUPONT TA990 were used to measure the glass transition temperatures, T_g , of different samples at a $10^\circ\text{C}/\text{min}$ heating rate, under argon or nitrogen atmospheres. The onset value was always taken. The increase of T_g with reaction time, at a given temperature, was determined by using several DSC pans filled with reactants (10 mg or 20 per pan), placed in an oven at the selected temperature. The pans were removed from the oven at different times and scanned in the DSC. Vitrification was assigned to be the time at which the T_g becomes equal to the cure temperature.

The time at which phase separation began (i.e., the cloud-point for a particular sample and cure temperature), was recorded with a light transmission device previously described.²² The use of light in the visible region led to an observable alteration of the dispersed particles having diameters in the order of $0.1 \mu\text{m}$. Since the final particle-size distribution was between 0.1 and $1 \mu\text{m}$ (see next part of the series), the term cloud-point arbitrarily refers to the time at which phase separation was first observed using light in the visible region. Figure 2 shows how the cloud-point time, t_{cp} , and the phase separation interval, Δt_{cp} were determined from the light-transmission recorded at a particular cure temperature.

The viscosity during different isothermal cures was monitored with coaxial-cylinder viscometer with shear rates equal to 100 s^{-1} or 0.65 s^{-1} (both a Contraves-Rheomat 115— and a Haake-Rotovisco RV3—were used).

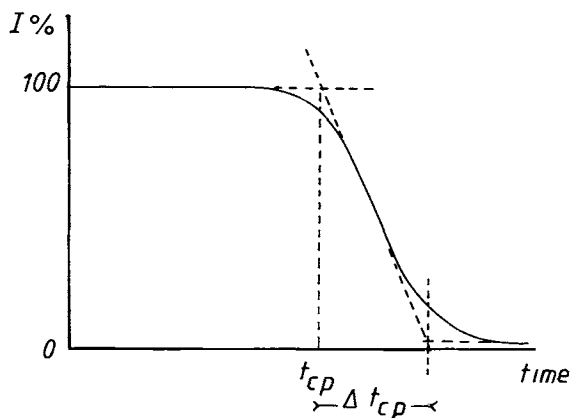


Fig. 2. Determination of t_{cp} and Δt_{cp} from cloud-point curves.

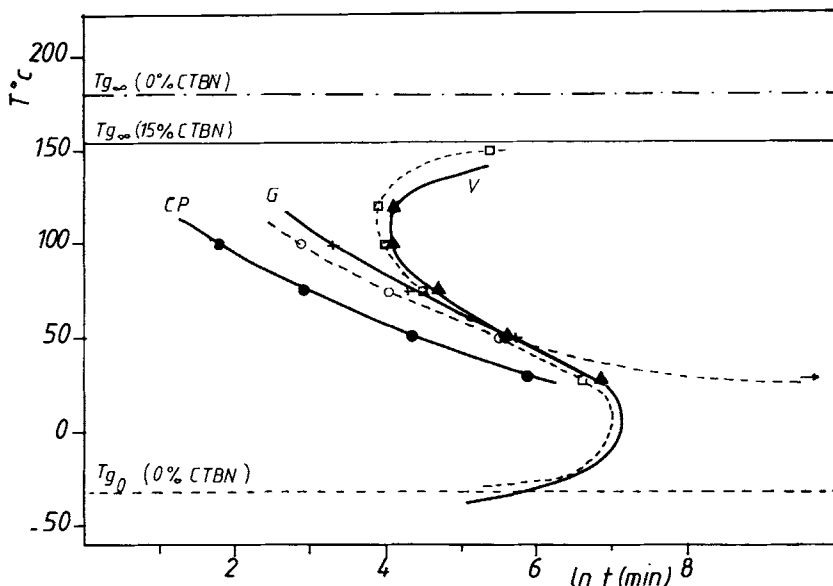


Fig. 3. Time-temperature-transformation diagram for the neat system (dashed lines) and a formulation with 15% rubber (solid lines) (C.P. = cloud-point, G = gelation, V = vitrification).

RESULTS AND DISCUSSION

Time-Temperature-Transformation (TTT) Diagram

The overall influence of the ETBN addition on this particular system is presented in the form of a TTT diagram²⁰ and an example is shown in Figure 3 for the neat and the 15% rubber-modified systems. The times for gelation, vitrification, and phase separation are determined as described in the experimental part. Similar TTT diagrams can be obtained with different amounts of rubber. Representative results at two different isothermal curing temperatures, T_i , and with three different amounts of rubber are given on Table I. The addition of rubber leads to a delay in vitrification. The addition of a 15% R also leads to a slight but significant delay in gelation, consistent with results reported for a similar system based on MNDA comonomer⁸ instead of 3DCM.

TABLE I
Examples of Partial Results Concerning the Phase Transition Times for Different Amounts of Rubber at Two Isothermal Curing Temperatures

% R	[OH] ₀ /e ₀	$t \pm 3\%$ (min) at $T = 50^\circ\text{C}$			$t \pm 3\%$ (min) at $T = 75^\circ\text{C}$		
		t_{cp}	t_{gel}	t_{vit}	t_{cp}	t_{gel}	t_{vit}
0	0.015	—	270	246	—	60	90
6.5	0.023	118.5	260	270	30	60	115
10.6	0.029	105	255	267	24	60	130
15.0	0.036	79	295	276	18.6	74	110

The temperature at which gelation and vitrification take place simultaneously, $_{\text{gel}}T_g$, is practically the same for the neat and rubber-modified thermosets (i.e., close to 55°C).

Phase separation is completed very rapidly at a time well before gelation or vitrification has occurred, in agreement with our previous results for the system based on MNDA,⁸ but in disagreement with what was reported by Chan et al.²⁰ (however, even in this case, more than 90% of the intensity decrease took place before gelation).

The maximum T_g of the 15% rubber-modified matrix, ${}_E T_{g\infty}$, is 25°C less than the value for the neat matrix. This implies that a significant amount of rubber remains in solution in the continuous phase. This explains the delay in vitrification. The influence of the amount of rubber on the decrease of ${}_E T_{g\infty}$ will be discussed later.

Conversion versus Time Curves

In order to analyze the influence of rubber on kinetics, conversion versus time curves for samples containing different rubber amounts and isothermally cured at 50°C and 75°C were determined by SEC. Figure 4 shows the results for samples containing two different amounts of rubber and a cure temperature of 50°C. Similar results have been obtained for different amount of rubber and at 50°C or at 75°C.

It can be seen that the curves for the neat and the rubber-modified systems are different from the beginning of the reaction to $x = 0.30$ – 0.35 and after,

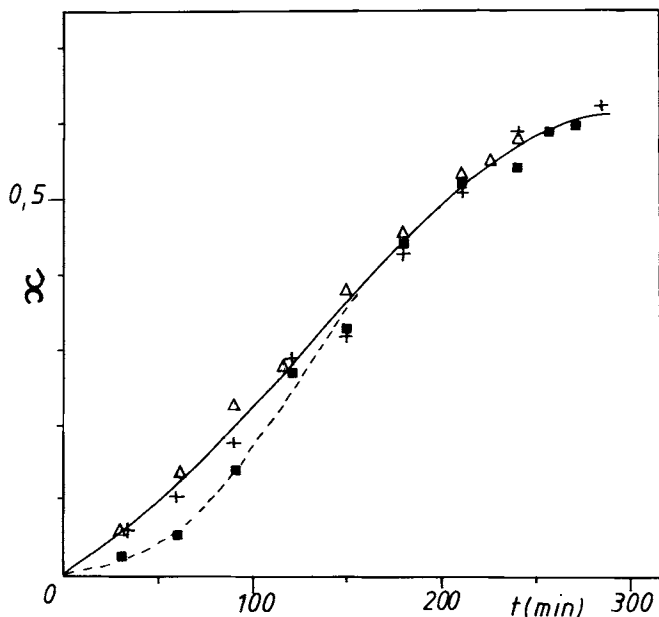


Fig. 4. Conversion vs time at 50°C, determined by SEC, for samples containing different % of rubber by weight: ((■) 0%, (△) 10, 6%, (+) 15%).

within the scatter of experimental results, no influence of rubber was evident. The curves become closer after the phase separation.

From our previous results for the neat system,¹⁹ taking into account a dilution effect and the fact that the initial hydroxyl concentration $[\text{OH}]_0$ depends on the amount of rubber (linkage $-\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{C}-$), and also



assuming no influence of phase separation, the influence of the percentage of rubber on the kinetics of the reaction could be estimated. Theoretical curves plotted in Figure 5 show that for the rubber modified system compared to the neat system, the autocatalytic mechanism by $[\text{OH}]_0$ is predominant at the beginning of the reaction; on the contrary, dilution is the dominant factor after $x \cong 0.15$ (but does the dilution effect have a physical sense after phase separation?).

We have a rather good correlation between experimental results (Fig. 4) and predictions (Fig. 5). The higher reactivity for the experimental results for the rubber-modified systems at the first stages of the reaction, compared to the expected values, can be explained by a higher amount of catalyst present than the initial $[\text{OH}]_0$ we have calculated. The catalyst could have been provided, for example, from impurities initially present in the CTBN (sodium chloride. . .) or introduced during the adduct synthesis (triphenyl phosphine). Therefore, due to this catalyst effect, the cross-over of the rubber-modified curves with the neat curve occurs later.

Exactly the same trends were obtained for the other cure temperature. The observed delay in gelation for samples with 15% rubber can be explained by an increase in gel conversion rather than a retardation of the kinetics.

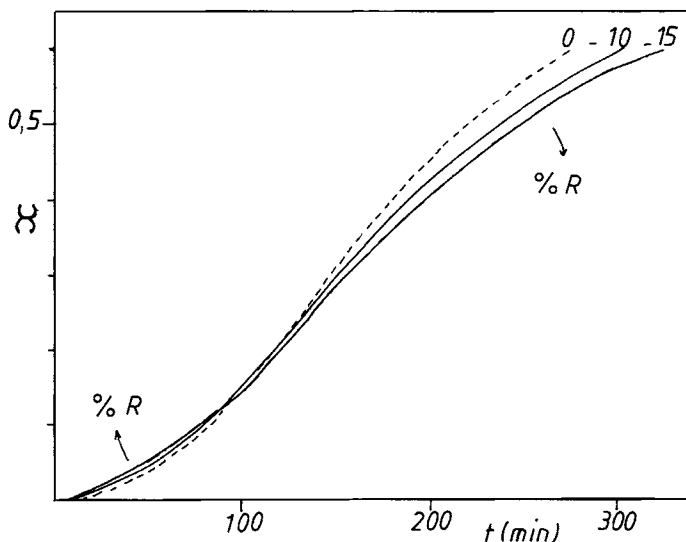


Fig. 5. Conversion vs time at 50°C calculated from the results for the neat system (----) and taking into account dilution effects and the initial hydroxyl amount $[\text{OH}]_0$, for samples containing different % of rubber.

The cloud-point and gelation times have been determined previously (Table I).

When this information is used together with the kinetic curves, the conversion at the cloud point, x_{cp} , and at gelation, x_{gel} , may be obtained as a function of rubber concentration as shown in Table II.

The value $x_{gel} = 0.60$ has been explained in the previous publication on the neat system¹⁹ by the fact that the ratio, r , of the secondary to the primary amino-hydrogen is equal to 0.4. The conversion, x_{gel} , is nearly the same for the 6.5% and 10.6% rubber-modified systems, but is slightly but significantly higher for the 15% rubber system. The quite high value of $x_{gel} = 0.63$ cannot be explained by a change in the r value. But, after phase separation ($x_{cp} = 0.17$), it may be inferred that there is a differential segregation of the monomers and low molecular weight species from the matrix of the dispersed phase. This would lead to a nonstoichiometric matrix and would have an effect on the delay in gelation observed for the systems with higher amounts of rubber.

Therefore, more than 10% of rubber are necessary to significantly disturb the build-up of the network. Similar conclusions have been found for a quite different system based on dicyandiamide (DDA) after an analysis of the soluble fractions extracted from the final network.²¹

Cloud-points versus Rubber Concentration

Cloud-point times as a function of rubber concentration are shown on Figure 6. Using the kinetic curves, the times can be transformed to the conversion at the cloud point, x_{cp} . In order to verify the matching of time scales, and also to be faster, several samples were extracted from the light transmission apparatus at the cloud point and rapidly frozen. The reaction extent was then determined by SEC following the usual procedure.

The results from both methods are shown in Figure 7 and confirm the validity of the experimental procedure. Although there is a significant scattering of experimental results, it may be stated that the conversion at the cloud point does not depend significantly on temperature (in the range 50–75°C) but does depend markedly on rubber concentration. These findings were in fact qualitatively predicted by a thermodynamic description of the system using the Flory-Huggins equation, and assuming that the components are monodisperse and also that no reaction takes place between the ETBN and the epoxy-diamine copolymer (ref. 9 Figs. 2 and 4). It is evident that the ETBN rubber can react with the amine group and work is in progress to experimentally model this effect on the thermodynamic diagrams.

TABLE II
Conversion at the Cloud Point (x_{cp}) and at Gelation (x_{gel}) for Different Amounts of Rubber at Isothermal Curing Temperature $T_i = 50^\circ\text{C}$

% R	x_{cp} (± 0.01)	x_{gel} (± 0.01)
0	—	0.60
6.5	0.28	0.59
10.6	0.26	0.59
15.0	0.17	0.63

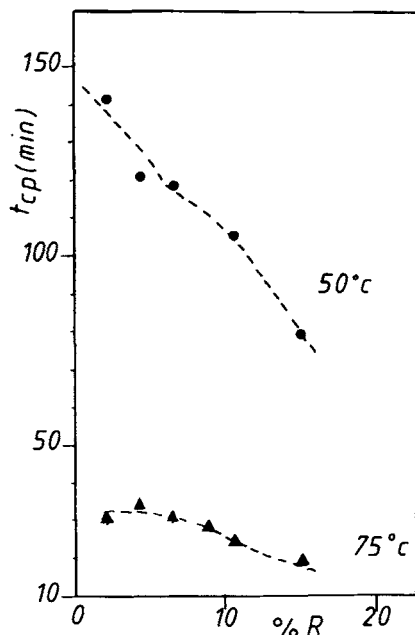


Fig. 6. Cloud-point times vs rubber concentration for two cure temperatures (50°C and 75°C).

We only have one result for the similar system based on MNDA,⁸ but it seems that the extent of reaction at the cloud point for the 15% R system is higher than for the one based on 3DCM (i.e., $x_{cp} = 0.23$ instead of 0.17).

Influence of the Rubber Concentration on the Viscosity

The viscosity rise during polymerization will now be considered. Figures 8 and 9 represent the influence of temperature and rubber concentration on the

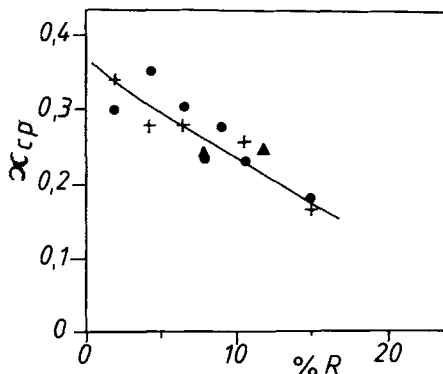


Fig. 7. Conversion at the cloud-point as a function of the rubber concentration. Results determined from the matching of cloud-point times and conversion versus time determinations: (+) 50°C, (●) 75°C; results determined from the direct determination of conversion at the cloud-point: (○) 50°C, (▲) 75°C.

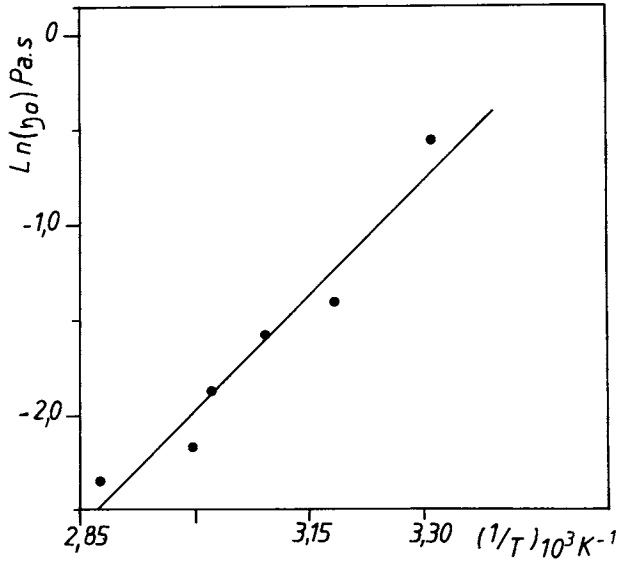


Fig. 8. Arrhenius representation of the initial viscosity of the neat epoxy-diamine system.

initial viscosity. As shown by Fig. 8, the initial viscosity of a stoichiometric epoxy-diamine formulation devoid of rubber may be represented by:

$$\text{Ln } \eta_0(\text{Pa.s}) = -14.09 + 4037/T(K) \tag{1}$$

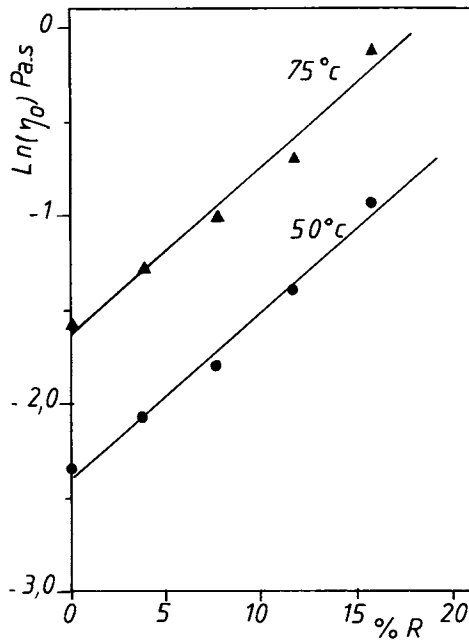


Fig. 9. Influence of the rubber concentration on the initial viscosity of the system for two different temperatures: (●) 50°C, (▲) 75°C.

Equation (1) gives an apparent activation energy equal to $E_\eta = 33.6$ kJ/mol.

Figure 9 shows a linear dependence of $\text{Ln } \eta_0$ on the amount of rubber added to the formulation. The following eq. (2) correlates all the experimental results for the initial viscosity:

$$\text{Ln } \eta_0 (\text{Pa.s}) = -14.09 + \frac{4037}{T(\text{K})} + 0.09[\% \text{ R}] \quad (2)$$

The viscosity rise during polymerization at 50°C is shown in Figure 10 for formulations containing different amounts of rubber. In this figure, with this scale, it is clearly seen that while all formulations containing rubber may be roughly represented by a single curve (even we have some differences between 6.5%–10.6% and 15%), the system devoid of rubber deviates from the master curve. After $t = 180$ min the viscosity, η , is higher for the neat system. This is consistent with the results obtained previously with the similar system based on MNDA.⁸

It is interesting to now compare the results in Fig. 10 with those presented in Fig. 4 (x vs. time) especially since the kinetics of the reactions are quite similar and independent of the amount of rubber present (after 150–200 min of reaction to the gel point). When we compare Figs. 4 and 10, it is clear that for the same extent of reaction, x , the viscosity is higher for the neat system than for the rubber-modified systems. Thus, we can conclude that the large differences observed in viscosity behaviour are not due to kinetic behaviour. However, the viscosity tends to infinity at the same time that we observe insoluble fractions for the neat system but not for the rubber-modified systems. The significance of the viscosity measurements after gelation for the rubber-modified systems is not clear.

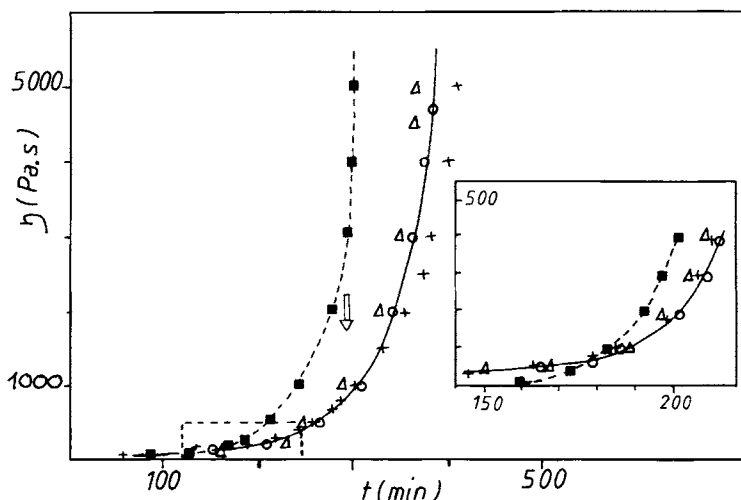


Fig. 10. Viscosity rise as a function of time at 50°C for formulations containing different amounts of rubber: (■) 0%, (○) 6.5%, (△) 10.6%, (+) 15%, shear rate 0.65 s^{-1} (arrows indicate the gelation field observed from the determination of insoluble fraction—Table I).

Any constitutive equation expressing the viscosity changes during a thermoset polymerization must take into account the fact that the viscosity goes to infinity at the gel point. As the weight-average molecular weight, \overline{M}_w , shows the same behaviour, it is common to propose a power dependence of viscosity, η , on \overline{M}_w ²³:

$$\eta/\eta_0 = (\overline{M}_w/\overline{M}_{w_0})^m \quad (3)$$

where η_0 and \overline{M}_{w_0} are the initial viscosity and weight-average molecular weight.

Since \overline{M}_w is related to the conversion, x , through the statistics of network formation, there is a relationship between η and x .²⁴ The parameter m can be determined experimentally.

For a large number of linear polymers, m varies from 1 for low molecular weight species, to about 3.4 for polymers with long entangled chains. Experimental studies on rheological changes during network polymerizations have found m values lying in the range 1 to 2.6.²³

However, the behaviour of a two phase system is more complex: m values greater than 3.4 have been observed when phase separation takes place during the viscosity rise in polyurethane (PU) polymerization.²⁵

Our results for η versus time are reported in Figure 11 on an expanded scale but only during the first steps of the polymerization (i.e., before the gel point). On this scale, the viscosities of the rubber-modified systems are higher than the viscosity of the neat system (these differences observed with this scale, can explain the discrepancies noticed previously between the results of Montarnal et al.⁸ and Wang and Zupko²⁶). The onset of phase separation obtained from Table I is indicated by arrows. The cross-over point of the curves for the systems with 15%, 10.6%, and 6.5% of rubber, is consistent with the phase separation phenomena and confirms its influence on the viscosity behaviour.

After the phase separation, the viscosity of the overall system, for a given $x > x_{cp}$, depends on the viscosities (\overline{M}_w) and the volume fractions of the matrix and the disperse phase. Contrary to the PU systems, the viscosity rise in rubber-modified epoxies is lower compared to the homogeneous system without rubber.

Since we do not know the values of the different parameters and their dependence on x , we are not able to improve our model for the rubber modified systems. We can only conclude from Fig. 10 that the behaviour depends slightly on the initial amount of rubber.

As the time t_{cp} and the conversion x_{cp} at the cloud point decrease (Tables I and II), an increase in the rubber amount leads to phase separation in a less viscous medium. Figure 12 shows the decrease in viscosity at the cloud point produced by an increase in the initial amount of rubber for two different isothermal curing temperatures. This has a bearing on the resulting morphologies as will be discussed in the next part of this series.

$T_{g_{\infty}}$ of the Matrix versus Rubber Concentration

The maximum glass transition temperature, ${}_E T_{g_{\infty}}$, of the matrix after a complete cure cycle will now be analyzed. Figure 13 shows that there

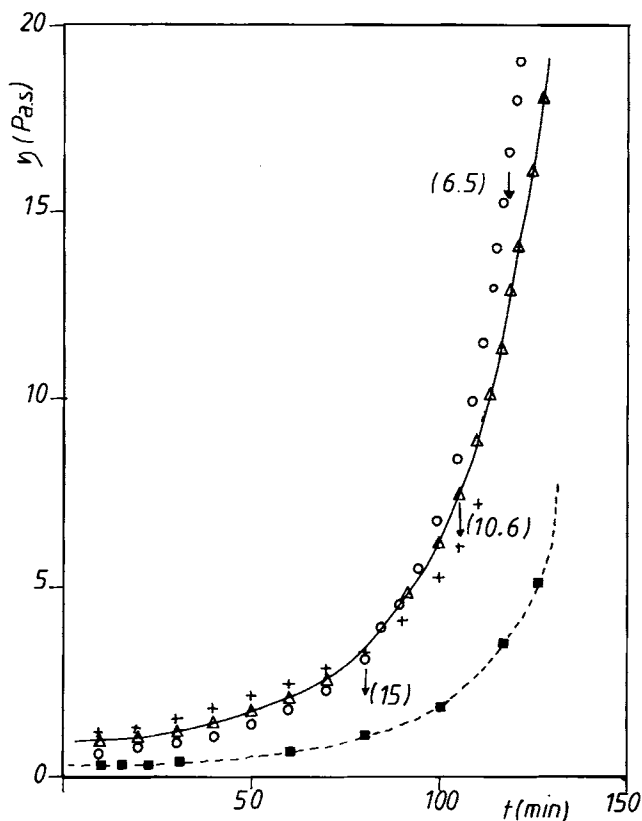


Fig. 11. Initial viscosity rise as a function of time at 50°C for formulations containing different amounts of rubber, shear rate 100 s^{-1} (arrows indicate the viscosity value at the cloud point (η_{CP}): (■) 0%, (○) 6.5%, (△) 10.6%, (+) 15%.

is practically no effect of the selected isothermal cure temperature, T_i , on ${}_E T'_{g\infty}$, for formulations containing the same initial amount of rubber. This agrees with results reported for other systems, as discussed in the introduction.^{8,20}

Figure 14 shows the variation of ${}_E T'_{g\infty}$, with the initial rubber amount in the formulation and two different cure cycles. Again, no effect of the cure temperature on ${}_E T'_{g\infty}$, is evident for a given rubber concentration. However, the rubber amount has a significant influence on the maximum glass transition temperature (i.e., increasing the initial rubber fraction, decreases the ${}_E T'_{g\infty}$, value). This must be attributed to the increase in the amount of rubber dissolved in the matrix on the end of the polymerization. The experimental points may be roughly represented by two straight lines. Then intersection represents the critical concentration, where phase inversion takes place: $(\% R)_{crit} = 24\%$.

An estimation of the theoretical value of $(\% R)_{crit}$ may be obtained by applying the Flory-Huggins equation to the mixture of R (assumed to be a monodisperse compound with a molecular weight equal to the number average molecular weight of the initial CTBN and the epoxy-amine solvent (assumed to be a pure compound with a number average molecular weight

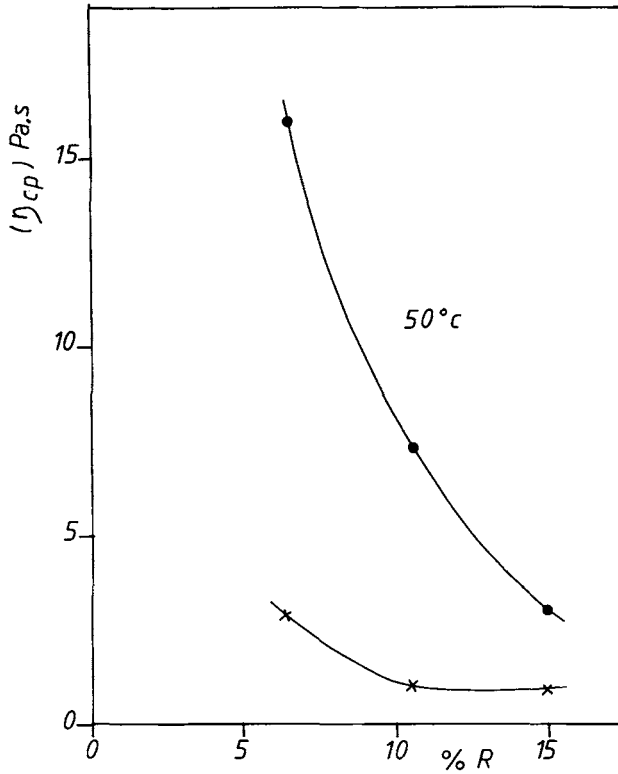


Fig. 12. Viscosity at the cloud point as a function of the rubber amount in the formulation, for two different cure temperatures.

equal to that of the neat system at the conversion of phase separation).¹⁰ Again we assumed no reaction between the rubber and the epoxy-amine copolymer.

The volume fraction of rubber at the critical point is given by²²:

$$\phi_R = 1/[1 + (V_{CTBN}/V_{E-A})^{1/2}] \quad (4)$$

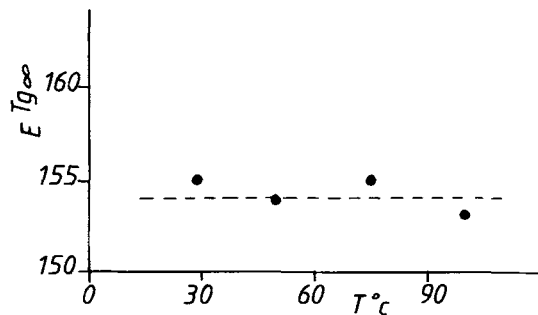


Fig. 13. Glass transition temperatures of the matrix, $E T_{g\infty}$, for formulations containing 15% rubber, precured at different temperatures, T_i and post-cured 14 h at 190°C.

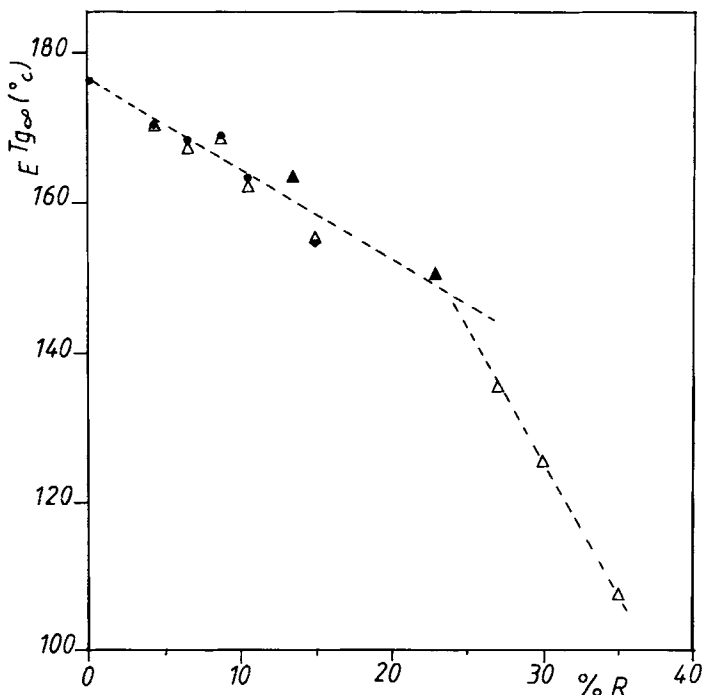


Fig. 14. Glass transition temperature of the matrix, ${}_{E}T_{g\infty}$, as a function of the initial amount of rubber, for formulations pre-cured at 50°C and 75°C, and post-cured 14 h at 190°C: (●) 50°C, (Δ) 75°C.

where V_{CTBN} and V_{E-A} represent the molar volumes of CTBN and the thermoset, respectively, at the conversion point of phase separation (both taken as pure compounds). Since the particular CTBN used in this study has a number average molecular weight, $\overline{M}_n = 3600$ g/mol, and a density, CTBN = 0.948 g/cm³, its molar volume is $V_{CTBN} = 3797.5$ cm³/mol. However, the initial molar volume of the stoichiometric thermoset may be defined by¹⁰:

$$V_{E-A} = (M_A + 2M_E)/3\rho_{E-A} \quad (5)$$

Since the diamine molecular weight is $M_A = 238$ g/mol, the epoxide molecular weight is $M_E = 348.6$ g/mol, and the density of the neat thermoset is $\rho_{E-A} = 1.127$ g/cm³, we get $V_{E-A} = 276.6$ cm³/mol.

On the other hand, for an $A_4 + E_2$ polymerization, the increase in molar volume with conversion is given by¹⁰:

$$V_{E-A} = V_{E-A}^0/(1 - 4x/3) \quad (6)$$

From Fig. 7, the conversion at the cloud point for the range close to the critical concentration, may be estimated as $x \cong 0.1$. Then, $V_{E-A} = 319$ cm³/mol, and the volume fraction of rubber of the critical point is:

$$\phi_R = 0.225$$

The corresponding mass fraction is

$$[\% \text{ R}]_{\text{crit}} = 0.196$$

Taking into account the assumptions of the thermodynamic model and the absence of reaction between the rubber and the epoxy-diamine copolymer, the agreement between predicted and experimental values can be considered reasonable.

Figure 14 shows that for concentrations smaller than the critical concentration, the decrease in ${}_E T_{g_{\infty}}$ may be represented by:

$${}_E T_{g_{\infty}} (K) = 449 - 1.21 [\% \text{ R}] \quad (7)$$

In order to estimate the amount of R dissolved in the matrix, the Fox equation²⁷ may be applied:

$$\frac{1}{{}_E T_{g_{\infty}}} = \frac{1 - W_R}{T_{g_E}} + \frac{W_R}{T_{g_R}} \quad (8)$$

where W_R is the mass fraction of rubber remaining as a solution in the matrix, $T_{g_E} = 449 \text{ K}$ is the glass transition temperature of the pure matrix (although other series of experimental runs gave values slightly higher (i.e., $T_{g_E} = 453 \text{ K}$), it was considered better to take the value from the same series of samples), and $T_{g_R} = 213 \text{ K}$ is the glass transition temperature of CTBN, determined using the same experimental procedure as for the rubber-modified epoxies (Manziona et al.⁶ report a value of T_{g_R} equal to 228 K for the same CTBN; the difference has to be attributed to the use of a different experimental technique—torsional braid analysis—and the definition of T_g as the midpoint of the transition rather than the onset value).

Replacing the experimental ${}_E T_{g_{\infty}}$ versus $\% \text{ R}$ relationship into Fox equation, we get:

$$W_R = \frac{1.092 [\% \text{ R}]}{449 - 1.21 [\% \text{ R}]} \quad (9)$$

Up to 20% R, the denominator may be taken as constant and W_R calculated approximately by:

$$\% W_R = [\% \text{ R}] / 4 \quad (10)$$

Thus, accepting the validity of the Fox equation, it may be stated that the matrix at the end of cure will maintain a rubber concentration equal to one fourth of the initial value.

CONCLUSION

The presence of epoxy-terminated butadiene-acrylonitrile rubber has the following effects on the formation of epoxy-diamine networks (at least for the selected system):

- The addition of rubber leads to a delay in vitrification. The addition of a 15% R leads also to a slight but significant delay in gelation.
- With rubber, compared to the neat system, the autocatalytic mechanism by $[\text{OH}]_0$ is predominant at the beginning of the reaction, but seems to have no effect after phase separation.
- With 15% rubber content, the gel conversion is higher than for the neat system. We observed an increase in gel conversion but no delay in kinetics. After phase separation ($x_{cp} = 0.17$), it may be assumed that there is a differential segregation of the monomers. This would lead to a non-stoichiometric matrix and would have an effect on the delay in gelation observed for the higher amounts of rubber.

Regarding the phase separation process, the following facts were shown:

- phase separation takes place completely well before gelation and vitrification
- the conversion at the onset of phase separation decreases with the increase in the rubber content, and does not depend significantly on temperature

*Influence of the rubber concentration on the viscosity:

- The initial viscosity increases with the rubber content.
- For the same extent of reaction, $x > x_{cp}$, the viscosity is higher for the neat system than for the rubber modified systems. The large differences observed in viscosity behaviour are not due to kinetics.
- After the phase separation, the viscosity of the overall system, for a given $x > x_{cp}$, depends on the viscosities (\overline{M}_w) and the volume fraction of the matrix and the dispersed phase.

*Influence of the rubber concentration on T_g :

- The maximum T_g of the rubber-modified matrix, ${}_E T_{g\infty}$, does not depend on cure temperature for a given rubber concentration. This means that the volume of the dispersed phase is determined by thermodynamic rather than kinetic considerations.⁹ This effect seems to be valid for several epoxy-amine systems.^{8,20}
- The value of ${}_E T_{g\infty}$ decreases in a roughly linear way with the initial amount of rubber added to the formulation (i.e., the more rubber that is initially introduced, the more remains in the matrix of the end of polymerization).
- The rubber concentration when phase inversion is observed, as determined from the abrupt decrease in T_g , is close to the theoretical prediction from a Flory-Huggins model with the assumption of monodisperse reactants.

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