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Phase diagram of different epoxy-amine precursors modified with a thermoplastic: Effect of structure of epoxy-amine system on miscibility

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ABSTRACT

The miscibility of a thermoplastic with the precursors of different epoxy-amine systems was analyzed thermodynamically in which the dependence of interaction parameter on temperature and composition χ (T, ϕ) and the polydispersity of components were considered. The epoxy-amine precursors were different only in the nature of amino groups, which were provided by a monoamine and a diamine in different proportions. Cloud-point curves were measured for five unreacted modified systems resulting that miscibility of the system increased with the proportion of monoamine. The thermodynamic analysis was realized in two steps: first, the model was applied to each system individually and secondly, a general equation for χ (T, ϕ) depending on the monoamine–diamine proportion was searched and used to analyze all systems together. Theoretical calculations of cloud-point curves, shadow curves, spinodal curves, critical points, vitrification curves and species distributions were realized and discussed for those systems.

1. Introduction

Epoxy resins are generally used as advanced composite matrix materials due to their good properties and performances. However these materials show poor resistance to the initiation and propagation of cracks [1,2]. The toughness of these thermosets may be improved by the incorporation of rubbery or thermoplastic components which are initially miscible with the reactive monomers but are segregated in the course of polymerization leading to a randomly dispersed phase. This mechanism is denominated Polymerization Induced Phase Separation (PIPS) [3,4].

Different types of morphologies can be generated by the PIPS mechanism [5]. The morphology developed during phase separation determines the final properties and applications of these modified materials.

The knowledge of the process of phase separation is fundamental for explaining (or predicting) the developed morphologies. For that, a first step is to make a reasonable thermodynamic analysis of phase separation and to obtain the phase diagrams of mixtures before and during the polycondensation of the thermoset [4,6,7].

The study of the miscibility of the modifier in the mixture of epoxy precursors before reaction is important to select a suitable cure temperature and to calculate the interaction parameter of the unreacted mixture, which may be used for the analysis of phase separation during polymerization [8,9]. The used cure temperature must be chosen carefully: on the one hand, it should produce the complete miscibility of the modifier in the initial mixture of the thermoset precursors; and the other, it should lead to a phase separation during the reaction of thermoset, hopefully before the gelation.

Different thermodynamic theories for polymer solution have been developed during the last years, the best known is the Flory–Huggins lattice theory [10,11]. Koningsveld and Staverman extended this model and developed general calculation methods for liquid–liquid equilibrium of polydisperse polymer solutions where the interaction parameter is composition-dependent [12].

The aim of this work is to analyze thermodynamically the phase separation of a thermoplastic in the precursors of several epoxy-amine systems by means of a model based on the Flory–Huggins lattice theory. The studied epoxy-amine systems were different only in the nature of amino group, which were provided by a monoamine (MA) and a diamine (DA) in different proportions, so that the resulting polymer would vary from a linear polymer (epoxy-MA) to a highly crosslinked polymer (epoxy-DA).

There are not in the literature experimental studies about systems modified with thermoplastic polymers in which the molecular structure of an epoxy resin has been modified of continue and controlled form by means of formulation, in preselected concentrations of a monoamine and a diamine, as it is our purpose.

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In addition, relationships between the molecular structure of epoxy resin and the thermodynamic properties were investigated and established [13]. A general equation for interaction parameter (χ) as a function of the MA–DA structure of the systems was proposed and used to obtain the phase diagrams of unreacted systems.

The obtained general equation of χ will be used in a future work for the analysis of phase separation during the polymerization (PIPS) of these systems.

The thermodynamic analysis was realized following the strategy described in a previous paper [14], in which, one of the systems of this study was analyzed (epoxy-DA). The application of this model to the rest of the systems will show the effect of the MA–DA proportion on the miscibility of the systems as well as on species distributions in the separated phases.

2. Experimental

2.1. Materials

The thermoplastic modifier was a polystyrene (PS) with a number and weight- average molecular weight of $M_n = 140\,000$ and $M_w = 230\,000$, respectively (polydispersity index of 1.64). The epoxy-amine systems were always constituted by stoichiometric amounts of epoxy groups and amino hydrogens. The epoxy precursor was a diglycidylether of bisphenol A (DGEBA, Araldite GY260) with a mass per mole of epoxy groups equal to 188 g mol^{-1}. The amino hydrogens were provided by the monoamine (MA), α-aminodiphenylmethane (ADM), and the diamine (DA), 4,4′-methylenebis (2,6 diethylaniline) (MDEA), in different proportions. A total of five different epoxy-amine systems were studied, in which the origin of amino group was: 100%MA, 75%MA–25%DA, 50%MA–50%DA, 25%MA–75%DA and 100%DA expressed as percentage of amino equivalents.

These materials were commercial products and were used as-received, without purification. The chemical structures and characteristics of the different materials are shown in Table 1.

The blends were prepared as follows: first, PS was dissolved in epoxy prepolymer at room temperature using methylene chloride as solvent, which was later evaporated for a day at room temperature followed by several hours at 140 °C. In a second step, the PS/DGEBA blend was taken out of the oven at 120 °C and the corresponding amounts of mono and diamine were added at room temperature. The resulting solutions were mixed for 2 min and then cooled in ice. Immediately after preparing the samples, their cloud points were measured.

2.2. Techniques

A light transmission device with a He–Ne laser beam was employed to determine the cloud point temperatures, T_{cp}, of unreacted mixtures. For that, the temperature of blend was increased until a homogeneous solution was obtained, kept constant during several minutes and then decreased at a cooling rate in the order of 0.5 °C min^{-1}. At a certain temperature, the mixture became turbid due to the phase separation, leading to a decrease in the intensity of transmitted light. T_{cp} was measured at the onset temperature of the decline of light. The union of the T_{cp} obtained for different modifier proportions of a blend determines the experimental cloud point curve (CPC) of that blend.

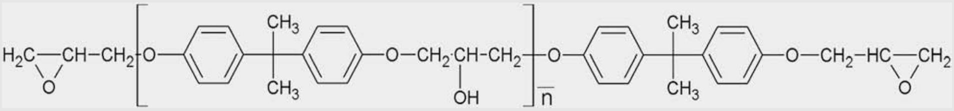
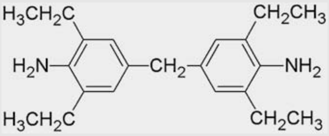
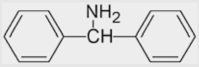
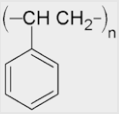
Although the systems were potentially reactive, the temperatures and times of analysis were minimized doing the advance of chemical reaction negligible.

3. Theoretical basis

3.1. Model development

The phase diagram of a pseudobinary blend consists of two curves: the cloud point curve (CPC) which separates the one-phase area and the two-phase area; and the vitrification curve which separates the liquid phase area from the solid or vitreous phase [14]. In the UCST case, the vitrification curve crosses the CPC at

Table 1
Characteristics and chemical structure of the materials.

Material	Supplier	Structure	Molar mass (g mol^{-1})	Density (g cm^{-3})
DGEBA	Ciba–Geiby Araldite GY260		376, $n = 0.13$	1.20
MDEA	Aldrich		310.5	1.35[a]
ADM	Aldrich		183.26	1.064
PS	Aldrich		$M_n = 140\,000$, $M_w = 230\,000$	1.04

[a] From Ref. [14].

a certain modifier concentration known as Bergham point, whereas in the LCST case, it never crosses the CPC.

The vitrification curve can be estimated from the Couchman equation given by:

$$\ln T_g = \frac{W_1 \Delta cp_1 \ln T_{g_1} + W_2 \Delta cp_2 \ln T_{g_2}}{W_1 \Delta cp_1 + W_2 \Delta cp_2} \tag{1}$$

where the subscripts 1 and 2 indicate the two components of the blend. W_i is the mass fraction of i component, and T_{g_i} and Δcp_i are, respectively the glass transition temperature and the heat capacity change at T_g of the i component.

The cloud point curve can be modelled using different theories and approaches. The theory most widely used for polymer blends is the Flory–Huggins lattice theory [15,16]. In our case, a model based on the Flory–Huggins theory modified by the approximations of Staverman and Koninsveld was employed. This way, the polydispersity of components was taken into account and the interaction parameter, χ, was considered dependent on both, temperature and composition [17,18].

The extended Flory–Huggins equation, written in terms of Gibbs free energy of mixing per mol of unit cell ($\overline{\Delta G}$) for a pseudobinary mixture is given by:

$$\overline{\Delta G} = \frac{\Delta G}{M} = R \cdot T \cdot \left(\sum_i \frac{\phi_{1i}}{r_{1i}} \ln \phi_{1i} + \sum_j \frac{\phi_{2j}}{r_{2j}} \ln \phi_{2j} + \phi_1 \phi_2 g(T, \phi_2) \right) \tag{2}$$

where M represents the amount of lattice sites in the system, R is the gas constant, T is the absolute temperature, the subscripts 1 and 2 stand for the two components of the system. The symbols i and j represent species of different molecular mass corresponding to 1 and 2 components respectively. ϕ is the volume fraction, r is the chain length defined as the ratio of the molar volume of the species with respect to a reference volume (V_{ref}). g is a function that depends on the temperature and composition and is related to the interaction parameter, χ, through the following expression:

$$\chi(T, \phi_2) = g(T, \phi_2) - \frac{\partial g(T, \phi_2)}{\partial \phi_2} \phi_1 \tag{3}$$

Several functions including different number of adjustable parameters have been proposed for $\chi(T, \phi_2)$ in the literature [19,20]. In our case, as usual [21], $\chi(T, \phi_2)$ was defined as the product of a temperature-dependent term, $D(T)$, and a concentration-dependent term, $B(\phi_2)$, given by:

$$\chi(T, \phi_2) = D(T) \cdot B(\phi_2) \tag{4}$$

$$D(T) = A + \frac{B}{T} \tag{5}$$

$$B(\phi_2) = \frac{1}{1 - c\phi_2} \tag{6}$$

where A, B and c are adjustable model parameter which vary for each system.

Several elements that determinate the phase separation process can be calculated starting from Eq. (2): cloud point curve, shadow curve, spinodal curve and critical point [22].

3.1.1. Cloud point curve (CPC) and shadow curve (SC)

The cloud-point curve and the shadow curve give the compositions in cloud point conditions of the matrix phase and the emergent phase, respectively.

Both curves are calculated by applying the condition of phase equilibrium, i.e. equating the chemical potentials of each component in the matrix phase (α) and in the emergent phase (β), as follows:

$$\Delta\mu_{1i}^{\alpha} - \Delta\mu_{1i}^{\beta} = 0 \tag{7}$$

$$\Delta\mu_{2j}^{\alpha} - \Delta\mu_{2j}^{\beta} = 0 \tag{8}$$

The expression for the chemical potential can be derived from Eq. (2). Then, substituting the obtained expressions for $\Delta\mu$ in Eqs. (7) and (8) and using also Eqs. (3)–(6), the following system of equations for the calculation of phase equilibrium is obtained.

$$\sigma_1 - \left[\left(\sum_i \frac{\phi_{1i}^{\beta}}{r_{1i}^{\beta}} - \sum_i \frac{\phi_{1i}^{\alpha}}{r_{1i}^{\alpha}} \right) + \left(\sum_j \frac{\phi_{2j}^{\beta}}{r_{2j}^{\beta}} - \sum_j \frac{\phi_{2j}^{\alpha}}{r_{2j}^{\alpha}} \right) \right] + D(T) \cdot \left(\frac{\phi_2^{\beta^2}}{1 - c\phi_2^{\beta}} - \frac{\phi_2^{\alpha^2}}{1 - c\phi_2^{\alpha}} \right) = 0 \tag{9}$$

$$\sigma_2 - \left[\left(\sum_i \frac{\phi_{1i}^{\beta}}{r_{1i}^{\beta}} - \sum_i \frac{\phi_{1i}^{\alpha}}{r_{1i}^{\alpha}} \right) + \left(\sum_j \frac{\phi_{2j}^{\beta}}{r_{2j}^{\beta}} - \sum_j \frac{\phi_{2j}^{\alpha}}{r_{2j}^{\alpha}} \right) \right] + D(T) \cdot \left[\frac{1}{c} \ln \left(\frac{1 - c\phi_2^{\beta}}{1 - c\phi_2^{\alpha}} \right) - \left(\frac{\phi_2^{\beta}\phi_1^{\beta}}{1 - c\phi_2^{\beta}} - \frac{\phi_2^{\alpha}\phi_1^{\alpha}}{1 - c\phi_2^{\alpha}} \right) \right] = 0 \tag{10}$$

where σ_1 and σ_2 are the separation factors of components 1 and 2 respectively. The value of σ determines the fractionation extension of each molecular species between the two equilibrium phases. Its definition is:

$$\sigma_1 = \frac{1}{r_{1i}} \ln \frac{\phi_{1i}^{\beta}}{\phi_{1i}^{\alpha}} \tag{11}$$

$$\sigma_2 = \frac{1}{r_{2j}} \ln \frac{\phi_{2j}^{\beta}}{\phi_{2j}^{\alpha}} \tag{12}$$

In addition to Eqs. (9) and (10), another equation can be added, coming from a mass balance for emergent phase, i.e.

$$\phi_1^{\beta} + \phi_2^{\beta} = 1 \tag{13}$$

3.1.2. Spinodal curve (SPC)

This curve represents the stability limit of a homogeneous phase. The thermodynamic requirement of spinodal curve is that the second derivative of the Gibbs free energy with respect to the composition be identical to zero, i.e.

$$\frac{\partial^2 \Delta G}{\partial \phi_2^2} = 0 \tag{14}$$

Combining Eq. (14) with Eqs. (2)–(6) the following equation for SPC is obtained:

$$\frac{1}{r_{1w}\phi_1} + \frac{1}{r_{2w}\phi_2} - D(T) \left(\frac{2}{1 - c\phi_2} + \frac{c\phi_2}{(1 - c\phi_2)^2} \right) = 0 \tag{15}$$

where r_{1w} and r_{2w} are the weight average relative molar volumes of the 1 and 2 components, respectively.

3.1.3. *Critical point*

It is the point in which the binodal and spinodal curves coincide. At this point, the matrix phase and the emergent phase have the same composition. Besides, it supposes the limit of an inversion in the separated phases. At the critical point, it must be simultaneously satisfied that the second and third derivates of the molar Gibbs free energy with respect to the composition be zero, i.e.

$$\frac{\partial^2 \Delta G}{\partial \phi_2^2} = \frac{\partial^3 \Delta G}{\partial \phi_2^3} = 0 \tag{16}$$

Combining Eq. (16), with Eqs. (2)–(6) the following equation for critical point is obtained.

$$\frac{r_1 z}{(r_{1w}\phi_1)^2} - \frac{r_2 z}{(r_{2w}\phi_2)^2} - D(T)\left(\frac{3c}{(1-c\phi_2)^2} + \frac{2c^2\phi_2}{(1-c\phi_2)^3}\right) = 0 \tag{17}$$

where r_{1z} and r_{2z} are the zeta averages of the relative molar volumes of the 1 and 2 component.

3.2. *Approaches used in the model*

The application of thermodynamic model to the different studied systems required for various approaches and considerations:

Each of the studied systems, which are formed by different epoxy precursors modified with PS (%PS + DGEBA/%DA–%MA (1:1)), was considered a system consisting of two components: on the one hand, the 1 component represents the precursors of epoxy-amine polymer; and the other, the 2 component represents to PS.

The 1 component (the precursors of epoxy-amine polymer) consists of three species of different sizes: DGEBA, MDEA and ADM, which are mixed in different proportions according to each system, maintaining the epoxy-amine system always stoichiometric. Thus, for example, for the DGEBA/50%MA–50%DA system, for every four DGEBA molecules, will be two monoamine molecules and one diamine.

The 2 component (PS) is formed by a species distribution of different molecular mass, which was obtained by applying the theoretical Schulz–Zimm distribution [23] to the number and weight average molecular weight of our PS, i.e.

$$W(X) = \frac{Y^{h+1}}{\Gamma(h+1)} \cdot X^h \cdot \exp(-Y \cdot X) \tag{18}$$

where $W(X)$ is the mass fraction of the X-mer, $h = [(\overline{X}_w/\overline{X}_n) - 1]^{-1}$, $Y = h/\overline{X}_n$, and Γ is the gamma function. For our PS, $\overline{X}_n = 1346$, $\overline{X}_w = 2212$.

To use the model is necessary to define a reference volume. The molar volume of PS monomer has been taken as reference volume for all the systems ($V_{\text{ref}} = 100\ \text{cm}^3\ \text{mol}^{-1}$).

To obtain the phase diagram, the thermodynamic model was applied to the experimental cloud point curves, therefore, the experimental CPCs of the different systems were first determined.

4. Results and discussion

Fig. 1 shows the cloud point curves obtained experimentally for the five system of study (DGEBA mixed with: 100%DA, 75%DA–25%MA, 50%DA–50%MA, 25%DA–75%MA and 100%MA modified with different amounts of PS). The curve corresponding to the PS + DGEBA/100%DA system was reported in a previous paper [14].

All the systems showed an upper critical solution temperature behaviour (UCST), meaning miscibility of the systems increases with temperature.

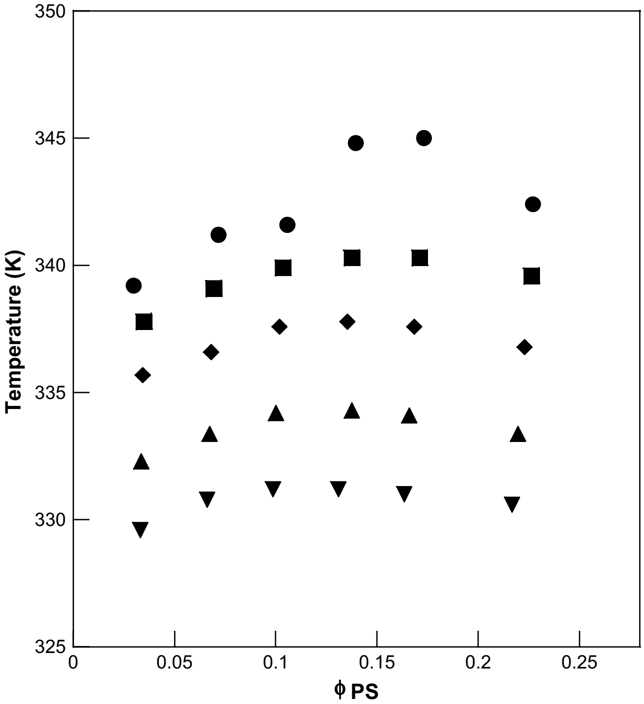


Fig. 1. Experimental cloud-point curves for five unreacted DGEBA/MDEA–ADM (1:1) systems modified with PS. The MDEA–ADM proportions were: 100%MDEA (●), 75%MDEA–25%ADM (■), 50%MDEA–50%ADM (◆), 25%MDEA–75%ADM (▲) and 100%ADM (▼).

A trend for the location of the CPC depending on the molecular structure of epoxy-amine system was obtained: the CPC of system shifted to lower temperatures by increasing the proportion of MA (or decreasing DA) in the system. This means that the monoamine increases the miscibility of PS in the epoxy-amine system, in the studied composition range.

The thermodynamic analysis was realized in two steps using the model described above. First, the model was applied to each measured CPC individually, obtaining the adjustable parameters *A*, *B* and *c* for each individual system. In a second step, a general equation for χ as a function of the molecular structure MA–DA of the systems was searched and proposed; then, it was used to realize the thermodynamic analysis on all systems together.

The procedure followed to apply the model to each CPC was similar to that developed by Kamide et al. [24]. So, using the equations of phase equilibrium (9) and (10), and the equation for the mass balance of emergent phase (13), a system of three equations and four unknowns (σ_1, σ_2, $D(T)$ and c) was obtained. The used strategy to solve this problem was described in a previous paper [14] in which the phase separation for the PS + DGEBA/100%DA system was analyzed. In short, this strategy consisted of determining first c, using the position of experimental threshold point; and then, the system was resolved, getting $D(T)$, σ_1 and σ_2 for each experimental point. The *A* and *B* adjustable parameters for each system were obtained from linear adjustment of the corresponding values of $D(T)$ with the inverse of temperature (Eq. (5)). This way, the values of *A*, *B* and *c* were calculated individually for each system and are shown in Table 2.

All adjustable parameters (*A*, *B* and *c*) followed a trend with the structure molecular MA–DA of the system. Thus, *A* and *c* decreased with increasing proportion of monoamine, while *B* increased.

The term $A/(1 - c\phi_2)$ is related to the excess entropy contribution to the free energy due to the self-association of solvent molecules. The *A* parameter provides a correction for the assumption of random mixing. The progressive decrease of *A* parameter

Table 2
Adjustable parameters of χ ($\chi(T,\phi_2) = (A + B/T)\cdot 1/(1 - c\cdot\phi_2)$) obtained for different DGEBA/%MA–%DA systems modified with PS.

%MA–DA	*A*	*B*	*c*
100%DA	0.1394	11.753	0.669
75%DA–25%MA	0.0937	28.998	0.652
50%DA–50%MA	0.0858	33.203	0.634
25%DA–75%MA	0.0718	39.164	0.626
100%MA	0.0568	45.478	0.607

with the MA/DA ratio of the system means that there is less self-association of solvent molecules when the proportion of MA increases (or DA decreases).

The term $(B/T)/(1 - c\phi_2)$ is related to the enthalpy contribution to the free energy. The *B* parameter is a measure of the mismatching of solubility parameter of both components [25,26]. The increase of *B* parameter with the MA/DA ratio of the system means that the mismatching of solubility parameters of PS and the epoxy pseudocomponent increased when the proportion of MA increased.

The *c* parameter was a positive value for all systems. It indicates an increase of the interaction parameter when increasing the PS concentration in the blend. The decrease of *c* with the increase of the MA/DA ratio causes a decrease of χ when the proportion of MA increases.

In a second step of this analysis, a general equation for χ depending on the MA–DA composition of the system was sought, which is able to describe adequately the experimental CPCs of all studied systems. The following equation was used:

$$\chi\left(T,\phi_2,\underline{N}_{\mathrm{MA}}\right) = \left(A(\underline{N}_{\mathrm{MA}}) + \frac{B(\underline{N}_{\mathrm{MA}})}{T}\right)\cdot\left(\frac{1}{1 - c\left(\underline{N}_{\mathrm{MA}}\right)\cdot\phi_2}\right) \tag{19}$$

where $\underline{N}_{\mathrm{MA}}$ represents the number fraction of amino equivalents provided by the monoamine.

The usual shape of the equation for χ remained, but now, the *A*, *B* and *c* parameters are not constant. Our purpose was to look for an expression for *A*, *B* and *c* as a function of the proportion of monoamine equivalents ($\underline{N}_{\mathrm{MA}}$).

For that, an alternative would be to use as expressions of *A*, *B* and *c*, equations resulting from the adjustments of the respective values of *A*, *B* and *c* obtained in the analysis of the individual systems as a function of proportion of monoamine.

However, in this work we attempted to develop an expression for χ which is only function of the χ of the systems whose amino groups provided only of the monoamine or the diamine (PS + DGEBA/100%DA and PS + DGEBA/100%MA called neat systems for us) and certain molecular parameters of systems such as the molar volume of epoxy system.

The obtained interaction parameters for neat systems are given by the following equations, as shown in Table 2.

$$\begin{aligned}\chi_{\mathrm{MA}}(T,\phi_2) &= \left(A_{\mathrm{MA}} + \frac{B_{\mathrm{MA}}}{T}\right)\cdot\left(\frac{1}{1 - c_{\mathrm{MA}}\cdot\phi_2}\right)\\ &= \left(0.0568 + \frac{45.478}{T}\right)\cdot\left(\frac{1}{1 - 0.6068\cdot\phi_2}\right)\end{aligned} \tag{20}$$

$$\begin{aligned}\chi_{\mathrm{DA}}(T,\phi_2) &= \left(A_{\mathrm{DA}} + \frac{B_{\mathrm{DA}}}{T}\right)\cdot\left(\frac{1}{1 - c_{\mathrm{DA}}\cdot\phi_2}\right)\\ &= \left(0.1394 + \frac{11.753}{T}\right)\cdot\left(\frac{1}{1 - 0.669\cdot\phi_2}\right)\end{aligned} \tag{21}$$

where the MA and DA subscripts represent the PS + DGEBA/100%MA and PS/DGEBA/100%DA systems, respectively.

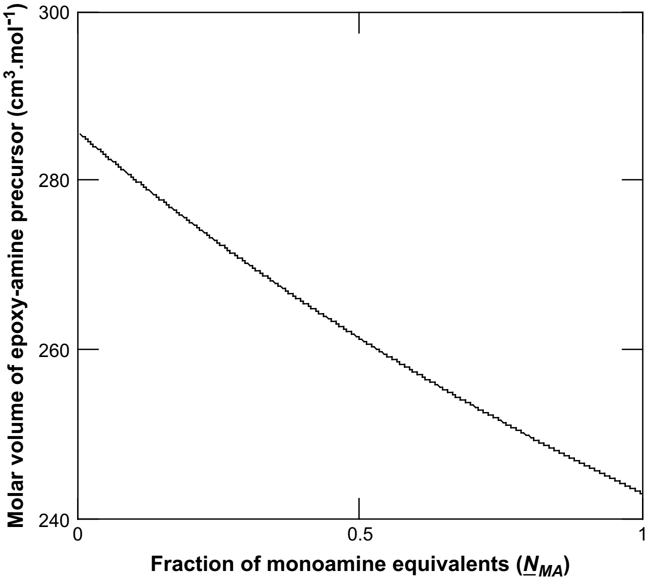


Fig. 2. Variation of the molar volume of the precursors of DGEBA/MDEA–ADM (1:1) system as a function of the fraction of monoamine equivalents ($\underline{N}_{\mathrm{MA}}$) in the system.

The molar volume of the precursors of the stoichiometric epoxy-amine system as a function of proportion of monoamine equivalents present at the same is given by:

$$V\left(\underline{N}_{\mathrm{MA}}\right) = \frac{\dfrac{M_{\mathrm{MA}}}{2\cdot\rho_{\mathrm{MA}}}\cdot\underline{N}_{\mathrm{MA}} + \dfrac{M_{\mathrm{DA}}}{4\cdot\rho_{\mathrm{DA}}}\cdot\left(1 - \underline{N}_{\mathrm{MA}}\right) + \dfrac{M_{\mathrm{EB}}}{2\cdot\rho_{\mathrm{EB}}}}{\dfrac{1}{2}\cdot\underline{N}_{\mathrm{MA}} + \dfrac{1}{4}\cdot\left(1 - \underline{N}_{\mathrm{MA}}\right) + \dfrac{1}{2}} \tag{22}$$

where M_{MA}, M_{DA}, M_{EB} and ρ_{MA}, ρ_{DA}, ρ_{EB} are respectively the molecular masses and densities of the monoamine, diamine and epoxy. $\underline{N}_{\mathrm{MA}}$ varies from zero for the DGEBA/100%DA system to one for the DGEBA/100%MA system.

Fig. 2 shows the variation of the molar value of the epoxy-amine pseudocomponent with the proportion of monoamine present in the system.

A decline in the molar volume of epoxy-amine pseudocomponent with the increase of the MA proportion was obtained from the volume corresponding to DGEBA/100%DA system ($V_{\mathrm{DA}} = 285.55$ cm^3/mol) to the volume for the DGEBA/100%MA system ($V_{\mathrm{MA}} = 242.78$ cm^3/mol).

Different equations for χ were proposed, resulting that the best fitting the experimental data is given by the following equations:

$$A\left(\underline{N}_{\mathrm{MA}}\right) = \frac{\left(1 - \underline{N}_{\mathrm{MA}}\right)\cdot A_{\mathrm{DA}}\cdot V_{\mathrm{DA}} + \underline{N}_{\mathrm{MA}}\cdot A_{\mathrm{MA}}\cdot V_{\mathrm{MA}}}{V_{\mathrm{MA-DA}}\left(\underline{N}_{\mathrm{MA}}\right)} \tag{23}$$

$$B\left(\underline{N}_{\mathrm{MA}}\right) = \frac{\left(1 - \underline{N}_{\mathrm{MA}}\right)\cdot B_{\mathrm{DA}}\cdot V_{\mathrm{DA}} + \underline{N}_{\mathrm{MA}}\cdot B_{\mathrm{MA}}\cdot V_{\mathrm{MA}}}{V_{\mathrm{MA-DA}}\left(\underline{N}_{\mathrm{MA}}\right)} \tag{24}$$

$$c\left(\underline{N}_{\mathrm{MA}}\right) = \left(\frac{(1 - \underline{N}_{\mathrm{MA}})\cdot c_{\mathrm{DA}}}{V_{\mathrm{DA}}} + \frac{\underline{N}_{\mathrm{MA}}\cdot c_{\mathrm{MA}}}{V_{\mathrm{MA}}}\right)\cdot V_{\mathrm{MA-DA}}\left(\underline{N}_{\mathrm{MA}}\right) \tag{25}$$

As shown, in these equations involved only the values of *A*, *B* and *c* of neat systems (100%DA and 100%MA) and the relationship between the molar volume of neat system (V_{MA} and V_{DA}) and the molar volume of mixture MA–DA system ($V_{\mathrm{MA-DA}}(\underline{N}_{\mathrm{MA}})$) which is a function of proportion of MA.

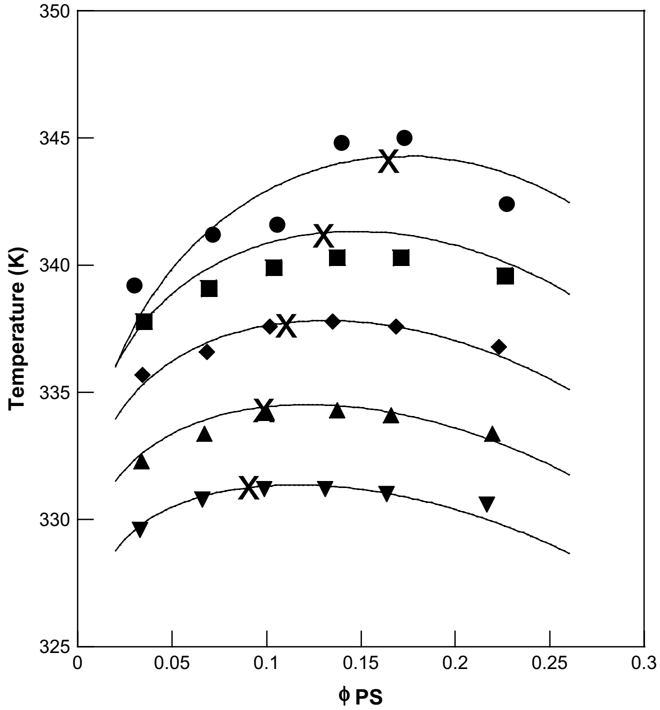


Fig. 3. Comparison of CPC obtained theoretically (—) and experimentally (symbols) for five unreacted PS + DGEBA/MDEA–ADM (1:1) systems where the proportions MA–DA were: 100%MDEA (●), 75%MDEA–25%ADM (■), 50%MDEA-50%ADM (◆), 25%MDEA-75%ADM (▲) and 100%ADM (▼). The position of critical point (X) is also indicated for each system.

These expressions taken as parameter value that obtained by the balanced sum of the parameter of neat systems, but correcting by the difference of molar volume.

Making $\underline{N}_{\mathrm{MA}}$ equals zero and one in Eqs. (23)–(25), the χ for the PS + DGEBA/100%MDEA system and the PS + DGEBA/100%ADM system are obtained, respectively.

To check the validity of the general equation of χ given by Eqs. (23), (24) and (25), the experimental CPCs of different systems were compared with the theoretical CPCs resulting from applying the model using this general equation of χ to the respective studied systems ($\underline{N}_{\mathrm{MA}} = 0, 0.2, 0.5, 0.75$ and 1). The result is shown in Fig. 3, where the position of critical point for each system is also indicated. The critical point is shifted to lower composition of modifier when the proportion of MA increased. For any relation MA–DA, the critical point was located between the values of 0.09 and 0.163 corresponding to the 100%MA and 100%DA systems, respectively.

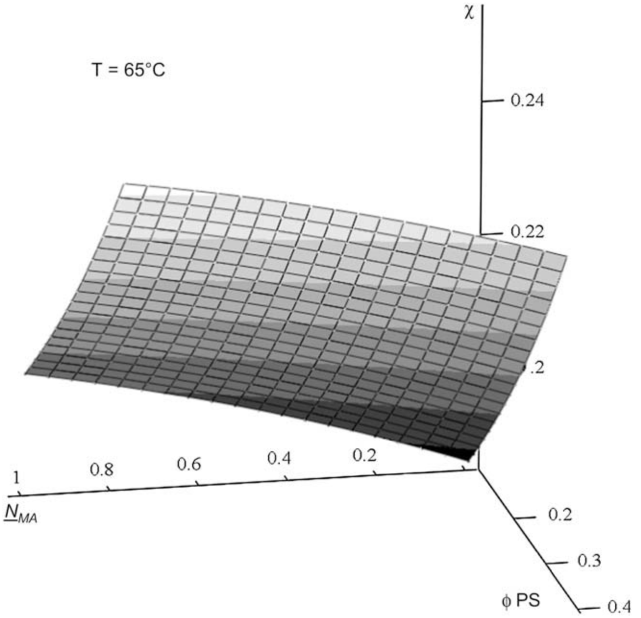


Fig. 4. Interaction parameter, χ, as a function of volume fraction of PS, ϕ_{PS}, and the fraction of amino equivalents provided by monoamine, $\underline{N}_{\mathrm{MA}}$, for a fixed temperature of 65 °C.

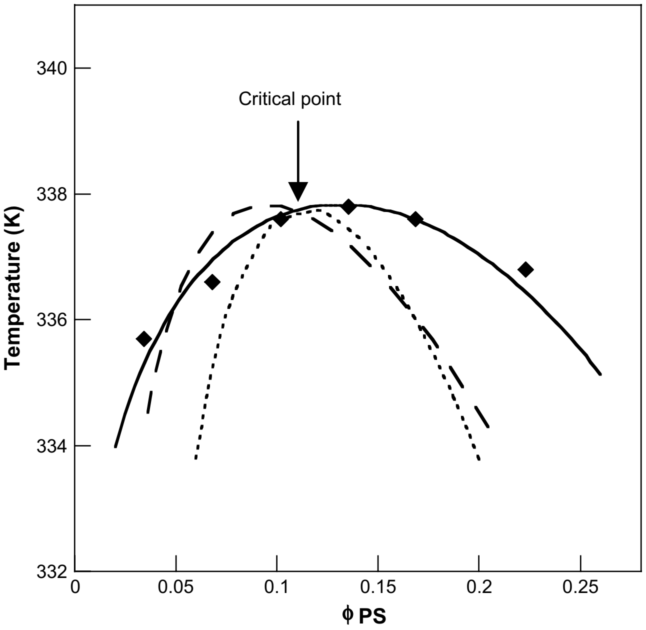


Fig. 5. Phase separation behaviour of the unreacted DGEBA/50%MDEA–50%ADM (1:1) system modified with PS: experimental (◆) and calculated (solid line) cloud point curve, shadow curve (dashed line), spinodal curve (dotted line) and location of critical point.

Fig. 3 shows a very good adjustment between the theoretical and experimental CPCs, verifying the validity of the equation found for χ.

Luckily, a valid equation for χ depending on the MA–DA proportion of system was found, in which neither the CPCs of mixture MA–DA systems or any parameter resulting from adjustments have been used. Only molecular features of the systems (molar volume) and the χ of neat systems involved in this general equation for χ.

The importance of having a valid equation for χ depending on MA–DA structure is that the phase diagram for systems with any ratio MA/DA could be obtained.

Fig. 4 shows the variation of interaction parameter with the equivalent fraction of monoamine and the volume fraction of PS at a temperature intermediate to the CPCs of systems. An increase of interaction parameter with the proportion of MA and with the proportion of PS was obtained.

Accordingly, the greatest miscibility in systems with higher MA proportion cannot be attributed to enthalpic factors, since the interaction parameter increased with the MA proportion. It should only be attributed to entropic factors because of the smaller size of

Table 3
Values of glass transition temperature (T_g) and the heat capacity change at T_g (Δcp) for PS and the precursors of DGEBA/100%MDEA (1:1) and DGEBA/75%MDEA-25%ADM (1:1) systems.

Component	T_g (°C)	Δcp (J/g °C)
PS	100.11	0.288
DGEBA/100%DA	−19.79	0.574
DGEBA/75%DA–25%MA	−26.09	0.466

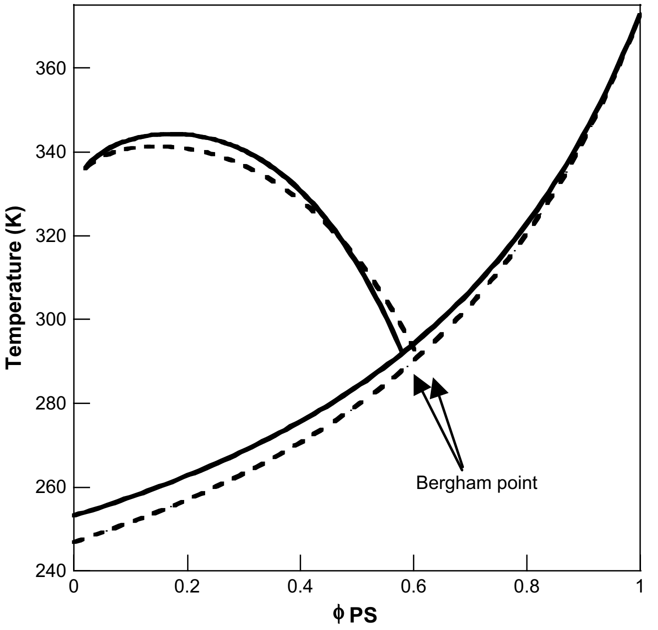


Fig. 6. Calculated cloud point curve and vitrification curve for the unreacted PS + DGEBA/100%MDEA (1:1) (solid line) and PS + DGEBA/75%MDEA-25%ADM (1:1) (dashed line) systems. The intersection of the vitrification and cloud point curves gives the Bergham point.

the precursors of epoxy-amine systems when the proportion of MA increases, as was reflected in Fig. 2. By decreasing the size of molecules, the entropy of system increases reducing the Gibbs free energy of mixing and increasing the miscibility of system [27].

In addition to the CPC, the other elements that define the process of phase separation were estimated using this general χ: the shadow curve (from Eqs. (9) and (10)), the spinodal curve (from Eq. (15)) and the critical point (from Eq. (17)). Fig. 5 shows these elements for one of the systems: PS + DGEBA/50%MA–50%DA.

With the considerations used in this model, the critical point was located to lower compositions of modifier than the threshold point.

The phase diagram is completed with the vitrification curve. These curves were calculated only for two systems: PS + DGEBA/100%DA and PS + DGEBA/75%DA–25%MA. For other systems, this curve could not be calculated because we did not get to observe the T_g of epoxy precursors of those systems since they should be temperatures below measured range of our DSC.

Table 3 shows the values of T_g and Δcp for the epoxy precursors and PS used to obtain the vitrification curves from Eq. (1).

The Bergham point (Fig. 6) was observed to a volume fraction of PS of 0.61 and 0.58 for the systems PS + DGEBA/100%DA and PS + DGEBA/75%DA–25%MA, respectively. Therefore, in the range of studied composition (0–30%PS), phase separation occurs before the vitrification of systems.

When the phase separation occurs, the species of the components are distributed between the separated phases, but do not similarly. To characterize to the separated phases, thermodynamic calculations of species distributions of both components (epoxy-amine precursor and PS) in each separated phase were realized for the cloud point conditions [28]. The results were analyzed and discussed in terms of the proportion of MA–DA and the proportion of PS in the systems.

In the matrix phase, the distributions of both components were equal to the respective distributions in the homogeneous phase for any composition of PS and any ratio MA/DA. It is due to that in cloud point conditions, the amount of species present in the emergent phase is negligible compared to the one present in the matrix phase. On the contrary, in the emergent phase, the species distributions were different depending on the proportion of PS and also the proportion of MA–DA in the system.

Fig. 7 shows the species distributions of PS in the emergent phase for cloud point conditions. In Fig. 7a, for different initial compositions of PS at a fixed MA–DA proportion; and in Fig. 7b, for different MA–DA proportions at a fixed PS proportion.

It is observed that the distribution of PS was narrower and richer in species of lower molecular weight, when the initial proportion of PS or the ratio MA/DA increased.

The observed trend in the distribution of PS with the initial proportion of PS was attributed, as is described in previous papers [14,29], to the change in the nature of emergent phase, which

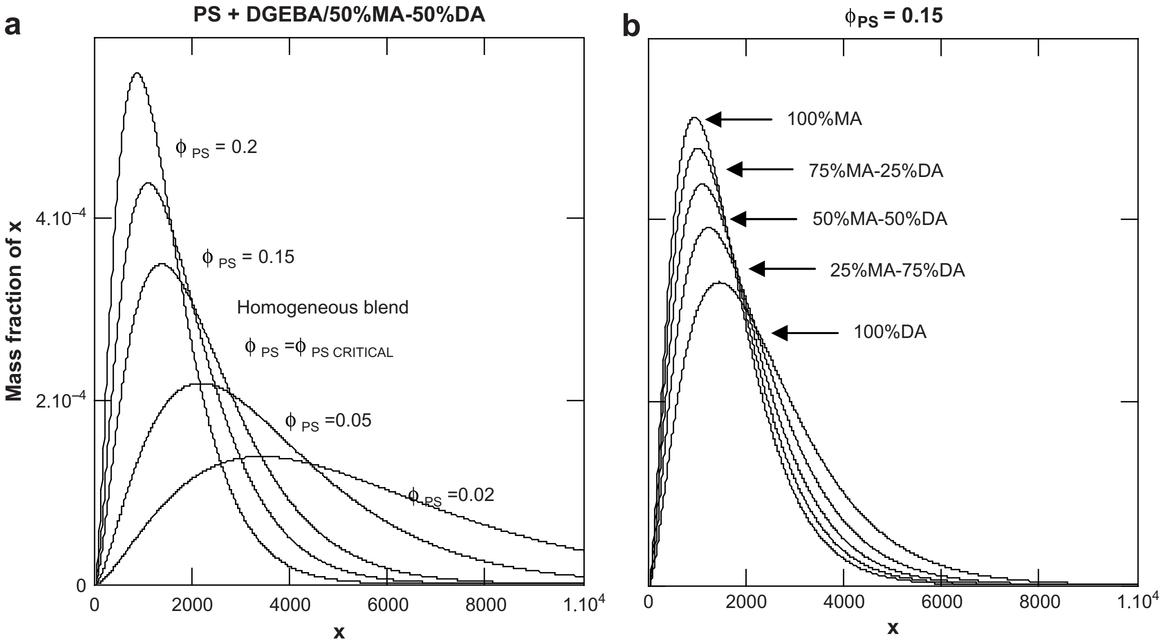


Fig. 7. Calculated species distributions of PS in the emergent phase: a) for the PS + DGEBA/50%MDEA-50%ADM (1:1) system at different initial volume fraction of PS; b) for different proportions MA–DA of the PS + DGEBA/MDEA-ADM (1:1) system, at a fixed ϕ_{PS} of 0.15.

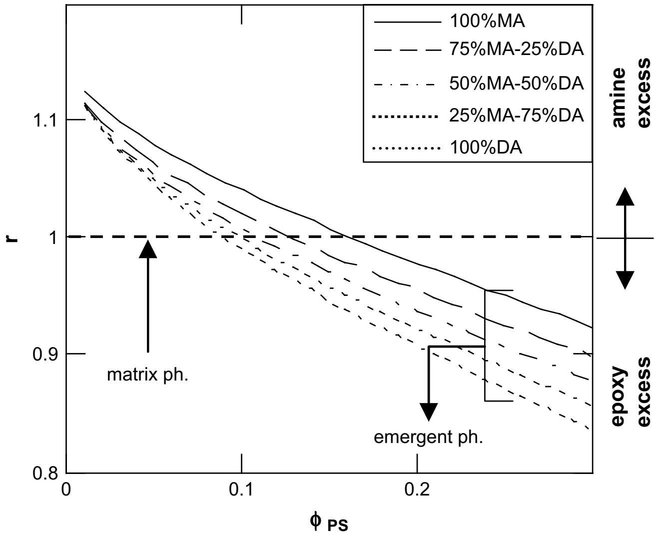


Fig. 8. Ratio of the amine/epoxy equivalents in each separated phase in cloud point conditions for different initial volume fraction of PS and different MA–DA proportion of the PS + DGEBA/MA–DA system.

becomes richer in epoxy-amine precursors, when the proportion of PS increases, containing thus fewer heavy PS molecules.

As for the effect of the MA–DA structure in the PS distribution, it was observed that for any initial PS proportion, an increase in the MA proportion caused that the distribution of PS in the emergent phase was richer in light molecules. This trend is due to that when the MA proportion in the system increased the critical point is shifted to lower PS compositions. It lead to an emergent phase increasingly poor of PS, and consequently its distribution of PS will have less heavy molecules.

To study the species distribution of the other components of system (epoxy-amine precursor), the stoichiometric ratio of amino and epoxy groups in each separated phase was determined as a function of PS proportion for the different MA–DA systems [30,31]. This is shown in Fig. 8.

The stoichiometric ratio of amino and epoxy groups is defined by Eq. (26) where [MDEA], [ADM] and [DGEBA] are the molar concentration of MDEA, ADM and DGEBA, respectively.

$$r_S = \frac{4\cdot[\mathrm{MDEA}] + 2\cdot[\mathrm{ADM}]}{2\cdot[\mathrm{DGEBA}]} \tag{26}$$

In cloud point conditions, the matrix phase remained in all cases stoichiometric with the same number of epoxy groups than H–amino. The reason for this, as mentioned above, is that the composition of matrix phase remains the same as that of homogenous mixture.

On the contrary, in the emergent phase a departure from stoichiometry is observed, containing an amine excess at initial compositions of PS smaller than the critical point and an epoxy excess at greater compositions in all systems. The departure from stoichiometry is higher when the difference between the initial composition and the critical composition increases.

These trends can be explained by the difference in size of the species that constitute the epoxy precursor and because the modifier is always more compatible with the smallest species of another component. The molar volume of monoamine is smaller than that of diamine and the molar volume of diamine is smaller that the volume of DGEBA ($V_{\mathrm{ADM}} < V_{\mathrm{MDEA}} < V_{\mathrm{DGEBA}}$). Therefore, the PS-rich phase will dissolve more molecules of ADM and MDEA than molecules of DGEBA, leading to an excess of amino groups in this phase.

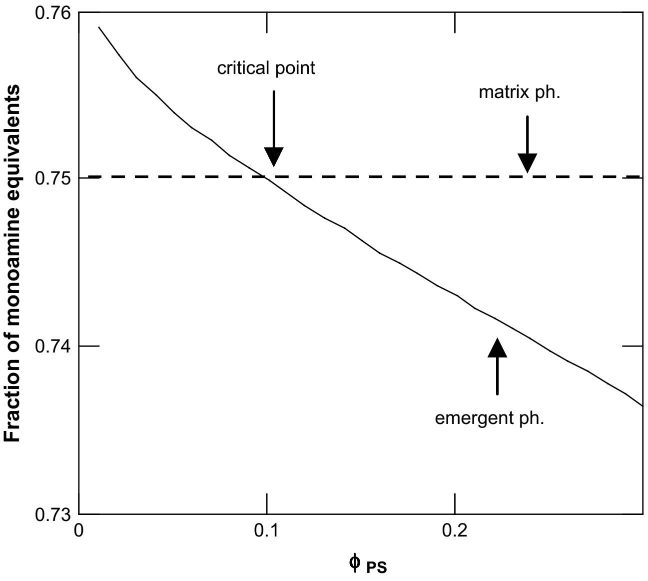


Fig. 9. Fraction of monoamine equivalents in each separated phase in cloud point conditions for the unreacted PS + DGEBA/75%ADM–25%MDEA system at different initial volume fraction of PS.

Following that reasoning, a variation in the proportion of amino equivalent provided by monoamine and provided by diamine in the emergent phase is expected to happen, which must depend on the modifier composition. As $V_{\mathrm{ADM}} < V_{\mathrm{MDEA}}$, at initial compositions of PS smaller than the critical point, the emergent phase is the richest in PS phase, and therefore dissolves more monoamine than diamine. On the contrary, at initial compositions of PS greater than the critical point, the emergent phase is the richest in epoxy-amine system phase and it will contain more diamine than monoamine. This fact is reflected in Fig. 9, for one of the studied systems

5. Conclusions

The miscibility of a PS in the precursors of several epoxy-amine systems was studied experimentally and thermodynamically. A total of five epoxy-amine systems were studied, in which the amino group were provided by a monoamine and a diamine in different proportions, but remaining the epoxy-amine system always stoichiometric. This way, the resulting polymer would vary gradually from a linear polymer (epoxy-MA) to a highly-crossed polymer (epoxy-DA).

Experimentally, cloud point curves for the five systems modified with PS were measured and reported. All systems showed an UCST behaviour. The obtained CPCs shifted to lower temperature when the MA proportion in the system increased (or DA proportion decreased), meaning that the monoamine produced an increase in the miscibility of systems.

Thermodynamically, an analysis of phase separation was realized to the five modified systems by means of a model based on the Flory–Huggins lattice theory and on the Staverman and Koningsveld approaches. In this model, the dependence of χ on temperature and composition $\chi\,(T, \phi)$ and the polydispersity of components were considered. The thermodynamic analysis was realized in two steps: first, the thermodynamic model was applied individually on the CPC of each system; and secondly, a general equation for χ dependent on the MA–DA composition which adjusts successfully the CPC of all systems was of search.

Fortunately, an equation of χ as a function of MA–DA structure in the system was found in which only intervened the χ of the neat systems (PS + DGEBA/100%DA and PS + DGEBA/100%MA) and the ratios of molar volumes. The importance of this general equation for χ is that, on the one hand, it was obtained without making experimental adjustments and without using the CPC of systems MA–DA mixture; and the other hand, it allows predict the CPC and the phase behaviour for systems with any MA–DA proportion.

The interaction parameter increased with the proportion of monoamine. Therefore, the increase of miscibility produced by monoamine should be assigned only to entropic factors (minor size of epoxy precursors when the ratio MA/DA increases) and not to enthalpic factors.

The cloud-point, shadow, spinodal curves and the critical point were estimated for each system from the proposed equation of χ. The phase diagrams were completed with the calculation of the vitrification curves, which was realized for two systems (PS + DGEBA/100%DA and PS + DGEBA/75%DA–25%MA). The critical point shifted to lower compositions of modifier as the proportion of monoamine increased (or DA proportion decreased) and it was located at lower composition of PS than the threshold point.

The species distributions of both components (PS and epoxy-amine precursors) in each separated phase in cloud-point conditions were calculated thermodynamically. In the matrix phase, the distributions were always equal to those in the homogeneous mixture. However, in the emergent phase, the species distributions varied for each MA–DA system and each composition of modifier. Thus, the distribution of PS in the emergent phase was more and more narrow and richer in the smallest species as the proportion of PS or the proportion of MA increased in the system. Explanations for the observed trends were given. The effect of the MA–DA structure on the distribution of PS was assigned to the variation of the position of the critical point in the different MA–DA systems.

The epoxy-amine system in the emergent phase had a departure from stoichiometry and a variation in the initial proportion of MA–DA. Thus at compositions of PS smaller than the critical point, an excess of amino groups was obtained of which the proportion of groups provide from MA was higher than it had initially. On the contrary, at compositions of PS greater than the critical point, an excess of epoxy groups occurred and the amino groups provided by the diamine increased with respect to that it had initially. These trends were explained by the different size of the components constituting of the system.

Acknowledgments

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