Phase Diagrams of Blends of Poly(phenylene ether), Polystyrene, and Diglycidyl Ether of Bisphenol A: Influence of the Molar Mass of Poly(phenylene ether)

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ABSTRACT: Phase diagrams of ternary blends of poly-(phenylene ether) (PPE, M_n = 1.2 and 12 kg mol^{-1}), polystyrene (PS, M_n = 22.5 kg mol^{-1}), and diglycidyl ether of bisphenol A (DGEBA) were experimentally obtained in an extended range of temperatures and fitted with the Flory–Huggins model using three binary interaction parameters. A significant increase in miscibility together with the appearance of an immiscibility loop was found for PPEs with M_n values comprised in the range between 1 and 10 kg mol^{-1}. This enables us to obtain initial homogeneous solutions in regions of high DGEBA concentrations, a possibility that was not previously reported for this ternary blend. This opens new possibilities for the toughening of epoxies replacing a single thermoplastic with a thermoplastic blend where both components (PS and PPE) are completely miscible. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1742–1747, 2006

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INTRODUCTION

Blends of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide), usually called poly(phenylene ether) (PPE), represent one of the few combination of polymers that are miscible over the whole composition range.[1–6] They have a negative heat of mixing[7] and also a negative volume of mixing[8] that evidence a favorable specific interaction. Processing of pure PPE is extremely difficult because of the small temperature window comprised between the glass transition and the decomposition temperature. At temperatures where its viscosity is low enough to facilitate processing, it undergoes decomposition. Blending PPE with PS leads to a decrease in the glass transition temperature and enables processing at lower temperatures. The PPE–PS blend forms the basis of a set of engineering thermoplastics.

In recent years, another way to facilitate processing of intractable polymers has been devised.[9–11] It consists of preparing a relatively concentrated solution of the polymer in a reactive solvent, the most typical one being an epoxy monomer based on diglycidyl ether of bisphenol A (DGEBA) together with a suitable hardener. Phase separation takes place in the course of the epoxy polymerization leading to a material consisting of a dispersion of crosslinked epoxy particles in a PPE matrix. In contrast to the use of miscible PS as a processing aid, the advantageous thermal and mechanical properties of pure PPE are recovered. Tuning of the final morphology and resulting properties can be achieved by adding some PS to the initial solution, to control the initial viscosity.[12] But, as both PPE and PS are only partially miscible with the DGEBA monomer, it is necessary to use a ternary phase diagram of the initial solution to select adequate processing conditions.[12] This ternary phase diagram must be regarded as a general basis for the analysis of the initial miscibility. The influence of the addition of a particular hardener could then be analyzed in a subsequent step.

The aim of this study is to investigate the possibility of processing these ternary blends in the region of high epoxy concentrations. Polymerization-induced phase separation starting from these solutions should lead to a dispersion of PPE/PS thermoplastic domains in an epoxy matrix or to bicontinuous phases, the latter being a desired morphology for toughening purposes.[13] The interest in replacing a single thermoplastic by a blend of two different thermoplastics lies in the possibility of modulating the properties of the thermoplastic phase by varying the ratio and molar
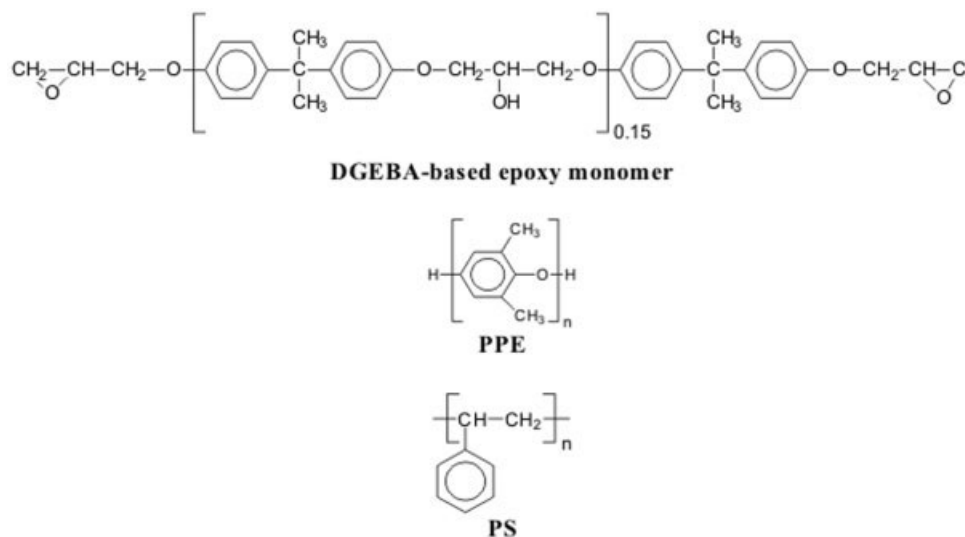
Figure 1 Chemical structures of the epoxy monomer and the polymers.

masses of the miscible thermoplastics. However, increasing the epoxy amount in the ternary blend rapidly leads to the immiscibility region.[12] A possible way to get a homogeneous solution with high DGEBA fractions is to decrease the molar mass of one of the thermoplastics. As PPE is less soluble with DGEBA than PS,[13] it was decided to study the effect of varying the molar mass of PPE in the phase diagrams of ternary blends. Two commercial PPEs (M_n = 1.2 and 12 kg mol^{-1}) and a single PS (M_n = 22.5 kg mol^{-1}) were used. Overall experimental trends were reasonably predicted using the Flory–Huggins (FH) model with three interaction parameters, one for each pair of components, and considering both polymers as monodisperse components. The FH model was then used to predict the influence of the PPE molar mass on the phase diagrams of PPE–PS–DGEBA blends. The possibility of obtaining homogeneous blends in the region of high DGEBA concentrations is discussed.

EXPERIMENTAL

Materials

Chemical structures of the polymers and the epoxy monomer are shown in Figure 1, and their characteristics are indicated in Table I.

Preparation of blends

Blends were prepared using CHCl$_3$ to aid the mixing process. The solvent was eliminated during 4 days under atmospheric pressure and one night under vacuum, at room temperature. Samples were then heated to 190°C, kept at this temperature for several minutes, and transferred to the cloud-point device.

Cloud-point curves

Cloud-point curves for binary and ternary blends were obtained using both a light transmission device and transmission optical microscopy (TOM) provided with a hot stage (Mettler FP82HT). Blends were kept several minutes at a temperature above the cloud-point curve and then cooled (at 1°C min^{-1} in the hot stage and at a variable rate comprised between 4 and 1°C min^{-1} in the light transmission device), down to the cloud-point temperature. Measurements were performed several times leading to reproducible values of cloud-point temperatures.

For the case of PPE–PS–DGEBA blends, cloud-point temperatures were obtained for constant values of DGEBA mass fractions, varying the relative amounts of PPE and PS. For example, a set of compositions

TABLE I
Characteristics of the Epoxy Monomer and the Polymers

Name	Supplier/Product	M_n (g mol^{-1})	M_w (g mol^{-1})	Density (g cm^{-3})
DGEBA	Huntsman (LY556)	382.6		1.17
PPE (HMW)	General Electric (Blendex 820)	12,000	25,000	1.06
PPE (LMW)	General Electric (SA 120)	1,200	2,520	1.06
PS	Polymer Source	22,500	28,800	1.08

containing 60 wt % DGEBA and 40 wt % PPE + PS (in relative proportions varying from pure PPE to pure PS) was prepared. Cloud-point temperatures (T_{cp}) of these solutions were experimentally determined leading to a curve of T_{cp} as a function of the relative amounts of PPE and PS. A set of these curves was obtained for different constant values of the initial DGEBA mass fraction. Interpolating in this set of curves at a particular temperature enabled to obtain cloud-point compositions belonging to the corresponding isotherm. This led to the experimental points plotted in the triangular phase diagrams.

RESULTS AND DISCUSSION

Phase diagrams and interaction parameters of the binary systems

The free energy per unit volume, ΔG, of a blend of components i and j, may be calculated in terms of the FH model.

$$(V_r/RT)\Delta G = (\phi_i/r_i)\ln\phi_i + (\phi_j/r_j)\ln\phi_j$$
$$+ g_{ij}(T, \phi j)\phi_i\phi_j \quad (1)$$

where R is the gas constant, V_r is a reference volume, ϕ represents a volume fraction, and r is the ratio of the molar volume of the corresponding component with respect to the reference volume. The first two terms in the right-hand side represent the combinatorial contribution to free energy (entropic contribution) while the last term represents the excess contribution to free energy. In this term, the heat of mixing plus other noncombinatorial effects are lumped in an empiric interaction parameter between the constitutional repeating units of both components, $g_{ij}(T, \phi_j)$, with the factor $\phi_i\phi_j$ accounting for the frequency of i–j contacts.
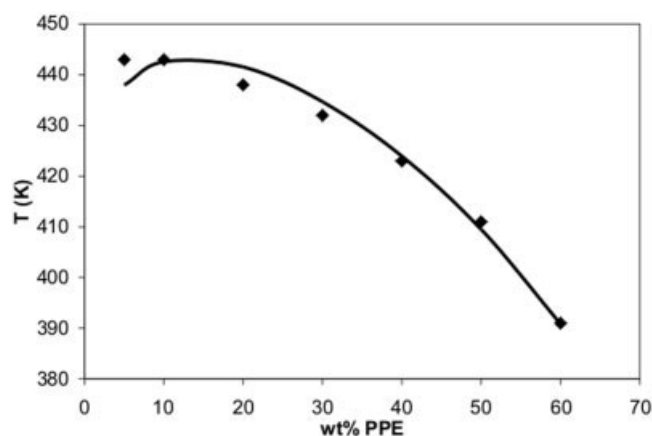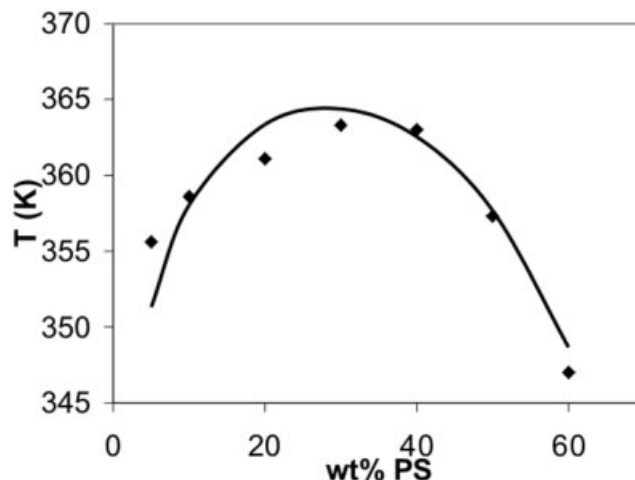
Figure 3 Cloud-point curve of the PS–DGEBA blend. Points are experimental values and the curve represents the best fitting obtained with the Flory–Huggins model.

In the simple FH model, the interaction parameter is expressed as a linear function of the reciprocal absolute temperature. But, in general, it is convenient to express the interaction parameter as a fitting function depending on temperature and composition (eventually it may be also expressed as a function of molar mass), to take into account different factors that contribute to the excess free energy.

In what follows, the three components will be designated with the following subscripts: DGEBA = 0, PPE = 1, and PS = 2. The interaction parameter of the PPE–PS pair, defined using the molar volume of the repeating unit of PS as the reference volume, was obtained from the literature.[14]

$$g_{12}(T) = 0.112 - 62/T \quad (2)$$

Equation (2) indicates that the interaction parameter increases with increase in temperature, which is characteristic of a lower-critical-solution-temperature (LCST) behavior (immiscibility region at high temperatures). However, the two-phase region is predicted at temperatures that are much higher than usual processing temperatures.[14]

The remaining two interaction parameters were obtained by fitting the corresponding experimental cloud-point curves shown in Figures 2 and 3.

For the PPE(HMW)–DGEBA blend, it was possible to fit the experimental curve using an interaction parameter $g_{01}(T)$ depending only on temperature. For this case, the reference volume was again taken equal to the molar volume of the repeating unit of PS, giving $r_0 = 3.39$ (for DGEBA) and $r_1 = 117.4$ (for the PPE of high molar mass, calculated using its number–average molar mass). The corresponding interaction parameter was expressed as:

Figure 2 Cloud-point curve of the PPE(HMW)–DGEBA blend. Points are experimental values and the curve represents the best fitting obtained with the Flory–Huggins model.

$$g_{01}(T) = A_{01} + B_{01}/T \qquad (3)$$

Chemical potentials of both components may be obtained from eq. (1) by standard procedures.[15] Equating the chemical potentials of each component in both phases leads to a couple of algebraic equations with the composition of the phase segregated at the cloud point and A_{01} and B_{01} as unknowns. The set of A_{01} and B_{01} values that minimized $\Sigma[T_{cp}(\text{predicted}) - T_{cp}(\text{exp})]^2$ was searched using the Levenberg-Marquardt algorithm included in Mathcad 2001 Professional. In this way, the best fit was obtained by an optimization procedure that includes all the experimental points in the same step. The best fit represented by the curve shown in Figure 2 corresponds to the following function:

$$g_{01}(T) = -0.394 + 264.1/T \qquad (4)$$

For the PS–DGEBA blend, the fitting of the experimental cloud-point curve required the use of an interaction parameter depending on both composition and temperature.[16,17] The following functionality of the interaction parameter defined by Prausnitz and coworkers was used to fit experimental results.[18]

$$g_{02}(T, \phi_2) = (A_{02} + B_{02}/T)[1/c(1 - \phi_2)]$$
$$\times \ln[(1 - c\phi_2)/(1 - c)] \qquad (5)$$

Again, using the molar volume of the constitutional repeating unit of PS as a reference volume led to $r_0 = 3.39$ (for DGEBA) and $r_2 = 216.3$ (for PS; this value is equal to its number–average degree of polymerization).

Deriving chemical potentials of both components and equating the expression for a given component in both phases, leads to two equations with the composition of the phase segregated at the cloud point, A_{02}, B_{02}, and c as unknowns. A similar optimization procedure as the one used for the PPE(HMW)–DGEBA pair led to the following expression for the interaction parameter:

$$g_{02}(T, \phi_2) = (-0.0371 + 71.2/T)$$
$$\times [1/0.627(1 - \phi_2)] \ln[(1 - 0.627 \phi_2)/(1 - 0.627)] \qquad (6)$$

The curve plotted in Figure 3 represents the fitting of the experimental cloud-point temperatures obtained with eq. (6).

Phase diagrams of the ternary blends

The phase diagram of the PPE(HMW)–PS–DGEBA blend is represented in Figure 4(a,b) (for clarity pur-
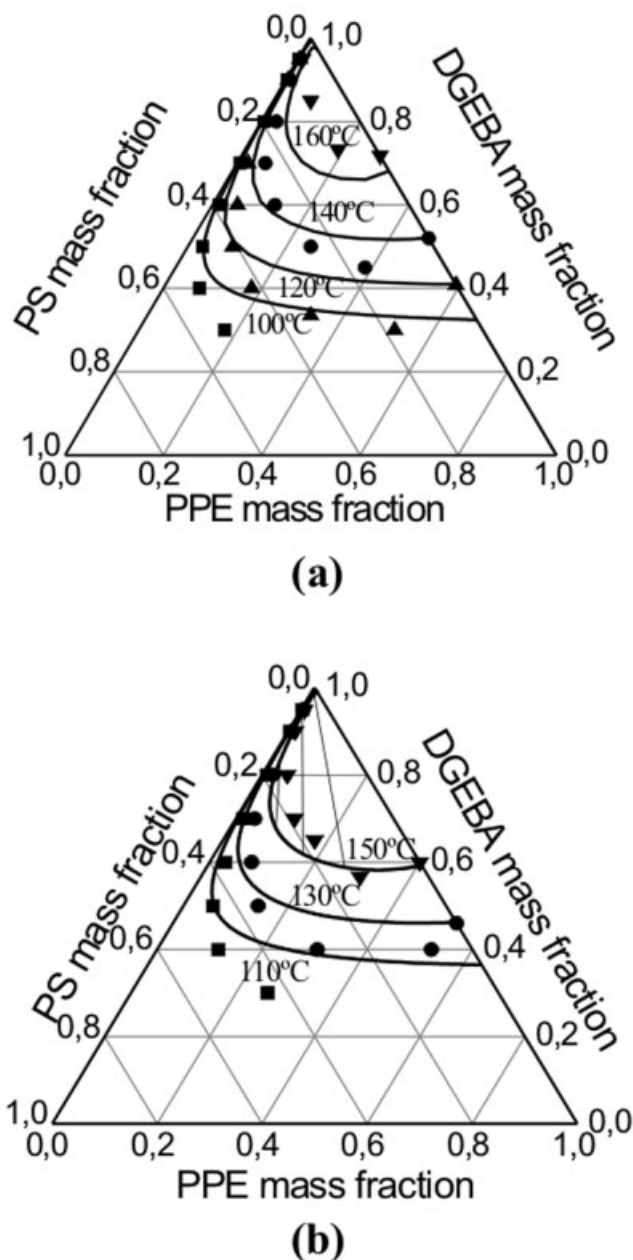

(a)

(b)

Figure 4 Phase diagram of the PPE(HMW)–PS–DGEBA blend. (a) Cloud-point curves for 100, 120, 140, and 160°C; (b) cloud-point curves for 110, 130, and 150°C. Points are experimental values, and curves represent the theoretical prediction using the Flory–Huggins model with three interaction parameters. Predicted tie lines at 150°C are shown. Blends located outside the corresponding isotherm in the lower part of the diagram, are homogeneous.

poses different sets of isothermal cloud-point curves are represented in the different diagrams). For a particular temperature, homogeneous solutions lie outside the corresponding isotherm, in the lower part of the triangular diagram. Therefore, for PPE(HMW), it was not possible to prepare homogeneous blends containing high mass fractions of DGEBA, except for formulations containing extremely low mass fractions of PPE.
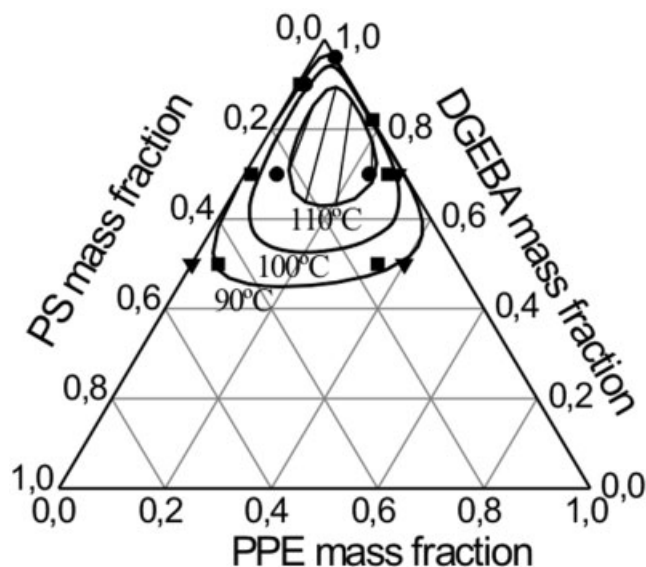
Figure 5 Phase diagram of the PPE(LMW)–PS–DGEBA blend with cloud-point curves for 90, 100, and 110°C. Points are experimental values and curves represent the theoretical prediction using the Flory–Huggins model with three interaction parameters. Predicted tie lines at 110°C are shown. Blends located outside the immiscibility loop for a particular temperature, are homogeneous.

Cloud-point curves for lower temperatures could not be obtained due to the occurrence of vitrification for compositions containing less than about 30 wt % DGEBA. The general trend is an increase in miscibility when increasing temperature.

Figure 5 shows the phase diagram of the PPE(LM-W)–PS–DGEBA blend. The decrease of the average molar mass of PPE led to a significant increase in miscibility and the appearance of an immiscibility loop at high temperatures. Formulations located outside the immiscibility loop are homogeneous. Therefore, the use of a low-molar-mass PPE enabled to obtain homogeneous solutions in ternary blends containing a high mass fraction of DGEBA.

An attempt to fit the experimental isotherms with the FH model written for the ternary blend was performed. In this case, the free energy per unit volume is written as:

$$(V_r/RT)\Delta G = (\phi_0/r_0) \ln \phi_0 + (\phi_1/r_1)$$

$$\ln \phi_1 + (\phi_2/r_2) \ln \phi_2 + g_{01}(T)\phi_0\phi_1$$

$$+ g_{02}(T, \phi_2)\phi_0\phi_2 + g_{12}(T)\phi_1\phi_2 \quad (7)$$

The same $g_{02}(T, \phi_2)$ function found for the binary system was assumed to be valid for the ternary blend with the hypothesis that, for a given temperature, the 0–2 contact energy depends on the fraction of sites surrounding the 0–2 pair that are occupied by "2" segments.

Chemical potentials of every component were derived by standard procedures.[15] Equating the chemical potential of a particular component in both phases leads to a set of three algebraic equations. They were solved fixing the temperature and the volume fraction of one of the components in one phase. Roots of the set of algebraic equations were searched using the Levenberg-Marquardt algorithm included in Mathcad 2001 Professional. They gave the volume fraction of a second component in the selected phase and the volume fraction of two of the components in the phase in equilibrium located at the end of the tie line. The volume fraction of the third component in both phases was obtained by making the summation of volume fractions equal to one. Several tie lines were determined with the same procedure starting from a different volume fraction of the selected component in one of the phases. Equilibrium curves were determined in this way for several temperatures. The molar volume of the repeating unit of PS was always taken as the reference volume, leading to $r_1 = 117.4$ for PPE(HMW) and 11.74 for PPE(LMW).

Predictions of the FH equation are shown by the continuous curves plotted in Figures 4 and 5. Some tie lines are also indicated. Model predictions fit the overall experimental trends, including the appearance of an immiscibility loop for the PPE(LMW)–PS–DGEBA blend (Fig. 5). For this blend, the model predicts complete miscibility at 120°C, but a small region of immiscibility was experimentally found at this temperature. Deviations of the model are expected to increase with the decrease in the average molar mass of PPE due to the failure of the assumption of monodisperse components. Polydispersity effects are more pronounced for low molar mass components due to their relatively high contribution to the combinatorial terms of the FH equation.

The thermodynamic model can be used to estimate phase diagrams when the molar mass of PPE is varied in a broad range. Figure 6 shows the isothermal phase diagram at 150°C predicted for PPEs of different molar masses. Increasing the molar mass of PPE beyond $M_n = 16$ kg mol^{-1} practically did not shift the immiscibility region, a fact that arises from the (almost) negligible contribution made by a high molar mass polymer to the combinatorial terms of the FH equation. For the same reason, the phase diagram is also valid for any PS of M_n higher than about 20 kg mol^{-1}.

Miscibility increases considerably when the selected PPE has a number–average molar mass in the range between 1 and 10 kg mol^{-1} and an immiscibility loop appears for the lowest part of this range. The presence of the immiscibility loop enables to increase the DGEBA fraction by selecting an appropriate temperature and an initial composition located outside the loop. Therefore, by selecting a PPE of low molar mass, the fraction of reactive solvent (DGEBA plus a hard-
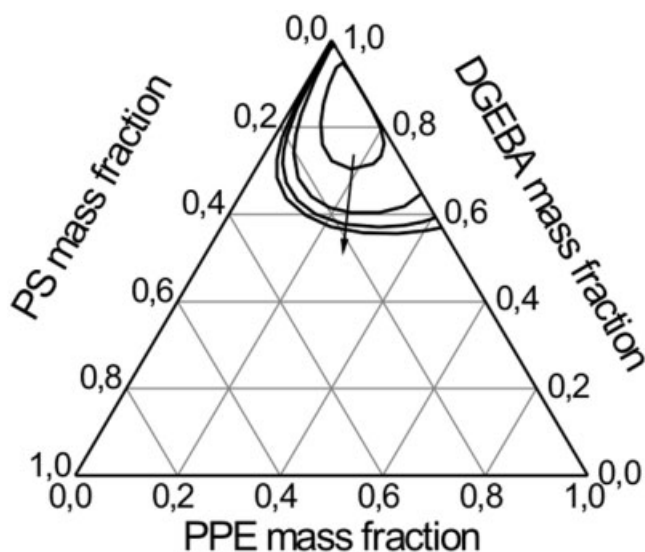
Figure 6 Phase diagram of PPE–PS–DGEBA blends at 150°C, for PPE with number–average molar masses of 4, 8, 12, and 16 kg mol^{-1} (increasing in the direction indicated by the arrow), and a PS with a number–average molar mass equal to 100 kg mol^{-1}.

ener) may be increased to a point where polymerization-induced phase separation generates a dispersion of PPE/PS domains in a continuous epoxy matrix or bicontinuous phases. This opens the possibility of toughening epoxies with PPE/PS blends. Properties of the thermoplastic phase can be modulated in a broad range by varying the ratio between both thermoplastics.

CONCLUSIONS

Experimental phase diagrams of PPE–PS–DGEBA blends could be reasonably fitted using the FH model with binary interaction parameters taken from the literature (for the PPE–PS pair), or obtained by fitting experimental cloud-point curves of binary blends (for PPE–DGEBA and PS–DGEBA pairs). To our knowledge, this is one of the few examples reported in the literature where the FH model is used with success to predict phase diagrams of blends of two polymers and a solvent, using information obtained from the corresponding binary systems and without employing extra fitting functions (e.g., a ternary interaction parameter).

The FH model was used to predict the effect of varying the molar mass of PPE on the initial miscibility of ternary blends. A significant increase in miscibility together with the appearance of an immiscibility loop was found for PPEs with M_n values comprised in the range between 1 and 10 kg mol^{-1}. This enables to obtain initial homogeneous solutions in regions of high DGEBA concentrations, a possibility that was not previously reported for this ternary blend. This opens new possibilities for the toughening of epoxies replacing a single thermoplastic with a thermoplastic blend where both components (PS and PPE) are completely miscible.

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