Thermodynamic Analysis of Phase Separation of a Thermoplastic in the Precursors of Different Epoxy-Amine Systems

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Summary: The miscibility of a thermoplastic, polystyrene (PS), with the precursors of several epoxy-amine systems has been studied thermodynamically and experimentally. The epoxy-amine systems were different only in the origin of amino groups, which were provided by a monoamine (MA) and a diamine (DA) in different proportions. Cloud-point curves (CPC) at conversion zero were reported for five modified systems with different MA-DA proportion. All CPCs showed an UCST behaviour. CPC shifted to lower temperatures when the ratio of MA/DA in the system increased, meaning that the MA produces an increase in the miscibility of the system. A model based on the Flory-Huggins theory was used for the thermodynamic analysis, in which the dependence of interaction parameter on temperature and composition, $\chi(T,\phi)$, and the polydispersity of components were considered. A general equation for $\chi(T,\phi)$ also depending on the MA-DA proportion was reached and used to obtain the phase diagram of the different systems. A high level of agreement between theoretical and experimental CPCs was obtained.

Keywords: Flory-Huggins theory; interaction parameter; molecular weight distribution; phase separation; thermodynamics

Introduction

Epoxy resins are generally used as advanced composite matrix materials due to their properties and performances. However these materials are brittle. The toughness of these materials may be improved by the incorporation of thermoplastic components which are initially miscible with the monomers, but are segregated in the course of polymerization leading to a randomly dispersed phase.[1]

The knowledge of the process of phase separation is fundamental for the processing and practical applications of these materials.[2] For that, a first step is to have the phase diagrams of mixtures before and during the polycondensation of thermoset.

Different thermodynamic theories have been developed in recent years, the most well-known is the Flory-Huggins lattice theory. Koningsveld and Staverman extended this model for polydisperse polymer solutions where the interaction parameter, χ, is composition-dependent.[3]

The aim of this work is to thermodynamically analyze 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, in which the polydispersity of components and the dependence of χ with temperature and composition were into account.

The studied epoxy-amine systems were different only in the nature of amino groups, 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 cross-linked polymer (epoxy-DA)

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In addition, we aimed to obtain a general equation for the interaction parameter, χ, as a function of the proportion of MA-DA in the system. This allows us to establish relationships between the composition of epoxy-amine system and the thermodynamic properties and also predict the behavior of phase of systems with any ratio MA/DA.[4]

As yet there are no published studies on systems modified with thermoplastic polymers, in which the molecular structure of epoxy system had been modified of continue and controlled manner by means of formulation, and this is the purpose of our work.

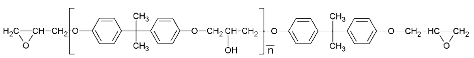
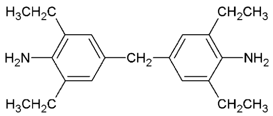
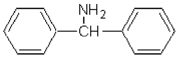
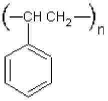
Experimental Part

The thermoplastic modifier was a polystyrene (PS) with a polidispersity index of 1.64. The epoxy-amine systems were always mixed in stoichiometric amounts of epoxy groups and amine hydrogens. The epoxy precursor (EB) was diglycidyl ether of bisphenol A (DGEBA). The amino hydrogens were provided by the monoamine (MA) α-aminodiphenilmethane (ADM) and the diamine (DA) 4,4′-methylenebis(2,6-diethylaniline) (MDEA). Five different epoxy-amine systems were studied, in which the origins of amino groups were: 100%DA, 75%DA-25%MA, 50%DA-50%MA, 25%DA-75%MA and 100%DA. The chemical structures and characteristics of the different materials are shown in Table 1.

The blends were prepared of the following way: First, the PS was dissolved in the epoxy prepolymer using methylene chloride (CH_2CL_2) as a solvent, which was later evaporated. Next, the corresponding amounts of mono and diamine were added at room temperature and mixed for approximately two minutes. To avoid the chemical reaction, the mixtures were immediately cooled on ice and then their cloud point temperatures were measured.

The cloud point temperatures were determined using a light transmission device with a He-Ne laser beam described elsewere.[5] Tcp were determined to the onset of the decrease in the intensity of transmitted light. The union of the Tcps obtained at different compositions of modifier for a specific system, defines the CPC of that system.

Table 1.
Characteristics of the materials.

Material	Supplier	Structure	Molar Mass ($g \cdot mol^{-1}$)	Density ($g \cdot cm^{-3}$)
DGEBA	Ciba – Geiby Araldite GY260		376 n = 0.13	1.20
MDEA	Aldrich		310.5	1.35a)
ADM	Aldrich		183.26	1.064
PS	Aldrich		Mn = 140000 Mw = 230000	1.04

a)from ref. [6]

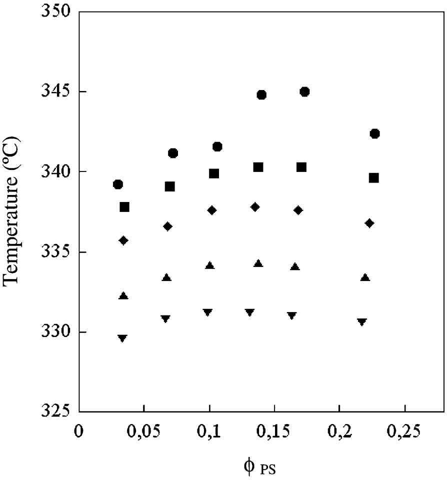


Figure 1.
Measured cloud-point temperatures vs. volume fraction of PS for five unreacted DGEBA/MDEA-ADM (1:1) systems modified with PS. The MDEA-ADM proportions were: 100%MDEA (●), 75%MDEA-25%ADM (■), 50%MDEA-50%ADM (◆), 25%MDEA-75%ADM (▲) and 100%ADM (▼).

Figure 1 shows the cloud point curves obtained experimentally for the five system of study modified with different amounts of PS. The curve corresponding to the PS+DGEBA/100%DA system was reported in a previous paper.[6]

All CPCs showed upper critical solution temperature behaviour (UCST), i.e. the miscibility of the systems increases with temperature. A displacement of the CPC to lower temperatures, when the ratio of MA/DA in the system increased, was obtained. This means that the monoamine produces an increase in the miscibility of the systems.

Thermodynamic Analysis

The thermodynamic analysis was performed by applying the model described below to the CPCs obtained experimentally. The analysis was realized using the Flory-Huggins model extended by the Staverman and Koningsveld approaches, in which the polydispersity of components and the dependence of the interaction parameter, χ, with temperature and composition were taken into account.[7,8] In this model, the Gibbs free energy of mixing per mol of unit cell ($\overline{\Delta G}$) for a polydisperse binary system is given by this equation,

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

where R is the gas constant, T is the absolute temperature, the subscripts 1 and 2 stand for the components 1 and 2. The symbols i and j represent species of different molecular mass corresponding to the components 1 and 2 respectively. ϕ is the volume fraction, r is the chain length defined as the ratio of he molar volume of the specie, with respect of a reference volume. And g is a function depending on the temperature and composition, which is related to the interaction parameter through the following expression,

$$\chi(T, \phi_2) = g(T, \phi_2) - \frac{\partial g(T, \phi_2)}{\partial \phi_2} \phi_1 \quad (2)$$

As usual,[9] in this work $\chi(T, \phi_2)$ was defined as the product of a temperature-dependent term, D(T), and a concentration-dependent term, $B(\phi_2)$, given by

$$\chi(T, \phi_2) = D(T) \cdot B(\phi_2) = \left(A + \frac{B}{T} \right) \cdot \frac{1}{1 - c \cdot \phi_2} \quad (3)$$

where A, B and c are adjustable model parameters, which are calculated by applying the model to the experimental cloud point data.

There are several elements that determine the process of phase separation [10]:1) the cloud-point curve and the shadow curve. These curves correspondingly give the compositions of the matrix phase and the emergent phase in cloud point conditions; 2) the spinodal curve representing the stability limit of a homogeneous phase, and 3) the critical point, i.e. the point in which the cloud-point, shadow and spinodal curves coincide, representing the limit of an inversion in the separated phase. These elements can be estimated from the previous equation (1), (2) and (3) as follows:

The cloud-point and shadow curves are calculated by equating the chemical potentials of components in the matrix phase (α) and in the emergent phase (β); i.e the condition of phase equilibrium, given by,

$$\Delta\mu_{1i}^{\alpha} - \Delta\mu_{1i}^{\beta} = 0 \tag{4}$$

$$\Delta\mu_{2j}^{\alpha} - \Delta\mu_{2j}^{\beta} = 0 \tag{5}$$

By calculating the chemical potential from equation (1) and replacing in equation (4) and (5), the following expressions for calculating equilibrium compositions are obtained:

$$\begin{aligned} \sigma 1 - \Bigg[& \left(\sum_{i} \frac{\phi_{1i}^{\beta}}{r_{1i}^{\beta}} - \sum_{i} \frac{\phi_{1i}^{\alpha}}{r_{1i}^{\alpha}} \right) \\ & + \left(\sum_{j} \frac{\phi_{2j}^{\beta}}{r_{2j}^{\beta}} - \sum_{j} \frac{\phi_{2j}^{\alpha}}{r_{2j}^{\alpha}} \right) \Bigg] + \mathrm{D(T)} \\ & \cdot \left(\frac{\phi_2^{\beta^2}}{1 - \mathrm{c}\,\phi_2^{\beta}} - \frac{\phi_2^{\alpha^2}}{1 - \mathrm{c}\,\phi_2^{\alpha}} \right) = 0 \end{aligned} \tag{6}$$

$$\begin{aligned} \sigma 2 - \Bigg[& \left(\sum_{i} \frac{\phi_{1i}^{\beta}}{r_{1i}^{\beta}} - \sum_{i} \frac{\phi_{1i}^{\alpha}}{r_{1i}^{\alpha}} \right) \\ & + \left(\sum_{j} \frac{\phi_{2j}^{\beta}}{r_{2j}^{\beta}} - \sum_{j} \frac{\phi_{2j}^{\alpha}}{r_{2j}^{\alpha}} \right) \Bigg] + \mathrm{D(T)} \\ & \cdot \Bigg[\frac{1}{\mathrm{c}} \ln \left(\frac{1 - \mathrm{c}\,\phi_2^{\beta}}{1 - \mathrm{c}\,\phi_2^{\alpha}} \right) \\ & - \left(\frac{\phi_2^{\beta} \phi_1^{\beta}}{1 - \mathrm{c}\,\phi_2^{\beta}} - \frac{\phi_2^{\alpha}\,\phi_1^{\alpha}}{1 - \mathrm{c}\,\phi_2^{\alpha}} \right) \Bigg] = 0 \end{aligned} \tag{7}$$

where σ_1 and σ_2 are adjustable parameters known as separation factors.

The spinodal curve is obtained by making the second derivative of the Gibbs free energy of mixing with respect to the composition identical to zero. This leads to the equation,

$$\begin{aligned} & \frac{1}{\mathrm{r}_{1\mathrm{w}}\phi_1} + \frac{1}{r_{2\mathrm{w}}\phi_2} - \mathrm{D(T)} \left(\frac{2}{1 - \mathrm{c}\,\phi_2} \right. \\ & \qquad \left. + \frac{\mathrm{c}\,\phi_2}{(1 - \mathrm{c}\,\phi_2)^2} \right) = 0 \end{aligned} \tag{8}$$

The critical point is obtained by satisfying simultaneously that the second and third derivates of the molar Gibbs free energy of mixing with respect to the composition are zero. This condition leads to the following equation,

$$\begin{aligned} & \frac{\mathrm{r}_1\mathrm{z}}{(\mathrm{r}_{1\mathrm{w}}\phi_1)^2} - \frac{\mathrm{r}_2\mathrm{z}}{(\mathrm{r}_{2\mathrm{w}}\phi_2)^2} - \mathrm{D(T)} \left(\frac{3\,\mathrm{c}}{(1 - \mathrm{c}\,\phi_2)^2} \right. \\ & \qquad \left. + \frac{2\,\mathrm{c}^2\phi_2}{(1 - \mathrm{c}\,\phi_2)^3} \right) = 0 \end{aligned} \tag{9}$$

where $\mathrm{r}_{1\mathrm{w}}$, $\mathrm{r}_{1\mathrm{z}}$ and $\mathrm{r}_{2\mathrm{w}}$, $\mathrm{r}_{2\mathrm{z}}$ are the weight and zeta averages of the relative molar volumes of the 1 and 2 components, respectively.

To apply the model to our study systems, different considerations were taken into account and several approaches were taken.

Each system was considered to consist of two components: on the one hand, the component 1 represents the precursors of epoxy-amine system and the other, the component 2 represents PS.

Component 1, epoxy-amine precursors, was composed of three species of different sizes (ADM, MDEA and DGEBA) mixed in different stoichiometric proportions, depending on the system studied.

Component 2, PS, consisted of a distribution of molecules of different sizes. The distribution for PS was obtained from the theoretical distribution of Schulz-Zimm, given by,

$$\mathrm{W(X)} = \frac{\mathrm{Y}^{\mathrm{h}+1}}{\Gamma(\mathrm{h}+1)} \cdot \mathrm{X}^{\mathrm{h}} \cdot \exp(-\mathrm{Y} \cdot \mathrm{X}) \tag{10}$$

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

The molar volume of the monomer of PS was taken as reference volume ($V_{ref} = 100\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$)

The thermodynamic analysis was carried out in two steps: First, the model was applied to the CPCs of the systems whose amino groups provided only monoamine or diamine (PS+DGEBA/100%DA and PS+DGEBA/100%MA, which we called neat systems). From the adjustment to experimental curves, the χ of the two systems (χ_{DA}, χ_{MA}) were obtained. In a second step, these two parameters (χ_{DA}, χ_{MA}) were used to look for a general equation for χ, as a function of the MA-DA proportion in the system, that adequately fits the experimental CPCs of the different MA-DA systems.

Therefore, firstly the model was applied individually to the CPCs of the neat systems: PS+DGEBA/100%DA and PS+DGEBA/100%MA. The procedure followed was similar to that developed by Kamide et al. A system of more unknowns than equations was obtained. The strategy used to solve this problem was described in a previous paper[6] in which the phase separation for our PS+DGEBA/100% MDEA system was analysed.The χ values obtained for the neat systems are given by the following equations,

$$\chi_{MA}(T,\phi_2) = \left(A_{MA} + \frac{B_{MA}}{T}\right) \cdot \left(\frac{1}{1 - c_{MA} \cdot \phi_2}\right) = \left(0.0568 + \frac{45.478}{T}\right) \cdot \left(\frac{1}{1 - 0.6068 \cdot \phi_2}\right) \tag{11}$$

$$\chi_{DA}(T,\phi_2) = \left(A_{DA} + \frac{B_{DA}}{T}\right) \cdot \left(\frac{1}{1 - c_{DA} \cdot \phi_2}\right) = \left(0.1394 + \frac{11.753}{T}\right) \cdot \left(\frac{1}{1 - 0.669 \cdot \phi_2}\right) \tag{12}$$

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

In a second step in this analysis, we aimed to find a general equation for χ depending on the MA-DA composition of the system, which would be able to adequately describe the experimental CPCs of the different systems. The following expression for the general equation of χ was used

$$\chi(\mathrm{T},\phi_2,\%_{\mathrm{MA}}) = \left(\mathrm{A}(\%_{\mathrm{MA}}) + \frac{\mathrm{B}(\%_{\mathrm{MA}})}{\mathrm{T}}\right) \cdot \left(\frac{1}{1 - \mathrm{c}(\%_{\mathrm{MA}}) \cdot \phi_2}\right) \tag{13}$$

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

As shown, the usual form of χ was maintained. But now, the adjustable parameters: A, B and c, are not constant, they are considered depending on monoamine proportion.

Therefore, the objective was to determine equations for A, B and c, as a function of the proportion of monoamine equivalents which reasonably fit the CPC of all systems studied.

In order to do this, we looked for an equation of χ, which was only function of the χ of the neat systems (100%DA and 100%MA) and certain molecular parameters of the systems, such as the molar volume of epoxy systems.

The molar volume of different epoxy-amine precursors ($\mathrm{V}_{\mathrm{MADA}}$) written according to the fraction of monoamine equivalents ($\%_{\mathrm{MA}}$) is given by the following equation,

$$\mathrm{V}_{\mathrm{MADA}}(\%_{\mathrm{MA}}) = \frac{\frac{\mathrm{M}_{\mathrm{MA}}}{2 \cdot \rho_{\mathrm{MA}}} \cdot \%_{\mathrm{MA}} + \frac{\mathrm{M}_{\mathrm{DA}}}{4 \cdot \rho_{\mathrm{DA}}} \cdot (1 - \%_{\mathrm{MA}}) + \frac{\mathrm{M}_{\mathrm{EB}}}{2 \cdot \rho_{\mathrm{EB}}}}{\frac{1}{2} \cdot \%_{\mathrm{MA}} + \frac{1}{4} \cdot (1 - \%_{\mathrm{MA}}) + \frac{1}{2}} \tag{14}$$

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.

The Figure 2 shows the variation of molar volume of the DGEBA/MA-DA precursors as a function of the proportion of monoamine equivalents.

The molar volume of epoxy-amine system decreased as the monoamine proportion in the system increased, from the molar volume corresponding to DGEBA/100%MDEA system ($\mathrm{V}_{\mathrm{DA}} = 285.55\ \mathrm{cm}^3/\mathrm{mol}$) to the molar volume for

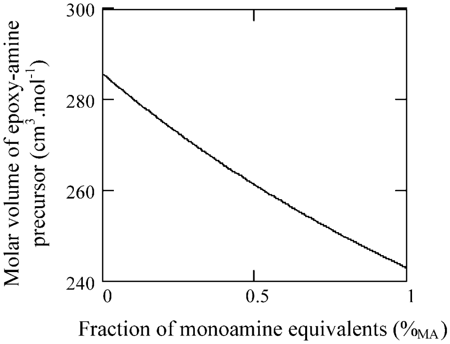


Figure 2.
Molar volume of the DGEBA/%MDEA-%ADM (1:1) precursor as a function of the fraction of monoamine equivalents (%ADM).

the DGEBA/100%ADM system (V_{MA} = 242.78 cm^3/mol).

Several equations for χ were tested, the equation that best fit the experimental CPCs was the following, given by the equation (15), (16) and (17).

$$A(\%_{MA}) = \frac{(1-\%_{MA}) \cdot A_{DA} \cdot V_{DA} + \%_{MA} \cdot A_{MA} \cdot V_{MA}}{V_{MA-DA}(\%_{MA})} \tag{15}$$

$$B(\%_{MA}) = \frac{(1-\%_{MA}) \cdot B_{DA} \cdot V_{DA} + \%_{MA} \cdot B_{MA} \cdot V_{MA}}{V_{MA-DA}(\%_{MA})} \tag{16}$$

$$c(\%_{MA}) = \left(\frac{(1-\%_{MA}) \cdot c_{DA}}{V_{DA}} + \frac{\%_{MA} \cdot c_{MA}}{V_{MA}}\right) \cdot V_{MA-DA}(\%_{MA}) \tag{17}$$

In these equations, the value of each parameter is obtained by the balanced sum of the corresponding parameters of neat systems, but modified by the ratio between the different molar volumes.

Results and Discussion

To check the validity of the equation found for χ (equation (15), (16) and (17)), the CPC obtained experimentally for the different systems were compared with the theoretical CPCs resulting from using this general χ equation in the model with the %MA values of 0, 0.25, 0.5, 0.75 and 1. The result is shows in Figure 3, where the critical point calculated for each system is too shown.

The critical point shifted to lower PS composition, from 0.163 to 0.09, as the ratio MA/DA in the system increased.

Figure 3 shows very good adjustment between the different theoretical and experimental CPCs, thus verifying the validity of the equation found for χ. The great coincidence between both theoretical and experimental curves in all the systems is surprising, as the CPCs of mixture MA-DA systems had not been used for determining χ.

This general equation for χ depending on MA-DA proportion in the system is of great importance because, on the one hand, it was obtained without making experimental adjustments, using only the molecular features of the systems and the χ of neat systems. And, on the other hand, the phase diagram for systems with any ratio MA/DA could be obtained.

The variation of χ with the proportion of PS and the MA-DA structure in the system is shown in Figure 4 for a temperature intermediate to the CPCs of studied systems.

χ increased with the MA proportion in the system for any composition of PS. Then, the greater miscibility of the systems with higher ratio MA/DA can not attributed to enthalpic factors, because χ increased when the MA proportion increased.[11] It must be only attributed to entropic factors; i.e to the reduction in size of the precursors of the epoxy-amine system when the ratio MA/DA increased, as shown in Figure 2.

In addition of the CPC and the critical point, the shadow and the spinodal curves were calculated for each system. Figure 5

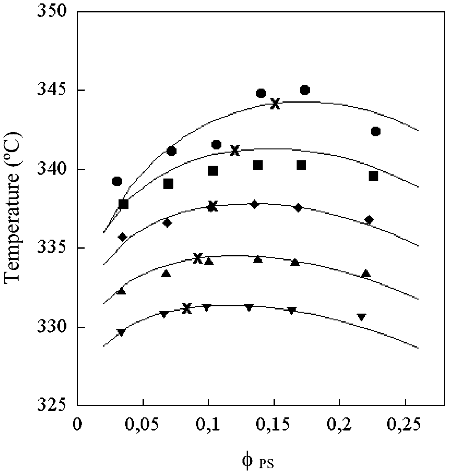


Figure 3.
Comparison of CPC obtained theoretically (–) and experimentally (symbols) for five unreacted PS + DGEBA/MDEA-ADM (1:1) systems where the proportions MA-DA were: 100%MDEA (●), 75%MDEA-25%ADM (■), 50%MDEA-50%ADM (◆), 25%MDEA-75%ADM (▲) and 100%ADM (▼). The position of critical point (X) is also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

shows these calculations for one of the intermediate systems, the PS + DGEBA/ 50%MDEA-50%ADM.

The critical point was located at a lower PS composition than the threshold point.

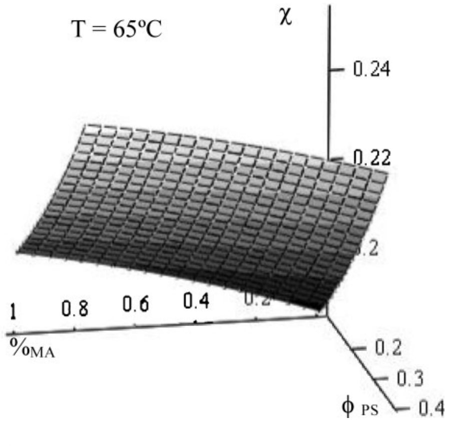


Figure 4.
Variation of the interaction parameter, χ, with the volume fraction of PS, ϕ_{PS}, and the fraction of amino equivalents provided by monoamine, $\%_{MA}$, at the temperature of 65 °C.

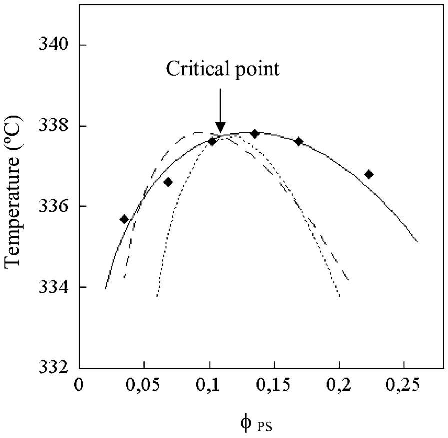


Figure 5.
Phase diagram of the unreacted DGEBA/50%MDEA-50%ADM (1:1) system modified with PS: experimental cloud point data (◆), calculated CPC (solid line), shadow curve (dashed line), spinodal curve (dotted line) and location of critical point.

Conclusion

The miscibility of PS in the precursors of several epoxy-amine systems was thermodynamically studied by means of a model based on the Flory-Huggins theory, in which the polydispersity of components and the dependence of the interaction parameter with temperature and composition, $\chi(T,\phi)$, were considered.

A total of five systems were studied, in which the amino groups were provided with a monoamine and a diamine in different proportion. All the systems studied showed an upper critical solution temperature behaviour. The miscibility of PS was different in each studied system, obtaining increased miscibility with the proportion of monoamine. This was attributed to entropic factors only, and not to enthalpic factors.

A general equation for the interaction parameter as a function of monoamine proportion was proposed, resulting to fit satisfactorily the cloud point curves of all studied systems. The general equation of χ was used to estimate the cloud-point, shadow and spinodal curves and the location of critical point of each studied system. The critical point shifted to smaller PS compositions when the proportion of monoamine in the system increased.

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