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Thermodynamic analysis of phase separation in an epoxy/polystyrene mixture

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Abstract

The phase separation process of an epoxy prepolymer based on diglycidyl ether of bisphenol A (DGEBA) with a thermoplastic polystyrene (PS) was thermodynamically studied in the frame of the Flory–Huggins theory. The thermodynamic treatment was carried out in two steps: first analysing the phase separation in cloud point conditions, and second analysing the advance of the phase separation for two compositions of 2 and 10% in volume of PS. The effect of the polydispersity of thermoplastic on phase separation was also studied. The polydispersity of PS produces a displacement of the threshold temperature to lower thermoplastic volume fraction (between 2 and 3%) and higher temperature value and the fact that the shadow curve and coexistence curves do not superimpose with the cloud point curve. Theoretical calculations of molecular weight distributions of PS at different degrees of phase separation were realized and different average molecular properties were obtained in each separated phase.

Keywords: Phase separation; Flory–Huggins equation; Thermoplastic-modified epoxy

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1. Introduction

In spite of the good properties and performances of epoxy resins, their poor resistance to the initiation and propagation of cracks is known. These brittle thermosets may be toughened by the incorporation of a rubbery or a thermoplastic second phase which be dispersed in the epoxy matrix [1].

In most cases these blends are prepared starting from a homogeneous solution of the modifier in the thermoset precursors and inducing phase separation during network formation. This mechanism is denominated polymerization induced phase separation (PIPS) [2].

The use of thermoplastic-toughened epoxies avoids usual drawbacks of rubber modification (i.e. reduction of yield strength, elastic modulus and glass transition temperature). The final properties of these modified materials are closely related with the morphologies generated in the process of phase separation [1]. These morphologies depend on the interrelation among thermodynamics (evolution of phase diagram with conversion), the competition between phase separation kinetics and polymerisation kinetics, and transformations of the polymer in the course of reaction (gelation, vitrification) [2,3].

Different polymer-solution theories have been developed during the last years, the best known is the Flory–Huggins lattice theory [4]. This theory was initially applied to monodisperse systems. A problem present in the thermodynamic analysis is the polydispersity of the components. To treat theses systems there are two ways. One way is consider the system as monodisperse or quasibinary approach. The other way take into account the polydispersity. Thus a modification in the Flory–Huggins theory is carried out where the different molecular size are represented by a molecular weight distribution function.

The aim of this paper is to make a thermodynamic analysis of phase separation in a thermoplastic epoxy prepolymer binary system using the Flory–Huggins model and to analyse the influence of the thermoplastic modifier

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polydispersity on the phase separation. First, experimental cloud-point curves (CPC) for binary system will be reported. In a second step, a thermodynamic analysis will be done, both in cloud-point conditions and when the phase separation is advancing.

Although the phase separation process in polymeric mixtures has been largely studied [5,6], there are few publications in which the effect of polydispersity has been treated thoroughly, calculating coexistence curves and molecular weight distributions. In this paper, we propose not only calculating but also to explain the evolution of the compositions and the molecular weight distributions in both phases as the phase separation advances.

2. Experimental

2.1. Materials

The epoxy prepolymer is based on diglycidyl ether of bisphenol A (DGEBA) whereas the thermoplastic modifier is a polystyrene (PS) with a polydispersity index equal to 1.64. These materials were commercial products and were used as received, without purification. Chemical structures, molar masses and densities of the material are indicated in Table 1 and Fig. 1.

When the polydispersity of some component of the system is taken into account in the thermodynamic analysis, it will be necessary to know its distribution species. The molecular weight distribution of PS is obtained by using a Schulz–Zimm (SZ) equation [7]

$$W(X) = \frac{Y^{h+1}}{\Gamma(h+1)} X^{h} \exp(-YX) \qquad (1)$$

where $W(X)$ is the mass fraction of the X-mer, $h = [(\bar{X}_w/\bar{X}_n) - 1]^{-1}$, $Y = h/\bar{X}_n$, and Γ is the gamma function. For our PS, $\bar{X}_n = 1346$, $\bar{X}_w = 2212$, $h = 1.556$ and $Y = 1.156 \times 10^{-3}$.

PS/DGEBA blends were prepared at room temperature using methylene chloride as solvent. This was evaporated during 1 day at room temperature followed by several hours at 140 °C.

2.2. Techniques

Cloud-point temperatures, T_{cp}, of PS/DGEBA mixtures were determined using a light transmission device (He–Ne laser beam) described elsewhere [8]. Temperature was increased until a homogeneous solution was obtained (140 °C), kept constant during several minutes and then decreased at a cooling rate of 2 K min^{-1}. At high temperatures, the polymer mixtures were homogeneous and therefore transparent; but when temperature was decreased the mixtures became turbid due to the phase separation. It leads to diminish the intensity of transmitted light. T_{cp} was determined at the onset temperature of the light transmission decrease (Fig. 2).

Table 1
Characteristics of the materials

	Supplier	Molar mass (g/mol)	Density (g/cm^3)
DGEBA	Ciba-Geigy Araldite GY260	376; $n = 0.13$	1.20
PS	Aldrich	$M_n = 140{,}000$; $M_w = 230{,}000$	1.04

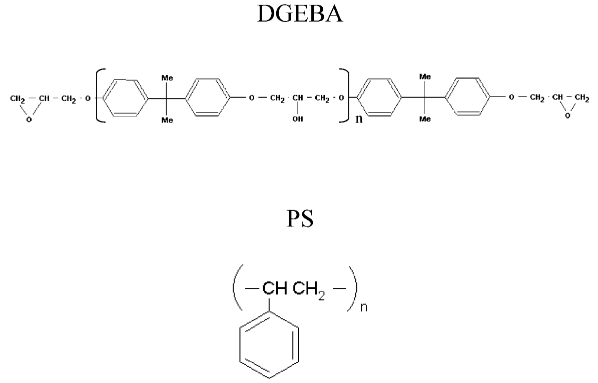

Fig. 1. Chemical structures of the epoxy prepolymer (DGEBA) and polystyrene (PS).

2.3. Thermodynamic analysis

The Flory–Huggins theory will be used to study the phase separation in polymer mixtures. The Flory–Huggins equation written in term of the Gibbs free energy of mixing per mol of unit cells, ΔG, for a binary system, is given by Ref. [9]

$$\Delta G = RT\left(\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi\phi_1\phi_2\right) \qquad (2)$$

where the subscript 1 stands for the epoxy, the subscript 2 represents the thermoplastic modifier, R is the gas constant, T is the absolute temperature, ϕ is the volume fraction, r_1 and r_2 are the ratios of the molar volumes of both components, defined on the basics of the number average

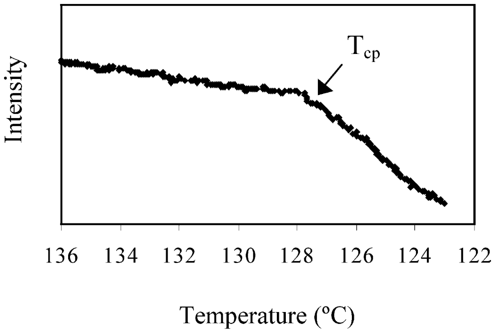

Fig. 2. Determination of the cloud point temperature.

molecular weight, with respect of the reference volume (V_R) normally defined as the molar volume of the smallest component (the epoxy prepolymer in the present case), i.e.

$$r_1 = \frac{V_{\mathrm{DGEBA}}}{V_R} = 1 \tag{3}$$

$$r_2 = \frac{V_{\mathrm{PS}}}{V_R} = 429.63 \tag{4}$$

and χ is the interaction parameter, which can not be determined experimentally and it is calculated applying the theory to the experimental data. In general, for an unreacted binary mixture, χ must be considered as a function of temperature and composition [10]. Here χ will be considered only as a function of the temperature. The fit with the thermodynamic model will determine whether a $\chi(T)$ relationship is enough for the description or if it is necessary to include the composition dependence.

Starting from this equation, several elements that determine the phase diagram of a binary polymer mixture can be calculated [6,11].

2.3.1. Binodal curve

This curve limits the zone of temperatures where the system is immiscible giving the temperatures and the compositions of the phases that are in equilibrium. It is defined by the equality of the chemical potentials of the components of the system in each one of the phases, i.e.

$$\Delta\mu_1^{\alpha} = \Delta\mu_1^{\beta} \tag{5}$$

$$\Delta\mu_2^{\alpha} = \Delta\mu_2^{\beta} \tag{6}$$

where α and β represent the matrix and emergent phases in equilibrium, respectively. These equations represent thermodynamic requirements for liquid–liquid phase at the cloud-point or coexistence conditions, under constant temperature and pressure.

2.3.2. Spinodal curve (SPC)

This curve represents the stability limit of the homogeneous mixture. Inside this limiting curve the mixture must be separated in two phases. The SPC thermodynamic requirement, at constant pressure and temperature, is that the second derivative of the Gibbs free energy with respect to the composition, be identical to zero, i.e.

$$\frac{\partial^2 \Delta G}{\partial \phi_2^2} = 0 \tag{7}$$

For a binary mixture of two polydisperse polymers the SPC is given by Eq. (8)

$$\frac{1}{r_{1\mathrm{w}}\phi_1} + \frac{1}{r_{2\mathrm{w}}\phi_2} - 2\chi = 0 \tag{8}$$

where $r_{i\mathrm{w}}$ is the weight average relative molar volume of the i component.

2.3.3. Critical point

It is the point in which the binodal and spinodal curves coincide. The matrix phase and the emergent phase have the same composition in the critical point; and, at composition of modifier higher than the critical composition, an inversion of phase is produced. 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.

$$\frac{\partial^2 \Delta G}{\partial \phi_2^2} = \frac{\partial^3 \Delta G}{\partial \phi_2^3} = 0 \tag{9}$$

The expression for a binary mixture of two polydisperse polymers is

$$\frac{r_1 z}{(r_{1\mathrm{w}}\phi_1)^2} - \frac{r_2 z}{(r_{2\mathrm{w}}\phi_2)^2} = 0 \tag{10}$$

where $r_{i\mathrm{w}}$ and r_{iz} are the weight and zeta averages of the relative molar volume of the i component.

For monodisperse species: $r_{in} = r_{i\mathrm{w}} = r_{iz}$

3. Results and discussion

The thermodynamic treatment was carried out in two different steps: first analysing the phase separation in cloud point conditions for compositions less than 30% in volume of PS, and second analysing the advance of phase separation when temperature of mixtures decreases for compositions of 2 and 10% in volume of PS.

To analyse the effect of thermoplastic polydispersity on phase separation, the analysis was realized in two ways: considering PS as a monodisperse specie and on the other hand taking account its polydispersity and then the results were compared. In the monodisperse case, all molecules of PS were considered equal with a molecular weight equal to the number average molecular weight. In the polydisperse case, the PS was characterized by a molecular weight distribution given by the Shulz–Zimm distribution. The DGEBA was always taken as monodisperse.

Numerical methods to analyze and calculate cloud point curves, spinodal curves, critical point and coexistence curves in mixtures have been proposed and discussed in the literature [5,12–19]. The procedure developed by Kamide et al. for quasibinary solutions [20] was used in this study.

3.1. Cloud point conditions

Fig. 3 shows the T_{cp} obtained experimentally for DGEBA/PS mixtures at different proportions. These temperatures determine the experimental cloud points curve (CPC). Our system is characterized by an upper critical solution temperature (UCST) behavior (i.e. miscibility increases with temperature).

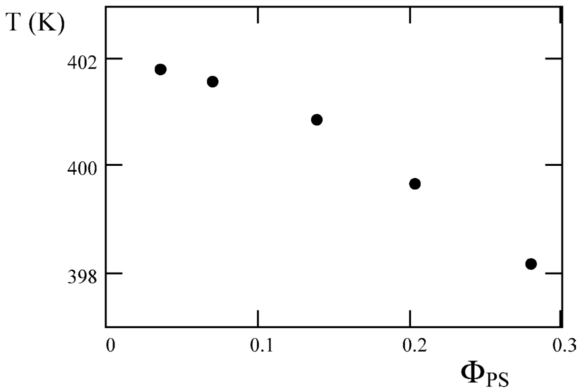

Fig. 3. Experimental cloud point temperatures vs volume fraction of PS for PS/DGEBA system.

The thermodynamic treatment requires the application of the phase equilibrium condition to each component, given by the following equations:

$$\Delta\mu_1^\alpha = \Delta\mu_1^\beta \tag{11}$$

$$\Delta\mu_{2j}^\alpha = \Delta\mu_{2j}^\beta \tag{12}$$

where $2j$ represents each one of the species of different molecular weight corresponding to the second component (PS).

The chemical potentials ($\Delta\mu$) may be obtained from Eq. (2) by the usual procedures [21]. Replacing $\Delta\mu$ in the expressions (11) and (12) leads to the equation for equilibrium calculation. For our system, the expressions are

$$\frac{1}{r_1}\ln\frac{\phi_1^\beta}{\phi_1^\alpha} - \left[\left(\frac{\phi_1^\beta-\phi_1^\alpha}{r_1}\right)+\left(\frac{\phi_2^\beta}{\bar{r}_{2n}^\beta}-\frac{\phi_2^\alpha}{\bar{r}_{2n}^\alpha}\right)\right] + \chi\left(\phi_2^{\beta^2}-\phi_2^{\alpha^2}\right) = 0 \tag{13}$$

$$\sigma_2 - \left[\left(\frac{\phi_1^\beta-\phi_1^\alpha}{r_1}\right)+\left(\frac{\phi_2^\beta}{\bar{r}_{2n}^\beta}-\frac{\phi_2^\alpha}{\bar{r}_{2n}^\alpha}\right)\right] + \chi\left(\phi_1^{\beta^2}-\phi_1^{\alpha^2}\right) = 0 \tag{14}$$

σ_2 is the separation factor, its value determines the fractionation extension of each molecular specie of the thermoplastic component between the two equilibrium phases. At a given pressure and temperature, σ_2, has the same value for all the $2j$ molecular species included in the thermoplastic distribution function. Its definition is:

$$\sigma_2 = \frac{1}{r_{2j}}\ln\frac{\phi_{2j}^\beta}{\phi_{2j}^\alpha} \tag{15}$$

In addition to the Eqs. (13) and (14), a mass balance for each of the two phases must be included in this analysis, i.e.

$$\phi_1^\alpha = 1-\phi_2^\alpha \tag{16}$$

$$\phi_1^\beta = 1-\phi_2^\beta \tag{17}$$

In cloud point conditions, that represent the onset of phase separation in the system, only a differential volume fraction of the emergent phase (R) is generated. Then, by making $R\to 0$, the following is obtained:

$$\phi_2^\alpha = \phi_2^0 \tag{18}$$

$$\phi_2^\beta = \sum_j \phi_2^\alpha w(r_{2j})\exp(\sigma_2 r_{2j}) \tag{19}$$

Besides

$$\frac{\phi_2^\alpha}{\bar{r}_{2n}^\alpha} = \sum_j \phi_2^\alpha \frac{w(r_{2j})}{r_{2j}} \tag{20}$$

$$\frac{\phi_2^\beta}{\bar{r}_{2n}^\beta} = \sum_j \phi_2^\alpha \frac{w(r_{2j})}{r_{2j}}\exp(\sigma_2 r_{2j}) \tag{21}$$

Then, by replacing Eqs. (16)–(21) in Eqs. (13) and (14), a system of two equations in two unknowns (σ_2, χ) is obtained and numerically solved for each experimental point.

In both treatments (mono and polydisperse) it was possible describe the dependence of calculated interaction parameters with experimental T_{cp} by means of a single linear relationship (Fig. 4) given by the following equations:

$$\text{Monodisperse PS} \Rightarrow \chi = -7.9275 + 3405.5\frac{1}{T} \tag{22}$$

$$\text{Polydisperse PS} \Rightarrow \chi = -8.9595 + 3817\frac{1}{T} \tag{23}$$

Substituting the respective dependence $\chi(T)$ in Eqs. (8), (13), (14) and (19) the spinodal curve and the temperatures (T_{cp}) and compositions of matrix and emergent phases (ϕ_2^α and ϕ_2^β) in cloud point conditions were obtained for each treatment. The critical points obtained by mean of Eq. (10) were, respectively, $\phi_{\mathrm{PS\ c\ mono}}=0.046$ and $\phi_{\mathrm{PS\ c\ poly}}=0.043$, for mono and polydisperse cases. The phase diagrams for both treatments of PS are shown in Figs. 5 and 6.

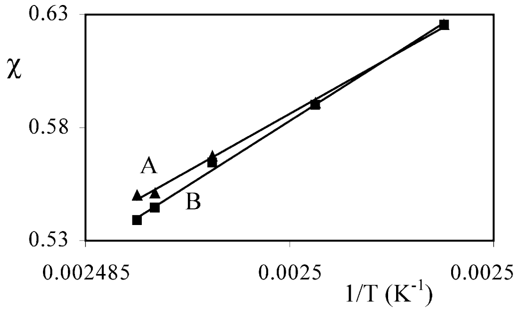

Fig. 4. Interaction parameter calculated vs $1/T_{cp}$ experimental. Curve A: PS monodisperse treatment; curve B: PS polydisperse treatment.

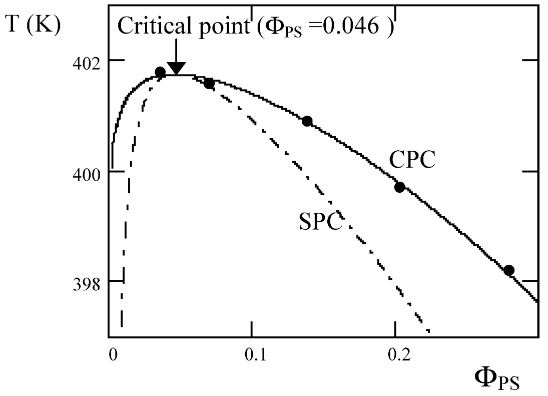

Fig. 5. Phases diagram of monodisperse PS/DGEBA system: experimental cloud point data (●), calculated cloud point curve (CPC), spinodal curve (SPC) and location of critical point.

At sight of the phase diagrams obtained, we can say that in both situations, the cloud point curve obtained with the thermodynamic model fits well to the experimental CPC, what means that a single $\chi(T)$ relationship is enough for the description and it is not necessary to include the composition dependence.

When polydispersity is taken account a new curve appears in the phase diagram, named shadow curve (SC). The shadow curve gives the compositions of the segregated phase (ϕ_2^β) in cloud point conditions. The compositions of the matrix phase (ϕ_2^α) are located on the cloud point curve. On the other side, when species are taken as monodisperse the compositions of both phases, matrix and emergent, are located on the CPC.

Comparing both diagrams, it was found that there is not great difference in the location of critical point. The principal variation is in the location of the miscibility gap (threshold temperature), so whereas in the monodisperse case the threshold temperature coincided with critical point, for the polydisperse case, it was displaced to lower modifier compositions (2–3% in volume) and higher temperature values. We can say that although the effect of polydispersity must be taken into account to fit experimental cloud point curves, the monodisperse assumption gives a reasonable approximation when macroscopic separation is considered.

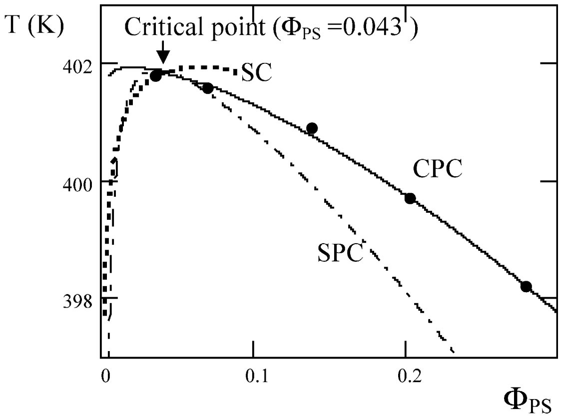

Fig. 6. Phases diagram of polydisperse PS/DGEBA system: experimental cloud point data (●), calculated cloud point curve (CPC), shadow curve (SC), spinodal curve (SPC) and location of critical point.

When polydispersity is considered, a thermodynamic calculation of the molecular weight distributions for both phases at different initial compositions can be realized. This calculation is shown in Fig. 7.

Fig. 7 shows that, the distribution of PS in the matrix phase is equal to the distribution in the homogeneous blend for any initial composition because in cloud point conditions the volume of emergent phase is negligible respect the volume of matrix phase and then only a differential PS fraction is present in the emergent phase. However, the distribution of PS in the emergent phase varies depending on the initial volume fraction of PS.

At the critical point, $\phi_{PS\ c} = 0.043$, as matrix and emergent phase have the same compositions then their distributions will be equal too and equals to the one of the homogeneous mixture. The critical point supposes the limit of a phase inversion, then:

- For initial compositions of PS less than critical point, $\phi_{PS}^0 < \phi_{PS\ c}$, the emergent phase is rich in PS and shows a broad distribution rich in high molecular weight of PS species.
- For initial compositions of PS greater than critical point, $\phi_{PS}^0 > \phi_{PS\ c}$, the emergent phase is poor in PS and, therefore, shows a narrow distribution rich in low molecular weight PS species.

3.2. Coexistence conditions

From a thermodynamic point of view the advance of phase separation for two initial compositions of 2 and 10% in volume of PS corresponding to lower and higher compositions than the critical point composition, respectively, is studied.

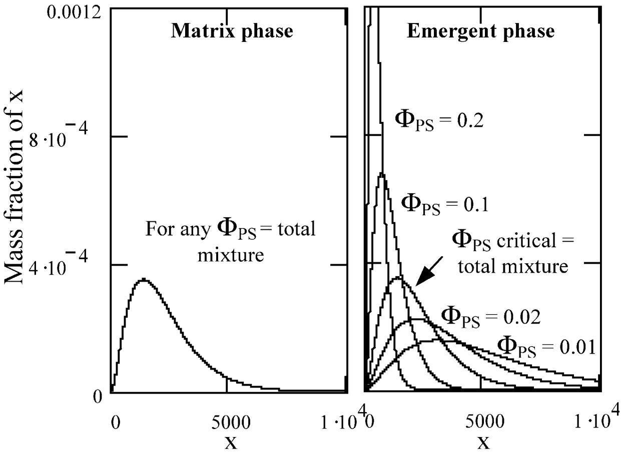

Fig. 7. Calculated molecular weight distributions for PS in the matrix and emergent phases in function of their degree of polymerization at different initial compositions.

Since the PS/DGEBA blend has an UCST behaviour miscibility increase with temperature and therefore when temperature decrease the phase separation advances. In this case, it is assumed that both phases attain equilibrium for every temperature.

The thermodynamic treatment in these conditions is similar to the previous case (i.e. cloud point conditions) and the same Eqs. (13) and (14) was used. In this case χ is known. The dependences $\chi(T)$ calculated in the previous section, given by Eqs. (22) and (23) corresponding, respectively, to mono and polydisperse situation, were utilized. When phase separation progress, the volume fraction of emergent phase, R, no longer is negligible and the compositions of the phase in equilibrium are given by:

$$\phi_2^{\alpha} = \sum \frac{\phi_2^0 w(r_{2j})}{R[\exp(\sigma_2 r_{2j}) - 1] + 1} \tag{24}$$

$$\phi_2^{\beta} = \sum \frac{\phi_2^0 w(ri)\exp(\sigma_2 r_{2j})}{R[\exp(\sigma_2 r_{2j}) - 1] + 1} \tag{25}$$

Moreover

$$\frac{\phi_2^{\alpha}}{\bar{r}_{2n}^{\alpha}} = \sum \frac{\phi_2^0 (w(r_{2j})/r_{2j})}{R[\exp(\sigma_2 r_{2j}) - 1] + 1} \tag{26}$$

$$\frac{\phi_2^{\beta}}{\bar{r}_{2n}^{\beta}} = \sum \frac{\phi_2^0 (w(r_{2j})/r_{2j})\exp(\sigma_2 r_{2j})}{R[\exp(\sigma_2 r_{2j}) - 1] + 1} \tag{27}$$

where ϕ_2^0 is the volume fraction of PS present in the initial mixture, in our case $\phi_{\mathrm{PS}}^0 = 0.02$ and $\phi_{\mathrm{PS}}^0 = 0.1$.

Then, by replacing Eqs. (16), (17) and (22)–(27) in Eqs. (13) and (14), a system of two equations with two unknowns was obtained. The system was solved for the two initial compositions at different temperatures, obtaining at each temperature R and σ_2. The compositions of each phase in equilibrium at different temperatures were then obtained from the Eqs. (24) and (25).

The evolution of volume fraction of the dispersed phase (R) as the phase separation progress was calculated and it is shown in Fig. 8. This evaluation was carried out taking into account the polydispersity of PS.

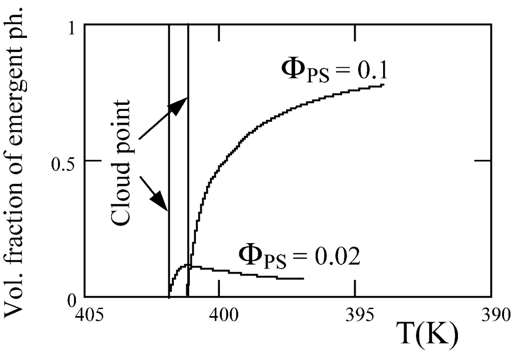

Fig. 8. Volume fraction of the emergent phase as a function of the temperature in the system PS/DGEBA for two initial compositions, $\phi_{\mathrm{PS}}^0 = 0.02$ and $\phi_{\mathrm{PS}}^0 = 0.1$.

Fig. 8 shows a fast increase in R in the temperature range near the cloud point for both compositions. In the case of the composition of 10% the value of R reached is considerably higher than the value reached at 2%. This could be because for the composition of 2% the emergent phase is the rich in PS whereas for the composition of 10% the emergent phase is the rich in epoxy and as the volume of epoxy is much larger than the volume of PS in the mixtures at these compositions, then it is reasonable that the volume of the phase rich in epoxy larger than the volume of phase rich in PS when phase separation is macroscopic. In both mixtures an almost constant value at low temperatures is reached; in the case of the mixture to 2%, R decreases slightly after going through a maximum.

The phase diagrams are obtained for both treatments mono and polydisperse (Figs. 9 and 10).

At a certain initial composition ϕ_2^0, the compositions of each phase in equilibrium, ϕ_2^{α}, ϕ_2^{β}, at different temperatures or at different degrees of phase separation are given by their corresponding coexistence curves.

In the monodisperse treatment (Fig. 9) the coexistence curves for any initial composition are located on the cloud point curve. On the contrary, in the polydisperse treatment (Fig. 10) the coexistence curves differ with initial composition and are located between the cloud point and shadow curves.

Usually, phase diagrams for quasibinary system (i.e. taking in account the polydispersity of the species) are presented using two sets of coordinates T–ϕ. They are different projections of the T–P–ϕ hypersurfaces representing states of polymer fractionation during the liquid–liquid macrophase separation of these systems.

In both treatments it is observed that as phase separation progress the phases are becoming purified, getting rich in PS the phase rich in PS and getting rich in epoxy the phase rich in epoxy. This is a consequence of a decrease of miscibility

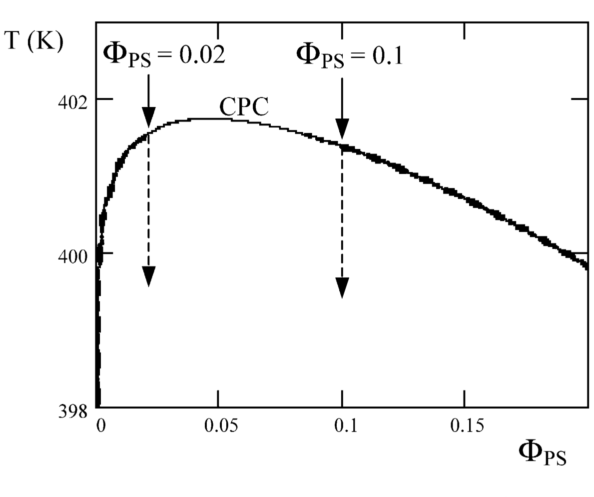

Fig. 9. Monodisperse PS/DGEBA system: coexistence curves for two initial volume fractions ϕ_{PS}^0, they are located on the cloud point curve (CPC).

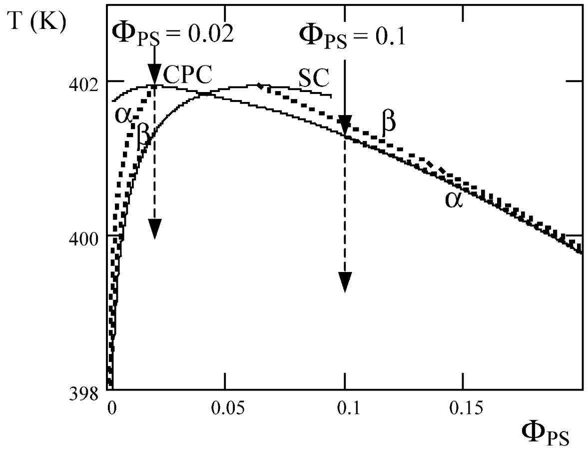

Fig. 10. Polydisperse PS/DGEBA system: coexistence curves (dotted lines) for two initial volume fractions ϕ^0_{PS}, cloud point curve (CPC) and shadow curve (SC). *α* and *β* represent the matrix and emergent phases, respectively.

when temperature decreases. The fact that phases are purifying could explain the light decrease of *R* when advance the phase separation for $\phi^0_{PS}=0.02$, (Fig. 8). For this composition although the emergent phase is the rich in PS the proportion of epoxy in this phase is very big, and then as phase separation progress, in the emergent phase it is produced in addition to the incorporation molecules of PS, the departure to a great extent of molecules of epoxy that initially had incorporated to this phase.

Molecular weight distributions of PS in both phases at different temperatures have been calculated for the initial compositions of 2 and 10% in volume of PS and they are shown in Figs. 11 and 12, respectively.

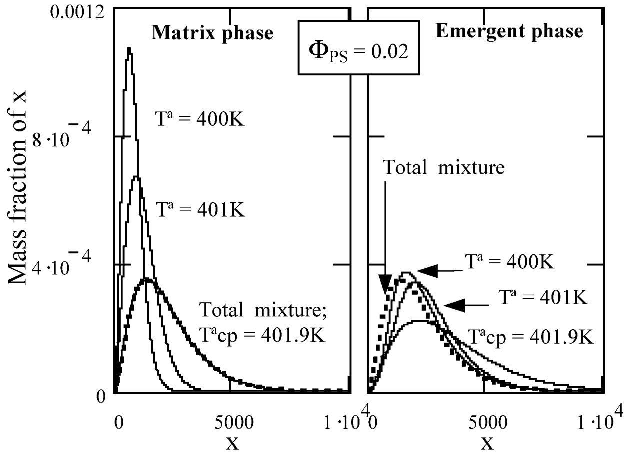

Fig. 11. Calculated molecular weight distributions of PS in the matrix and emergent phases at different temperatures for an initial volume fraction of PS $\phi^0_{PS}=0.02$. The dotted line represents the distribution of PS in the homogeneous mixtures.

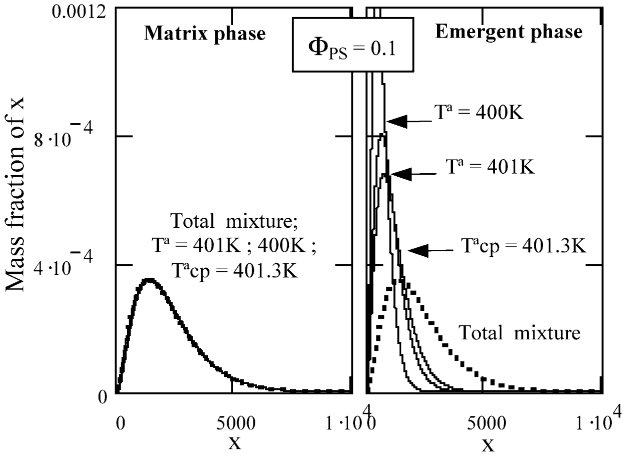

Fig. 12. Calculated molecular weight distributions of PS in the matrix and emergent phases at different temperatures for an initial volume fraction of PS $\phi^0_{PS}=0.1$. The dotted line represents the distribution of PS in the homogeneous mixtures.

The Figs. 11 and 12 allow us to know the thermodynamic evolution of the molecular weight distributions of PS. As phase separation progress the distributions of PS in the phases rich in epoxy (i.e. the matrix phase for composition $\phi^0_{PS}=0.02$ and the emergent phase for composition $\phi^0_{PS}=0.1$) are more and more narrow containing less weightly molecules. This could be explained because when decreasing temperature and becoming the blend less miscible, this phase will have less capacity to dissolve the most weightly molecules of PS.

As phase separation progress, the distributions of PS in the phase rich in PS (i.e. the emergent phase for composition $\phi^0_{PS}=0.02$ and the matrix phase for $\phi^0_{PS}=0.1$) are becoming equal to the distribution in the homogeneous blend. This could be explained because less and less weightly molecules of PS are incorporated coming from the phase rich in epoxy. For the composition $\phi^0_{PS}=0.1$, the distribution of PS in the matrix phase is equal to the distribution in the homogeneous mixture at cloud point condition and practically it does not vary as separation progress because the proportion of PS in the emergent phase is negligible.

4. Conclusions

A thermodynamic analysis of the phase separation process in PS/DGEBA binary system was performed in the frame of a Flory–Huggins theory. First, studying the separation in cloud point conditions for compositions less than 30% in volume of PS; and later studying the advance of the separation as the temperature of the mixtures diminishes for two compositions of 2 and 10% in volume of PS. A single relationship between the interaction parameter and temperature, $\chi(T)$, could reproduce experimental cloud point curve of mixtures of PS/DGEBA.

In order to analyse the effect of the polydispersity of PS on the separation, the treatment was done of two ways: on the one hand considering PS as a monodisperse component and on the other hand taking into account its polydispersity. It was found that, although the effect of polydispersity must be taken into account to realize a more exact analysis, the monodisperse assumption gives a reasonable approximation when macroscopic separation is considered.

In our PS/DGEBA system the consideration of the actual polydispersity of PS shifted the threshold temperature to lower thermoplastic volume fraction (between 2 and 3%) and higher temperature value (i.e. the system became more incompatible than is expected by assuming monodisperse PS). The effect of the polydispersity of PS caused also, that the curve that join the possible compositions of the emergent phase in cloud point conditions did not superimpose with the cloud point curve (CPC) generating a new curve known like shadow curve (SC). In addition, the polydispersity of PS made that the coexistence curves, curves that given the compositions of the phases in equilibrium at different stages of macrophase separation for a determined initial composition, did not overlap with the CPC either.

Molecular weight distributions of PS in each phase in cloud point conditions were calculated for different initial compositions. A differentiation between the distributions in the matrix and emergent phases was obtained. In cloud point conditions, the distributions of PS in the matrix phase were equal independently of the initial composition, whereas in the emergent phase they depended to a great extent on the initial composition. The thermoplastic polydispersity affect the liquid–liquid phase diagram causing molecular fractionation. As a consequence, the thermoplastic component has different average molecular properties in each equilibrium phase.

Moreover, the evolution of the molecular weight distributions as phase separation advances was calculated for the mixtures of compositions 2 and 10% in volume of PS. The distribution of PS in the PS-rich phase were becoming equal to the distribution in the homogeneous mixture, and the distributions of PS in the epoxy-rich phase were more and more narrow with lighter molecules. It could be because when separation advances mixture becomes more immiscible, and then the epoxy has minor capacity to dissolve the most weightly molecules of PS, which causes the migration of these molecules towards the PS-rich phase.

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References

[1] Riew CK, Kinloch AJ. Toughened plastic I: science and engineering. Advances in chemistry series. vol. 233. Washington, DC: American Chemical Society; 1993.

[2] Williams RJJ, Rozenberg BA, Pascault JP. Adv Polym Sci 1997;128: 95.

[3] Pascault JP, Williams RJJ. In: Paul DR, Bucknall CB, editors. Polymer blends, vol. 2. New York: Wiley; 2000. p. 379–415 [chapter 13].

[4] Flory JP. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.

[5] Borrajo J, Riccardi CC, Moschiar SM, Williams RJJ. In: Riew CK, editor. Rubber-toughened plastics. Advances in chemistry series, vol. 222. Washington, DC: American Chemical Society; 1989. p. 319 [chapter 14].

[6] Paul DR, Newman S. Polymer blends. vol. 1. California: Academic Press; 1987.

[7] Peebles LH. Molecular weight distributions in polymers. New York: Interscience, Wiley; 1971.

[8] Verchére D, Pascault JP, Sautereau H, Moschiar SM, Riccardi CC, Williams RJJ. Polymer 1989;30:107.

[9] Roe RJ, Zin WCH. Macromolecules 1980;13:1221.

[10] Kamide K, Matsuda S, Shirataki H. Eur Polym J 1990;26:379.

[11] Auad ML, Aranguren MJ, Borrajo J. Polymer 2001;42:6503.

[12] Kamide K. In: Jenkis AD, editor. Thermodynamics of polymer solutions: phase equilibria and critical phenomena. Polymer sience library, vol. 9. Amsterdam: Elsevier; 1990.

[13] Koningsveld R, Staverman AJJ. Polym Sci, Part A 1968;6:308.

[14] Solc K. Macromolecules 1970;3:665.

[15] Margit T. Rätzsch. Makromol Chem Macromol Symp 1987;12:101.

[16] Mumby SJ, Sher P. Macromolecules 1994;27:689.

[17] Riccardi CC, Borrajo J, Williams RJJ, Girard-Reydet E, Sautereau H, Pascault JP. J Polym Sci, Part B 1996;34:349.

[18] Riccardi CC, Borrajo J, Williams RJJ. Polymer 1994;35:5541.

[19] Ruseckaite RA, Williams JJ. Polym Int 1993;30:11.

[20] Kamide K, Matsuda S, Shirataki H. Eur Polym J 1990;26:379.

[21] Vázquez A, Rojas AJ, Adabbo HE, Borrajo J, Williams RJJ. Polymer 1987;28:1156.