Miscibility of epoxy monomers with carboxyl-terminated butadiene–acrylonitrile random copolymers

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Cloud-point curves for mixtures comprising epoxy monomers of the DGEBA type (diglycidyl ether of bisphenol A), rubbers of the CTBN type (carboxyl-terminated acrylonitrile–butadiene random copolymers) and, eventually, hardeners such as diamines are reported. It is shown that the miscibility of epoxy monomers with a particular rubber is very sensitive to the molar mass of the epoxy molecule.

The application of a simple Flory–Huggins lattice model, regarding both components as monodisperse, leads to the location of the critical point, coexistence curves and the estimation of the interaction parameter per unit volume (Λ). A correlation of the type $\Lambda = \Lambda_0 + \Lambda_T T$ was found, with a negative Λ_T. The decrease in miscibility observed when using a CTBN containing less acrylonitrile is explained from the change in the solubility parameter. Using CTBN as an adduct with the epoxy monomer leads to an increase in miscibility, which is explained by the copolymer effect. Systems based on epoxy–diamine copolymers prepared in the presence of CTBN adducts showed a complex behaviour including two maxima in cloud-point curves.

(Keywords: miscibility; phase separation; demixing; rubber-modified epoxy; toughening)

INTRODUCTION

Brittle thermosets may be improved by means of elastomeric components which are initially miscible with the thermosetting resin but are segregated in the course of polymerization, leading to a discrete, randomly dispersed rubbery phase. In particular, the use of carboxyl-terminated butadiene–acrylonitrile (CTBN) random copolymers is quite generalized for the toughening of epoxy networks[1]. Although it is evident that the phase-separation process in these systems is directly related to the miscibility of the CTBN with the epoxy system for a given temperature, composition and reaction extent, few experimental studies of cloud-point curves have been reported in the literature[2–4].

Wang and Zupko[2] made cloud-point measurements of mixtures of epoxy monomers based on the diglycidyl ether of bisphenol A (DGEBA) and CTBN with two different acrylonitrile contents. Upper critical solution temperature (*UCST*) behaviours were observed, with precipitation thresholds located at a CTBN volume fraction of about 0.07. This location was incorrectly assigned to the difference in molecular weights of both components and the corresponding variation of the combinatorial entropy of mixing. The position of the miscibility gap was shown to be very sensitive to the acrylonitrile (AN) content of CTBN. Decreasing the AN proportion from 17% to 10% led to an increase in the precipitation threshold temperature of about 73°C. This behaviour is explained by the increase in the difference between the solubility parameters of both components when decreasing the AN contents.

Montarnal *et al.*[3] discussed experimental aspects of the determination of cloud-point curves (CPC) and showed some results for DGEBA–CTBN systems. Of particular interest is the fact that an adduct of CTBN with DGEBA, i.e. a CTBN where the terminal carboxyl groups have been capped with epoxide groups of DGEBA, showed a shift of the miscibility gap to lower temperatures when compared with the pure CTBN–DGEBA system. Thus, the use of adducts increases the miscibility of both components.

Vàzquez *et al.*[4] reported cloud-point temperatures as a function of the CTBN amount in a DGEBA/DDS (diaminodiphenylsulphone) system, using an epoxy/amine ratio equal to 3.5 to avoid gelation. By describing the free energy of mixing by a Flory–Huggins equation, assuming that both oligomers were monodisperse, the interaction parameter could be obtained as a function of temperature.

The aim of this paper is to show the influence of several formulation parameters, i.e. molecular weight of the DGEBA monomer, type of CTBN and use of CTBN in the form of an adduct with DGEBA, on the miscibility gap of the system. Moreover, the meaning of cloud-point curves in relation to coexistence curves[5] will be discussed,

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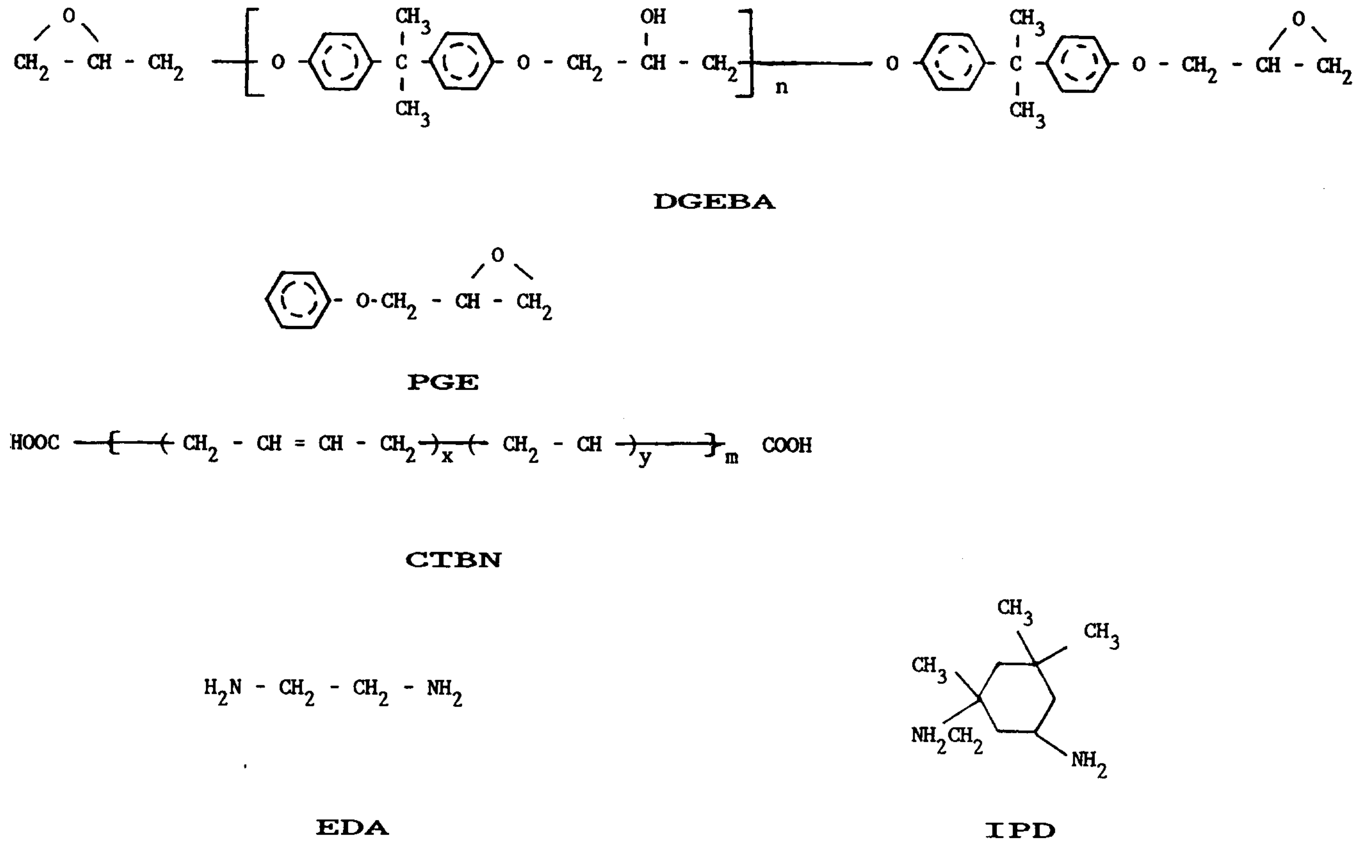

Figure 1 Basic reagents used in the different formulations: DGEBA, diglycidyl ether of bisphenol A; PGE, phenyl glycidyl ether; CTBN, carboxyl-terminated acrylonitrile–butadiene random copolymer; EDA, ethylene diamine; IPD, isophoronediamine

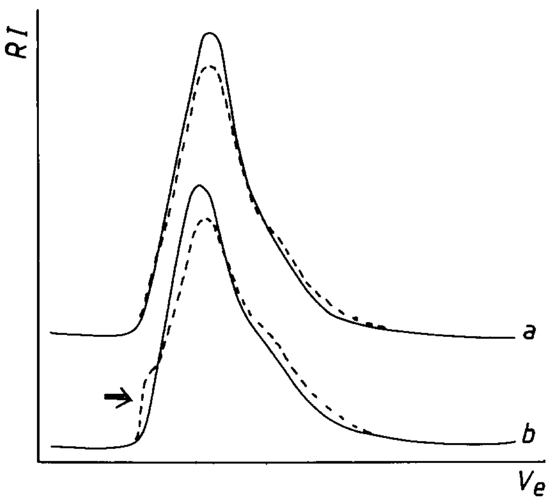

Figure 2 S.e.c. chromatograms (RI detector) for several CTBN copolymers: (a) full curve, CTBN ×8 and ×9 (same curve); broken curve, CTBN ×13; (b) full curve, CTBN ×15; broken curve, CTBN ×31 (the arrow shows a distinct fraction of high-molecular-weight molecules in CTBN ×31)

and a rough approximation for evaluating the interaction parameter in different cases will be presented. Finally, some preliminary results concerning the use of diamines as curing agents will be shown.

EXPERIMENTAL

Materials

The basic structure and properties of the reagents used in the different formulations are shown in *Figure 1* and *Tables 1* to *3*.

For DGEBA monomers (the term 'macromer' would be more appropriate because it accounts for the polydispersity; the term 'resin', very often used, is to be avoided because it is indistinctly applied to the monomer, to a whole formulation or to the final network), $\overline{M_n}$ and $\bar{n}$ are obtained assuming that the functionality is equal to 2. In fact, the structure of these monomers has been shown to be more complex[7].

For CTBN copolymers, only the most significant structure is shown in *Figure 1*, although other different structures are also present, i.e. vinyls arising from the reaction of butadiene by a 1,2-addition mechanism, pendant carboxyl groups, chain ends other than carboxyl groups, etc. *Figure 2* shows size exclusion chromatograms for several CTBN copolymers.

In what follows, DGEBA monomers and CTBN copolymers will be respectively identified by the mean value $\bar{n}$ and the number following 1300 in their commercial denomination.

Adducts

Adducts were prepared by reacting the carboxyl groups of the CTBN with an excess of DGEBA, in the presence of triphenylphosphine (TPP) as catalyst. The reaction was carried out at 85°C under a N_2 atmosphere and the conversion was measured either by chemical titration of carboxyl groups or by following the increase of the adduct peak appearing in s.e.c. (1% solutions to tetrahydrofuran, THF) when using a u.v. detector ($\lambda = 254\,\mathrm{nm}$)[8]. This last method is based on the fact that pure CTBN does not absorb radiation at 254 nm while the adduct does. So,

Table 1 Characteristics of epoxy monomers (DGEBA)

Producer	DER 332 Dow	Araldite GY 250 Ciba-Geigy	Bakelite 164 Bakelite	DER 337 Dow	Araldite GY 280 Ciba-Geigy
$\bar{M}_n$ (g mol^{-1})[a]	349	374	383	479	550
$\bar{n}$[b]	0.03	0.12	0.15	0.49	0.74
$\bar{M}_w/\bar{M}_n$[c]	1.03	-	1.06	1.35	1.64
δ (MPa$^{1/2}$)[d]	20.9	20.9	20.9	20.9	20.9
ρ (g cm^{-3})	1.17	1.17	1.17	1.17	1.17

[a] Determined by acid titration of epoxy groups and assuming the chemical structure shown in *Figure 1*
[b] Calculated from $\bar{M}_n$
[c] Determined by size exclusion chromatography
[d] Solubility parameter calculated by group contribution (Hildebrand model)

Table 2 Characteristics of CTBN copolymers

Hycar BF Goodrich	CTBN 1300 ×13	CTBN 1300 ×8	CTBN 1300 ×9	CTBN 1300 ×15	CTBN 1300 ×31
AN amount (%)[a]	26	18	18	10	10
eq. COOH/100 g[a]	0.057	0.052	0.067	0.050	0.050
COOH functionality[a]	1.8	1.8	2.3	1.9	1.9
$\bar{M}_n$ (g mol^{-1})[a]	3200	3600	3600	3600	3800
$\bar{M}_w/\bar{M}_n$[b]	2.13	1.94	1.99	1.92	2.09
ρ (25°C) (g cm^{-3})[a]	0.960	0.948	0.955	0.924	0.924
η (27°C) (Pa s)[a]	570	150	160	60	60
δ (MPa$^{1/2}$)[a]	18.7	17.9	17.9	17.3	17.3

[a] Data specified by BF Goodrich
[b] Determined by size exclusion chromatography

Table 3 Characteristics of diamines

Producer	Ethylenediamine (EDA) Carlo Erba	Isophoronediamine (IPD) Veba Chemie
$\bar{M}_n$ (g mol^{-1})	60	170
ρ(25°C) (g cm^{-3})	0.90	0.92
δ (MPa$^{1/2}$)	25.2[a]	19.6[b]

[a] Solubility parameter tabulated in ref. 6 as a Hildebrand parameter
[b] Calculated by group contribution (Hildebrand method)

Table 4 Values of the molar volumes of different adducts, V_A, and volume fraction of epoxy in the adduct, f_B

Adduct	V_A (cm^3 mol^{-1})	f_B
A-I ($\bar{n}$=0.03)	4414	0.121
A-I ($\bar{n}$=0.15)	4608	0.131
A-II ($\bar{n}$=0.12)	4674	0.123

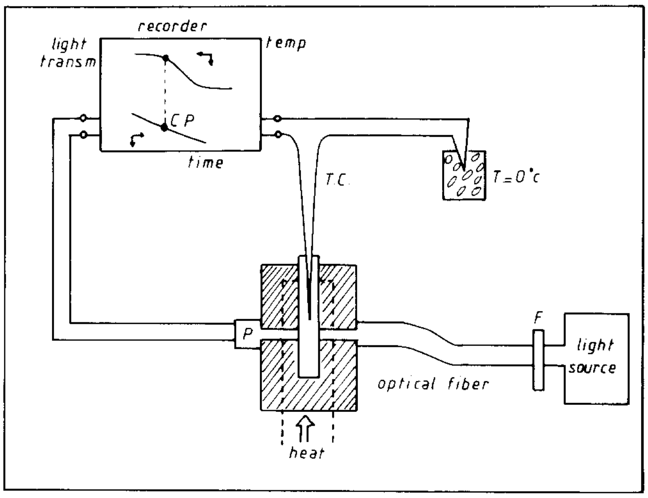

Figure 3 Schematic diagram of the device used for the determination of cloud-point curves: F, filter; P, photodetector; CP, cloud point

the area under the u.v. peak related to the area under the CTBN peak measured with the refractive-index detector, taken as a reference, gives a measure of the carboxyl conversion. Typical times for attaining an almost complete conversion were close to 4 h.

CTBN ×8 was the rubber selected for preparing adducts. Two types of adducts, using different epoxy excesses, were synthesized. Adduct I (A-I) was obtained by using 100 g epoxy monomer ($\bar{n}$=0.03 or 0.15), 60 g CTBN and 0.25 g TPP (final conversion close to 1). For adduct II (A-II), the following proportions were used: 100 g epoxy monomer ($\bar{n}$=0.12), 120 g CTBN and 0.50 g TPP (final conversion equal to 0.98).

Cloud-point curves (CPC)

Mixtures of CTBN (pure or adducts), with epoxy monomers, were carefully prepared by stir-mixing both components in desired volume (ϕ) or mass (ϕ_m) fractions, for about 10 min, at convenient temperatures to attain the homogeneous region (as judged by the transparency of the mixture). When using a diamine as a curing agent, it was added to the formulation after the CTBN–epoxy monomer mixture was complete, at an adequate temperature to produce the epoxy–amine reaction while avoiding amine volatilization (40°C for EDA and 120°C for IPD). In every case, mixtures were transferred to small sample tubes and degassed.

Figure 3 shows a schematic diagram of the light-transmission device used to obtain CPC. The basis of the experimental measurement is the decrease in the fraction of transmitted light at the time of phase separation, due to the difference in the refractive index

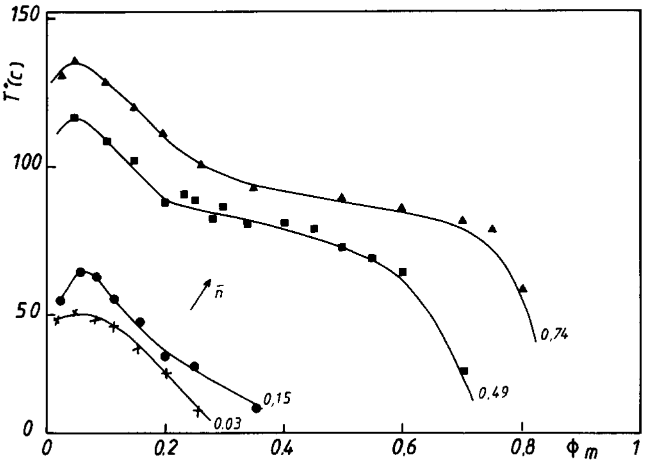

Figure 4 Cloud-point temperature vs. mass fraction of CTBN for mixtures of CTBN ×8 with epoxy monomers of different molar masses (different $\bar{n}$ values, see *Figure 1*)

of both phases (1.57 for pure DGEBA and 1.51 for pure CTBN). The use of light in the visible region implies that the attenuation effect will appear for dispersed particles having an order of diameters greater than 100 nm. The sample tube, containing a copper–constantan thermocouple, is introduced into the metallic block which is heated either by electrical resistance or by circulating oil coming from a thermostat. This provides the possibility of heating or cooling at different rates.

The determination of a particular cloud point (CP) was made by heating the sample to a temperature located at some 20°C higher than the CP, keeping it constant for 5–10 min, and decreasing it with a cooling rate in the order of $1°\mathrm{C\,min^{-1}}$. The CP determined from the resulting intensity vs. time curve is shown in *Figure 3*. Typically each point was measured 5–6 times. It was also verified that experimental values were in agreement with those obtained by heating at a rate of $0.2°\mathrm{C\,min^{-1}}$. Higher heating rates shifted the CP to higher temperatures ($\Delta T \simeq 2$–3°C for a $5°\mathrm{C\,min^{-1}}$ heating rate).

Macrophase separation

Selected samples were introduced into an oven and kept at a constant temperature in the heterogeneous region for several months. Phase stratification was considered complete when two clear phases well separated by a thin interface were observed. Phase compositions and molecular-weight distributions were obtained by s.e.c. measurements with the refractive-index detector and by nitrogen elemental analysis.

RESULTS AND DISCUSSION

Epoxy monomer (variable $\bar{n}$) – CTBN ×8 mixtures

CPC for mixtures of CTBN ×8 with epoxy monomers of different molecular masses, i.e. variable $\bar{n}$, are shown in *Figure 4* (a fifth curve, for $\bar{n}=0.12$, is plotted in *Figure 12*). A *UCST* is observed for every case as reported by Wang and Zupko[2]. Moreover, the curve for $\bar{n}=0.15$ is very close to the one reported by these authors for a similar system.

The most significant feature is the high sensitivity of the location of miscibility gaps as a function of the molecular mass of the epoxy monomer. Increasing $\overline{M}_n$ from 349 to $383\,\mathrm{g\,mol^{-1}}$ leads to an increase in the precipitation threshold temperature (maximum of CPC) of some 14°C. It is interesting to realize that increasing $\bar{n}$ also leads to a change in the chemical composition of the epoxy molecule, i.e. an increase in the concentration of secondary OH groups. In turn, this leads to a negligible change in the solubility parameter as shown in *Table 1* but the change in molecular mass has a pronounced effect on the miscibility gap location. This experimental fact supports the hypothesis used in theoretical models of phase separation in rubber-modified thermosets[4,9], where it was assumed that the very origin of the demixing of CTBN from the epoxy matrix was the increase in the average molecular weight of the thermoset during polymerization.

The shape of the CPC depends on CTBN polydispersity, particularly as reflected by the weight and higher-molecular-weight averages[10], as well as the polydispersity in the composition of CTBN random copolymer chains. It may be qualitatively stated that the dispersed phase segregated from mixtures with composition $\phi < \phi_c$ (composition of the critical point located somewhere at the right of the precipitation threshold[11]) will be rich in large CTBN chains containing the smallest proportion of acrylonitrile, i.e. having the smallest value of the solubility parameter (*Table 2*).

Although this is a very complex system from which to infer any reliable thermodynamic description of CPC, it is indeed interesting to locate expected binodal and spinodal curves obtained by applying the mean-field Flory–Huggins model assuming that both components are monodisperse with molar masses corresponding to the number average of the corresponding distributions. (Although it has been shown[12] that the spinodal curve depends only on the weight-average molecular weight and that the critical point depends on the weight-average and z-average molecular weights, the possible polydispersity in composition of CTBN molecules makes this refinement unnecessary.)

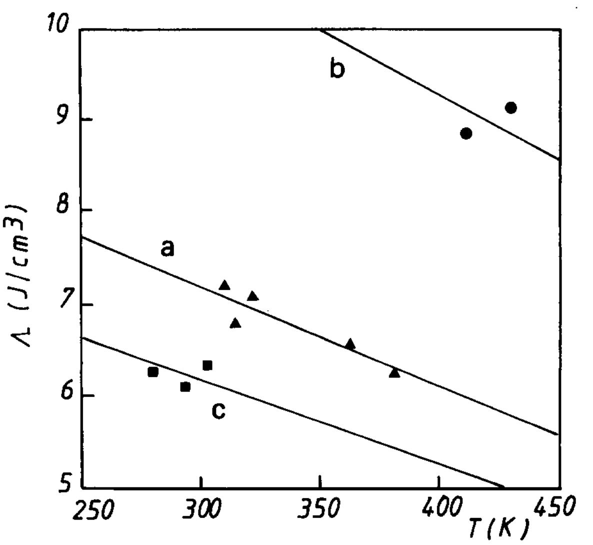

Figure 5 Interaction parameter per unit volume as a function of temperature: a, epoxy monomer (variable $\bar{n}$) – CTBN ×8; b, epoxy monomer ($\bar{n}=0.15$) – CTBN ×15 (×31); c, epoxy monomer ($\bar{n}=0.12$ or 0.15) – adduct (CTBN ×8)

The Gibbs free energy associated with the mixing of component A of molar volume V_A with component B of

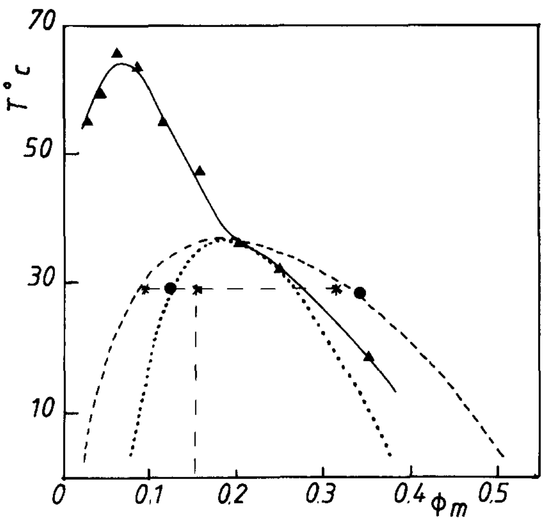

Figure 6 Experimental CPC (▲) and calculated binodal (broken line) and spinodal (dotted curve) curves, for the system DGEBA ($\bar{n}=0.15$) - CTBN ×8 ($T_c=37°C$). Asterisk and circle indicate experimental values of the composition of the two phases arising from the macroscopic separation produced in a sample of $\phi_{m0}=0.15$, kept for several months at 29°C: (*) SEC measurements; (●) nitrogen elemental analysis

molar volume V_B, expressed per unit volume of the mixture, is given by[13]:

$$\Delta G_{M|cm^3} = RT[(\phi_A/V_A)\ln\phi_A + (\phi_B/V_B)\ln\phi_B] + \Lambda\phi_A\phi_B \qquad (1)$$

where A and B denote CTBN copolymer and epoxy monomer, respectively, and ϕ_A and ϕ_B are the corresponding volume fractions.

The first term in equation (1) is the combinatorial part of the free energy of mixing arising from the Flory–Huggins model, and the second term represents the residual free energy of mixing. Equation (1) may also be regarded as a definition of the polymer–polymer interaction parameter Λ, expressed in unit of energy per unit volume.

Frequently, the interaction between both components is expressed using a χ parameter. When the composition dependence may be neglected, Λ and χ are related by:

$$\chi = \Lambda V_r/RT \qquad (2)$$

where V_r is a reference volume, normally defined as the molar volume of the smallest component (the epoxy monomer in the present case) or the molar volume of a polymer segment. As we intend to compare the miscibility of different systems, it is convenient to avoid the use of a reference volume and to express the interaction on a unit volume basis, by means of Λ.

The location of the binodal curve can be calculated by solving equation (1) for a common tangent in the plot of ΔG_M vs. ϕ_A. The spinodal curve arises from $\partial^2\Delta G_M/\partial\phi_A^2=0$, and the coordinates of the critical point, common to both curves, are the following:

$$\phi_{Ac} = V_B^{1/2}/(V_A^{1/2}+V_B^{1/2}) \qquad (3)$$

$$T_c = (2\Lambda_c/R)/(V_A^{-1/2}+V_B^{-1/2})^2 \qquad (4)$$

The mass fraction of CTBN may be calculated from the volume fraction by:

$$\phi_m = \phi_A\rho_A/(\phi_A\rho_A+\phi_B\rho_B) \qquad (5)$$

where the densities of the epoxy monomer, ρ_B, and CTBN copolymer, ρ_A, are shown in *Tables 1* and *2*, respectively.

By calculating the composition of the critical point from equations (3) and (5), the critical temperature T_c may be obtained from the experimental CPC. Using equation (4) with T_c expressed in kelvins, the critical value of the interaction parameter may be obtained.

When values of Λ_c are plotted as a function of T_c, a straight line is obtained as shown in *Figure 5* (curve A). This correlation may also be regarded as the function between the interaction parameter and temperature, for a particular epoxy monomer. Thus,

$$\Lambda = \Lambda_0 + \Lambda_T T \qquad (6)$$

Equation (6) assumes that there is no dependence of Λ on composition (this dependence has been shown to be fairly small for the polystyrene–polybutadiene pair[13]).

The best fit of experimental results gives $\Lambda_0 = 10.29\ \mathrm{J\,cm^{-3}}$ and $\Lambda_T = -1.042\times10^{-2}\ \mathrm{J\,cm^{-3}\,K^{-1}}$. The negative value of Λ_T may be explained using the same arguments as Roe and Zin[13]. Thus, from Flory's equation-of-state theory the interaction parameter per unit volume

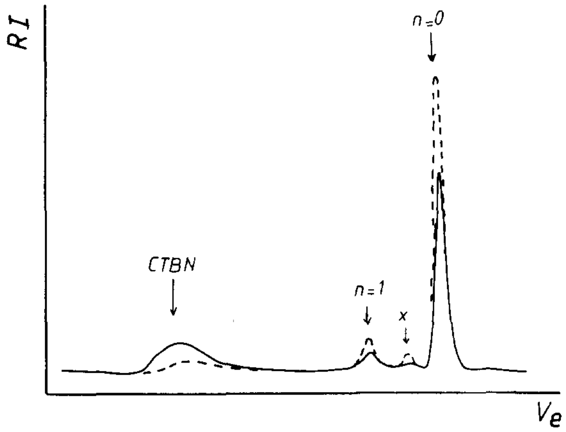

Figure 7 S.e.c. chromatograms (RI detector) of the two phases separated at 29°C from a DGEBA ($\bar{n}=0.15$) - CTBN ×8 mixture: full curve, phase rich in CTBN—less dense; broken curve, phase rich in epoxy monomer—more dense. See ref. 7 for the assignment of peaks $\bar{n}=0$, x and $\bar{n}=1$, for DGEBA monomer

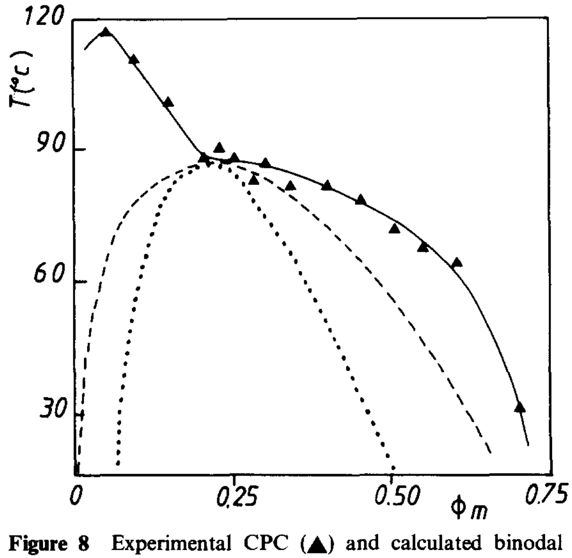

Figure 8 Experimental CPC (▲) and calculated binodal (broken curve) and spinodal (dotted curve) curves, for the system DGEBA ($\bar{n}=0.49$) - CTBN ×8 ($T_c=85°C$)

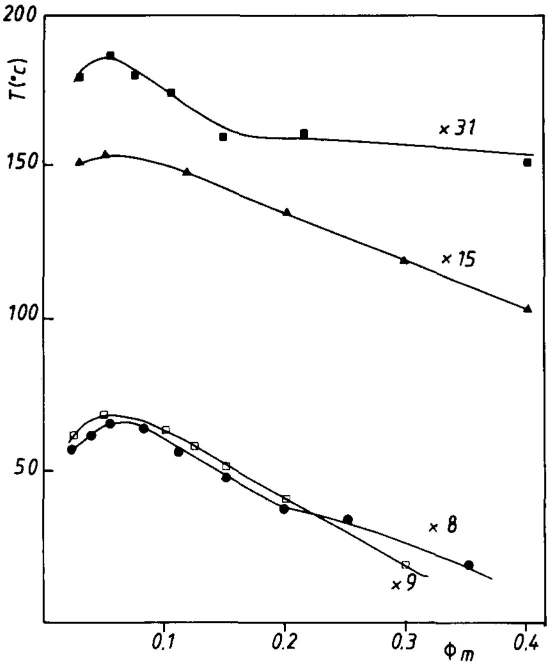

Figure 9 Cloud-point temperatures vs. mass fraction of CTBN for mixtures of DGEBA ($\bar{n}=0.15$) with several CTBN copolymers (identification in *Table 2*)

results as the addition of two terms: the first one gives the change in the energy density due to the foreign segment contact while the second one arises from the change in free volume on mixing. The first term is inversely proportional to the square of the specific volume and so has a negative temperature dependence. The second term has a positive dependence. The prevailing effect of the first term explains the observed negative temperature dependence[13].

Substituting equation (6) into equation (4), we get:

$$T_c = 2\Lambda_0/[R(V_A^{-1/2} + V_B^{-1/2})^2 - 2\Lambda_T] \qquad (7)$$

which accounts for the variation of the critical temperature with the molar volume of the epoxy monomer.

Figure 6 shows the calculated binodal and spinodal curves for the system DGEBA ($\bar{n}=0.15$) — CTBN ×8, plotted together with the experimental CPC for this particular mixture.

A sample with an initial composition $\phi_{m0}=0.15$ was kept for several months at 29°C until phase stratification was considered complete. S.e.c. chromatograms of both phases are shown in *Figure 7*. It can be seen that there is a net segregation of CTBN copolymer between both phases, the fraction of higher molar masses being greater in the phase richer in CTBN, as expected. By calculating the DGEBA concentration in each phase from the s.e.c. chromatogram, the mass fractions of CTBN in both phases may be estimated. Using nitrogen elemental analysis (acrylonitrile content) the phase compositions may also be obtained, assuming that the AN percentage of CTBN is the same in the two phases. The resulting values are plotted in *Figure 6*. The experimental points are located in the vicinity of the predictions of the simple thermodynamic model. Although a shift in these experimental compositions may be expressed when changing the initial composition[5], it is remarkable how a simple Flory–Huggins lattice model approximates the coexistence curves for macrophase separation. This adds to statements of others[13,14] that the Flory–Huggins equation represents the combinatorial term to a surprisingly good approximation.

Similar curves to those shown in *Figure 6* are observed for other $\bar{n}$ values. For example, *Figure 8* shows the case $\bar{n}=0.49$.

Epoxy monomer ($\bar{n}=0.15$) — CTBN (variable AN) mixtures

CPC for mixtures of a particular epoxy monomer ($\bar{n}=0.15$) with several CTBN copolymers are shown in *Figure 9*. CTBN ×8 and CTBN ×9 have the same AN amount and molecular mass but differ in the number and position of carboxyl groups (CTBN ×9 has a higher amount of carboxyl groups including pendant ones). They show similar miscibility behaviour with the epoxy monomer.

CTBN ×15 and CTBN ×31 have only 10% of AN. This leads to a decrease in the solubility parameter and a corresponding high increase in the cloud-point temperatures. The precipitation threshold temperature increases from 65°C for CTBN ×8 to 186°C for CTBN ×31. This high sensitivity to AN content must also affect the fractionation by composition for a particular type of CTBN, as previously discussed.

The higher values of cloud-point temperatures for CTBN ×31 when compared with CTBN ×15 may be ascribed to the increase in the rubber molecular mass (*Table 2*) and an increase in polydispersity due to the presence of a small fraction of high molecular weights (*Figure 2*). The determination of the CPC is, indeed, a sensitivity method for qualitatively testing the polydispersity of polymers[5].

CTBN ×13 has a high amount of AN (26%) and a corresponding high value of the solubility parameter. It is completely miscible with DGEBA ($\bar{n}=0.15$) down to the glass transition temperature of samples.

Critical interaction parameters for DGEBA ($\bar{n}=0.15$) mixed with CTBN ×15 or CTBN ×31 may be estimated using the same assumptions as in the previous section. The resulting values are shown in *Figure 5* (curve B). An arbitrary straight line showing a negative slope has been drawn as both Λ_0 and Λ_T must be increased with respect to values of curve A. Values of the interaction parameter are close to 9 J cm^{-3}. In the same temperature range, i.e. at 420 K, the interaction parameter for DGEBA ($\bar{n}=0.15$) mixed with CTBN ×8 (*Figure 5*, curve A) is $\Lambda = 5.9$ J cm^{-3}. Thus $\Lambda_{\mathrm{CTBN(10\%\ AN)}}/\Lambda_{\mathrm{CTBN(18\%\ AN)}} = 1.5$.

According to Roe and Zin[13], when the term giving the change in the energy density due to foreign segment contact prevails over the one giving the change in free volume on mixing, the interaction parameter may be written as $\Lambda = (\delta_B - \delta_A)^2$. Although this simple equation does not fit the values of Λ obtained from the thermodynamic model, one can compare the predicted ratio of Λ values with the value 1.5. Using the solubility parameters reported in *Tables 1* and *2*, we get

$$\Lambda_{\mathrm{CTBN(10\%\ AN)}}/\Lambda_{\mathrm{CTBN(18\%\ AN)}} = 1.44,$$

in reasonable agreement.

Application of the Flory–Huggins model with the assumptions discussed in the previous case permits the location of binodal and spinodal curves. As an example, *Figure 10* shows the particular case of DGEBA ($\bar{n}=0.15$) – CTBN ×31.

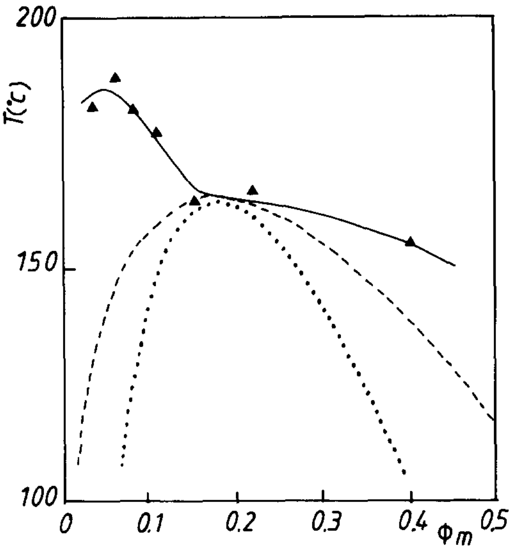

Figure 10 Experimental CPC (▲) and calculated binodal (broken curve) and spinodal (dotted curve) curves, for DGEBA ($\bar{n}$=0.15)–CTBN ×31 mixtures

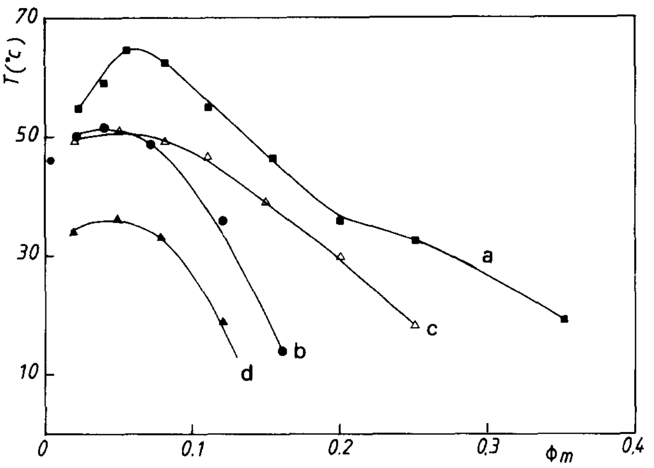

Figure 11 Cloud-point temperatures vs. mass fraction of CTBN ×8 for the following mixtures: a, DGEBA ($\bar{n}$=0.15) – CTBN ×8; b, DGEBA ($\bar{n}$=0.15) – A-I ($\bar{n}$=0.15); c, DGEBA ($\bar{n}$=0.03) – CTBN ×8; d, DGEBA ($\bar{n}$=0.03) – A-I ($\bar{n}$=0.03)

Epoxy monomer (variable $\bar{n}$) — CTBN ×8 adducts

Three different types of CTBN ×8 adducts were prepared as reported in the experimental section. They will be denoted by A-I ($\bar{n}$=0.03), A-I ($\bar{n}$=0.15) and A-II ($\bar{n}$=0.12). Cloud-point curves of these three adduct–epoxy monomer mixtures compared with the same systems using unmodified CTBN ×8 are shown in *Figures 11* and *12* (even when using an adduct the composition axis ϕ_m always refers to the mass fraction of pure CTBN in the mixture). In every case, the use of an adduct increases the miscibility of the systems for the same overall composition.

In order to calculate the location of the critical point by assuming a mixture of monodisperse components, it is necessary to calculate the molar volume of every adduct, V_A. Calculations will be illustrated for the adduct A-I ($\bar{n}$=0.15).

The number-average molecular weight of the adduct is defined as $\overline{M}_n$ = (mass of adduct)/(number of moles of adduct).

Initially, 100 g DGEBA (0.2614 moles) and 60 g CTBN ×8 (0.01667 moles) are mixed. Taking into account that the functionality of the epoxy monomer is 2 while that of CTBN is 1.8 (*Table 2*), the initial ratio of equivalents is given by r = eq. COOH/eq. epoxy = (1.8 × 0.0167)/(2 × 0.261) = 0.0574.

At any reaction extent of carboxyl groups, p_A, the reaction extent of epoxy groups, p_B, is given by:

$$p_B = r p_A$$

As in the synthesis of adduct A-I the reaction was carried out to completion, i.e.:

$$p_A = 1 \quad \text{and} \quad p_B = r = 0.0574$$

As both epoxide groups of a DGEBA molecule have the same reactivity, the probability of finding an unreacted DGEBA (B_{free}) is given by:

$$B_{free}/B_0 = (1 - p_B)^2 = (1 - r)^2 = 0.8885$$

and

$$B_{adduct}/B_0 = 1 - B_{free}/B_0 = 0.1115$$

Then, 11.15% of the initial DGEBA mass is incorporated into the adduct. This gives the mass of adduct = 60 g + 0.1115 × 100 g = 71.15 g.

The number of moles of adduct is given by the addition of the initial number of moles of CTBN plus the number of moles of DGEBA incorporated into the adduct less the number of moles of linkages (each linkage reduces the number of molecules in one unit). Then:

$$\text{number of moles} = 0.01667 + 0.02914 - 1.8 \times 0.01667 = 0.0158$$

This gives:

$$\overline{M}_n = 71.15/0.0158 = 4502 \text{ g mol}^{-1}$$

The adduct density ρ_A may be estimated by:

$$m_{adduct}/\rho_A = m_{epoxy}/\rho_{epoxy} + m_{CTBN}/\rho_{CTBN}$$

where m_{epoxy} and m_{CTBN} are the masses of both components in the adduct. This gives ρ_A = 0.977 g cm^{-3}.

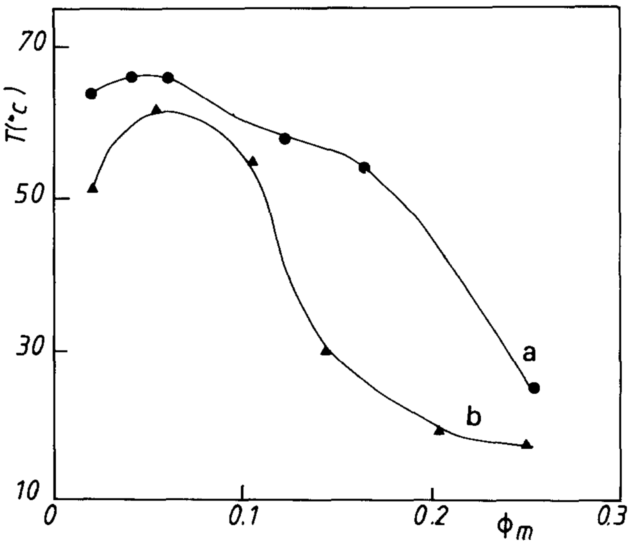

Figure 12 Cloud-point temperatures vs. mass fraction of CTBN ×8 for the following mixtures: a, DGEBA ($\bar{n}$=0.12) – CTBN ×8; b, DGEBA ($\bar{n}$=0.12) – A-II ($\bar{n}$=0.12)

The molar volume of the adduct, V_A, is given by:

$$V_A = \overline{M_n}/\rho_A = 4608\,\mathrm{cm^3\,mol^{-1}}$$

On the other hand, the volume fraction of epoxy in the adduct is calculated as:

$$f_B = (m_{epoxy}/\rho_{epoxy})/(m_{adduct}/\rho_A) = 0.131$$

Table 4 shows values of V_A and f_B for the three adducts. Using the values of V_A so obtained, the composition of the critical point, ϕ_{Ac}, arises from equation (3). By converting ϕ_{Ac} into ϕ_{mc} (mass fraction of pure CTBN in the adduct), critical temperatures T_c are obtained from the corresponding CPC depicted in *Figures 11* and *12*. The use of equation (4) leads to the values of critical interaction parameters which are plotted in *Figure 5* as a function of critical temperatures (curve C). The straight line corresponds to the best regression modifying both Λ_0 and Λ_T by the same amount, as is expected from the copolymer effect discussed in what follows.

It is interesting to compare the values of the interaction parameters for mixtures including adducts with respect to those containing unmodified CTBN and the same amount and type of epoxy monomer. For example, at a temperature $T = 300$ K, the ratio of the interaction parameters is $\Lambda_{adduct}/\Lambda_{unmodified\,CTBN} = 0.86$.

On the other hand, the decrease in the interaction parameter when using a random copolymer A–B mixed with B, as compared with the mixture of A and B, is given by[13]:

$$\Lambda_{A-B,B}/\Lambda_{A,B} = (1 - f_B)^2 \tag{8}$$

where f_B is the volume fraction of monomer B in the copolymer A–B. In our case (A = CTBN and B = epoxy), $f_B \simeq 0.125$ and $(1 - f_B)^2 = 0.766$. Because of the approximations involved in our thermodynamic analysis, the agreement may be considered reasonable.

Independently of the use of any model, the experimental fact is a shift of the miscibility gap to lower temperatures when using an adduct. As the adduct has a higher molar mass than pure CTBN, an effect which would shift the CPC to higher temperatures, the observed increase in miscibility can only be explained by a copolymer effect as previously discussed.

Epoxy–diamine copolymer mixed wth CTBN ×8 (pure or adduct)

Only preliminary results will be reported here for these complex mixtures to show some particular trends of the cloud-point curves. In order to work with liquid unreactive systems for cloud-point determinations, two different kinds of approaches have been used: (i) replacement of a significant fraction of the diepoxy (DGEBA) by a monoepoxy (PGE; *Figure 1*), and using a stoichiometric epoxy/amine ratio; (ii) use of an epoxy/amine ratio higher than the critical gelation ratio. In case (i) an unmodified CTBN was used whereas an adduct was used in case (ii).

Apart from the use of different diamines, the main difference between (i) and (ii) is the use of a CTBN which does not participate in the epoxy–amine polymerization in the first case, and a reactive one in the second case (this situation is closer to industrial practice than the first one). In both cases, the final system obtained after complete reaction is chemically inert at temperatures used to measure CPC.

(i) IPD, DGEBA ($\bar{n}$ = 0.15), PGE copolymer (molar ratio 2:1:6) + CTBN ×8. The epoxy–amine reaction was carried out at 120°C to completion, in the presence of different mass fractions of CTBN. Although phase separation takes place during polymerization, the molecular-weight distribution of the epoxy–amine copolymer, as determined by s.e.c. chromatograms, showed no significant difference when varying the CTBN amount, even for the case where CTBN was absent. The IPD, DGEBA ($\bar{n} = 0.15$), PGE copolymer had a number-average molecular weight around 1500 g mol^{-1} and a polydispersity index equal to 3.0.

The CPC of these mixtures is shown in *Figure 13*, revealing a similar behaviour with respect to systems described in previous sections.

(ii) EDA, DGEBA ($\bar{n}$ = 0.12) copolymer + A-II ($\bar{n}$ = 0.12). The critical gelation ratio for the reaction of a diepoxy with a diamine, in epoxy excess and assuming that both epoxy groups have equal reactivity and there are no substitution effects, is given by[15]:

$$r_c = \mathrm{eq.epoxy/eq.amine} = 3 \tag{9}$$

Mixtures with $r > r_c$ were prepared and the reaction was carried out to completion, at 40°C, in the presence of an adduct of CTBN:A-II ($n = 0.12$). As in the previous system, phase separation takes place during polymerization.

Figure 14 shows CPC for different r values as well as the curve obtained in the absence of diamine ($r \to \infty$). Increasing the amount of diamine in the mixture, i.e. decreasing r, leads to a significant increase in the location of the miscibility gap. This effect may be qualitatively explained by the increase in the number-average molecular weight, the polydispersity and the difference between solubility parameters of both components, when increasing the proportion of EDA in the formulation. A remarkable fact is the presence of a minimum in the CPC, giving rise to an increase in the cloud-point temperature with the adduct amount when shifting to the right of the minimum. This trend, which was also observed when EDA was replaced by diaminodiphenylsulphone[4], can be explained qualitatively by the fact that the adduct also reacts with the diamine, thus increasing its molar mass. The greater the adduct amount in the formulation, the higher the expected increase in its molar volume.

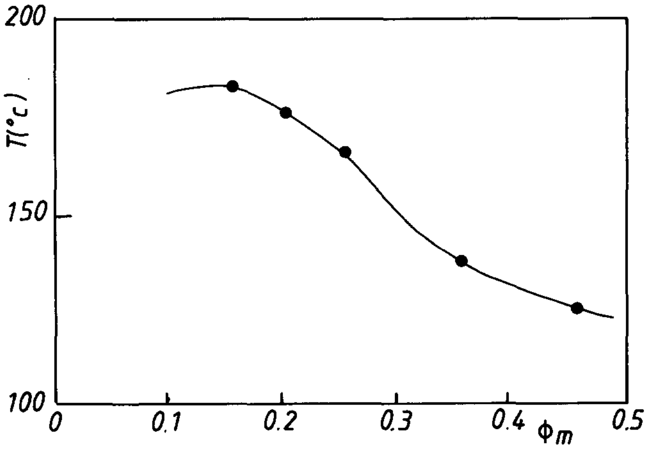

Figure 13 Cloud-point temperatures vs. mass fraction of CTBN for a mixture of IPD, DGEBA ($\bar{n}$ = 0.15), PGE copolymer (molar ratio 2:1:6) with CTBN ×8

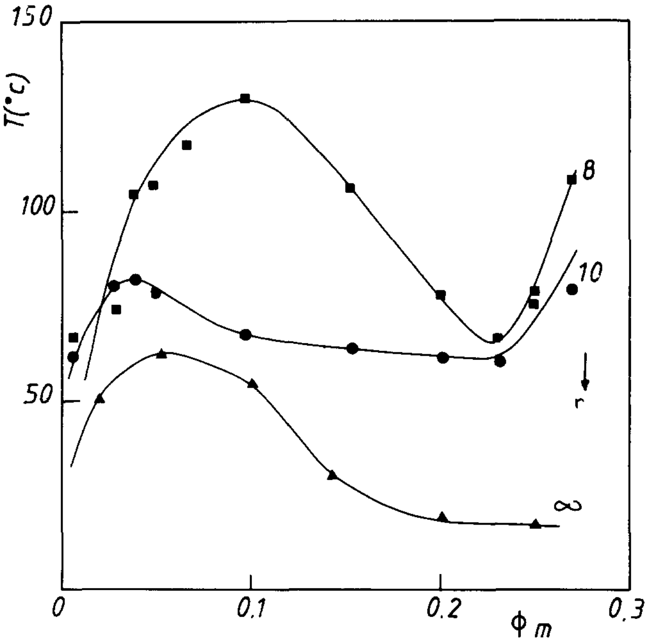

Figure 14 Cloud-point temperatures vs. mass fraction of CTBN for mixtures of EDA, DGEBA ($\bar{n}=0.12$) copolymers, with the adduct A-II ($\bar{n}=0.12$), for various r (r = eq. epoxy/eq. amine)

The miscibility of epoxy–diamine copolymers/CTBN mixtures is being further investigated in a systematic form, in order to give more support to the reported preliminary results.

CONCLUSIONS

The miscibility of epoxy monomers (DGEBA) with rubbers (CTBN) is very sensitive to the molecular weight of the epoxy molecule. A small increase in the number-average molecular weight (i.e. from 349 to 383 g mol^{-1}) leads to a significant shift in the miscibility gap to higher temperatures (i.e. $T = 14$°C in the precipitation threshold temperature). This effect outweighs the change in chemical structure, i.e the increase in concentration of secondary OH groups.

The application of a simple Flory–Huggins lattice model, regarding both components as monodisperse, leads to the location of the critical point and coexistence curves, as well as the estimation of the interaction parameter per unit volume (Λ). A correlation of the type $\Lambda = \Lambda_0 + \Lambda_T T$ was found, with a negative Λ_T. This agrees with results reported for other systems such as polybutadiene–polystyrene[13]. For a particular sample and temperature, experimental compositions belonging to the coexistence curve for macrophase separation are in close agreement with theoretical predictions.

Decreasing the acrylonitrile content of the CTBN decreases the miscibility. The increase observed in the estimated value of the interaction parameter is of the same order as the one predicted from the change in the solubility parameter of CTBN.

Using a CTBN as an adduct with the epoxy monomer, as is often done in industrial practice, leads to a shift of the miscibility gap to lower temperatures, in spite of the increase in molar mass. This is explained by the copolymer effect.

Epoxy–diamine copolymers mixed with CTBN may show a complex behaviour depending on the epoxy/amine stoichiometric ratio and the way in which the CTBN is used. When the polymerization is carried out in the presence of a CTBN adduct, the fact that it reacts through the epoxy ends, thus increasing its molar mass, leads to a significant decrease in miscibility from a certain value of CTBN concentration, i.e. a second maximum appears in the cloud-point curve. This effect is being investigated further.

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