

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

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ABSTRACT: Blends of poly(2,6-dimethyl-1,4-phenylene oxide), usually called poly(phenylene ether) (PPE), and polystyrene (PS) in a reactive solvent based on diglycidyl ether of bisphenol A (DGEBA), are used to facilitate processing of PPE. The process starts with an initial homogeneous solution and the final material is obtained by polymerization-induced phase separation. In this study, experimental phase diagrams of these ternary blends were obtained in an extended range of temperatures for two commercial PPEs of different molar masses ($M_n = 1.2 \text{ kg mol}^{-1}$ and 12 kg mol^{-1}). Overall experimental trends including the appearance of an immiscibility loop for the PPE(1.2 kg mol^{-1})-PS-DGEBA blend, were reasonably predicted using the Flory-Huggins (FH) model with interaction parameters obtained from the literature (for PPE-PS blends) or by fitting experimental cloud-point curves of the corresponding binary systems (for PPE-DGEBA and PS-DGEBA blends). The FH model was then used to predict the influence of the PPE molar mass on the 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} . Using a PPE of low molar mass opens the possibility of obtaining initial homogeneous solutions with a high fraction of the epoxy precursors. Polymerization-induced phase separation starting from these solutions can lead to a dispersion of thermoplastic domains in an epoxy matrix or to bi-continuous phases. What is significant is the fact that properties of the thermoplastic phase can be modulated by varying the ratio of both thermoplastics and the molar mass of PS. This opens new possibilities for the toughening of epoxies replacing a single thermoplastic with a thermoplastic blend.

Key words: blends; miscibility; phase diagrams; poly(phenylene oxide); polystyrene; thermodynamics

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 mixing⁷ and also a negative volume of mixing⁸ that evidence a favourable specific interaction. Processing of pure PPE is extremely difficult due to 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 in order 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 was 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 bi-continuous 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 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 vary the molar mass of PPE comparing phase diagrams of ternary blends obtained with two commercial PPEs ($M_n = 1.2 \text{ kg mol}^{-1}$ and 12 kg mol^{-1}). Overall experimental trends were reasonably predicted using the Flory-Huggins 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 will be 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 at atmospheric pressure and one night under vacuum, at room temperature. Samples were then heated to 190 °C, kept at this temperature during 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 located 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. A set of these curves enabled to determine compositions at the cloud-point at a constant temperature. Experimental points associated with isothermal cloud-point curves could then be plotted in the triangular phase diagrams.

RESULTS AND DISCUSSION

Phase diagrams and interaction parameters of the binary systems

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

$$g_{12}(T) = 0.112 - 62/T \quad (1)$$

Equation (1) indicates a lower-critical-solution-temperature (LCST) behavior. 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-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 free energy per unit volume, ΔG , of a blend of components 0 and 1, may be written as:

$$(V_r/RT)\Delta G = (\phi_0/r_0) \ln \phi_0 + (\phi_1/r_1) \ln \phi_1 + g_{01}(T)\phi_0\phi_1 \quad (2)$$

where R is the gas constant, V_r is the reference volume taken as the one of the repeating unit of PS, ϕ represents a volume fraction and r is the ratio of the molar volume of the corresponding component with respect to the reference volume ($r_0 = 3.39$ and $r_1 = 117.4$ for the PPE of high molar mass, calculated using its number-average molar mass). The usual functionality of the interaction parameter with temperature is taken:

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

Chemical potentials of both components may be obtained from eq. (2) 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:

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

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 co-workers was used to fit experimental results:¹⁸

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

The free energy per unit volume of this blend is written as:

$$(V_r/RT)\Delta G = (\phi_0/r_0) \ln \phi_0 + (\phi_2/r_2) \ln \phi_2 + g_{02}(T, \phi_2)\phi_0\phi_2 \quad (6)$$

where $r_2 = 216.3$.

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-DGEBA pair led to the following expression for the interaction parameter:

$$g_{02}(T, \phi_2) = (- 0.0371 + 71.2/T)[1/0.627(1 - \phi_2)] \ln[(1 - 0.627\phi_2)/(1 - 0.627)] \quad (7)$$

The curve plotted in Figure 3 represents the fitting of the experimental cloud-point temperatures obtained with eq. (7).

Phase diagrams of the ternary blends

The phase diagram of the PPE(HMW)-PS-DGEBA blend is represented in Figures 4a and 4b (for clarity purposes different sets of isothermal cloud-point curves are represented in the different diagrams). In the selected temperature range only the PPE-DGEBA pair exhibits partial miscibility. 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(LMW)-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.

The free energy per unit volume for the ternary blend is written as:

$$(V_r/RT)\Delta G = (\phi_0/r_0) \ln \phi_0 + (\phi_1/r_1) \ln \phi_1 + (\phi_2/r_2) \ln \phi_2 + g_{01}(T)\phi_0\phi_1 + g_{02}(T,\phi_2)\phi_0\phi_2 + g_{12}(T)\phi_1\phi_2 \quad (8)$$

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 value of r_1 was taken as 117.4 for PPE(HMW) and 11.74 for PPE(LMW).

Predictions of the Flory-Huggins 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 the higher contribution of the combinatorial terms of the FH equation.

The thermodynamic model can be used to predict 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 $M_n = 16 \text{ kg mol}^{-1}$ 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 Flory-Huggins 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 may be increased to the point where polymerization-

induced phase separation generates a dispersion of PPE/PS domains in a continuous epoxy matrix or bi-continuous phases. Properties of the thermoplastic phase can be modulated in a broad range by varying the molar mass of PS and the ratio between both thermoplastics. This opens the possibility of toughening epoxies with PPE/PS blends.

CONCLUSIONS

Experimental phase diagrams of PPE-PS-DGEBA blends could be reasonably fitted using the Flory-Huggins 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. The appearance of an immiscibility loop was found for PPEs of low molar masses. This enables to increase the fraction of DGEBA by selecting an appropriate temperature and an initial composition located outside the loop. For these solutions, polymerization-induced phase separation can generate a dispersion of PPE/PS domains in a continuous epoxy matrix or bi-continuous phases. What is significant is the fact that properties of the thermoplastic phase can be modulated by varying the ratio of both thermoplastics and the molar mass of PS. This opens new possibilities for the toughening of epoxies replacing a single thermoplastic with a thermoplastic blend.

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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

Figure Captions

Figure 1 Chemical structures of the epoxy monomer and the polymers.

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.

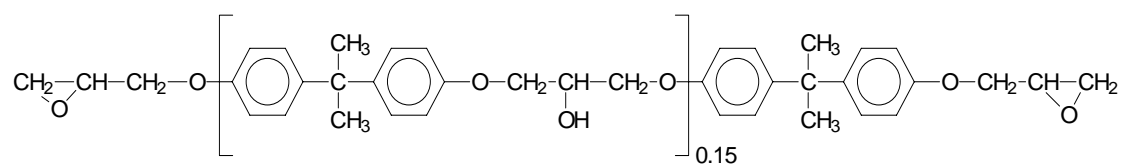
Figure 3 Cloud-point curve of the PS-DGEBA blend. Points are experimental values and the curve represents the best fitting obtained with the Flory-Huggins model.

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.

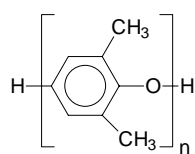
Figure 5 Phase diagram of the PPE(LMW)-PS-DGEBA blend with cloud-point curves for 90, 100 and 110 °C. Points are experimental values and curves represent the theoretical prediction using the Flory-Huggins model with three interaction parameters. Predicted tie lines at 110 °C are shown.

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.

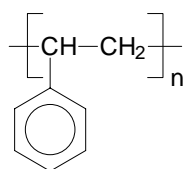
Figure 1



DGEBA-based epoxy monomer



PPE



PS

Figure 2

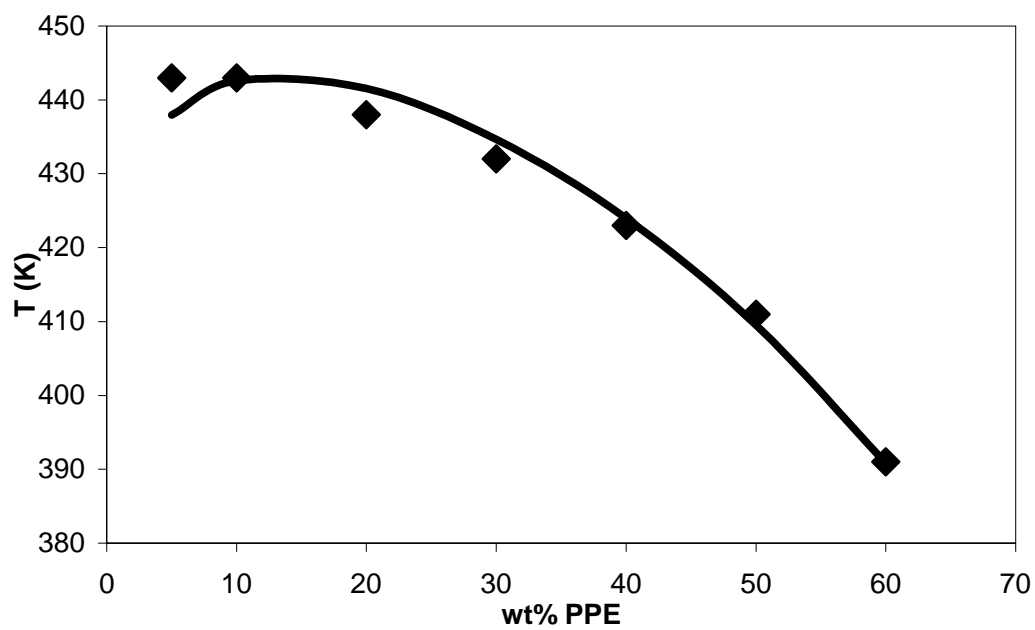


Figure 3

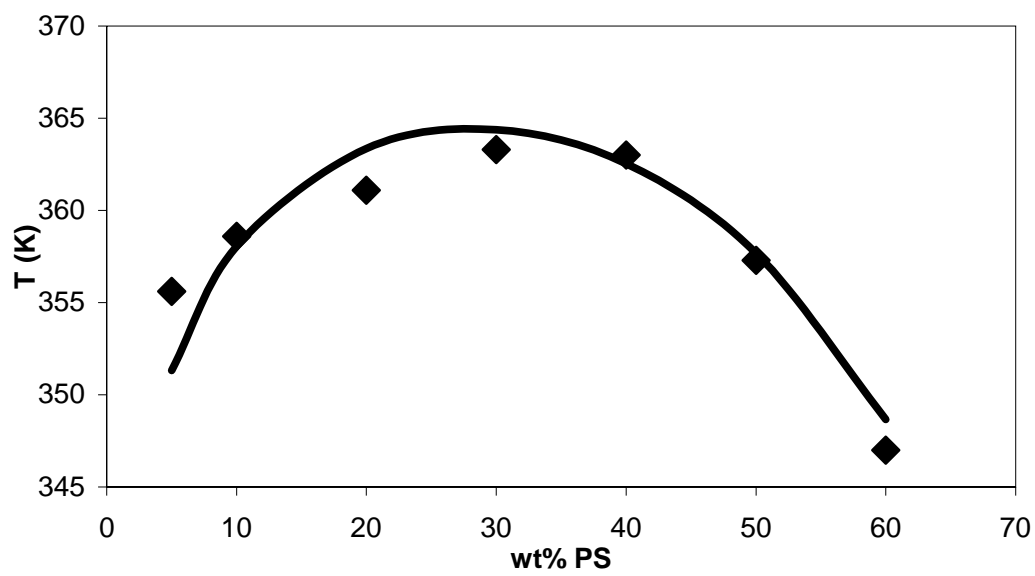
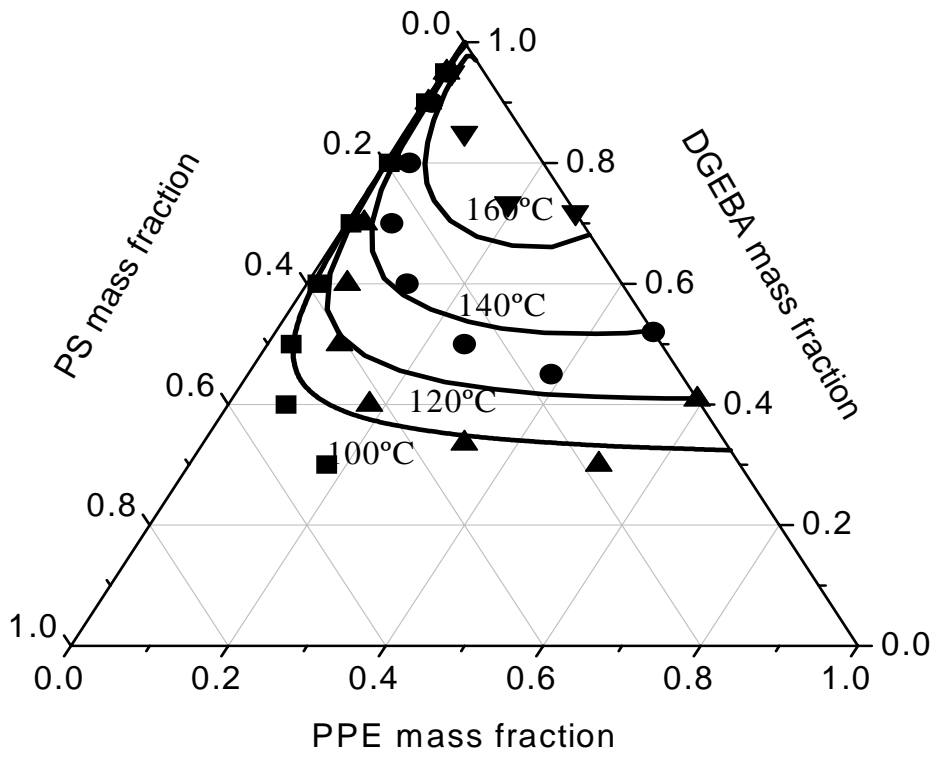
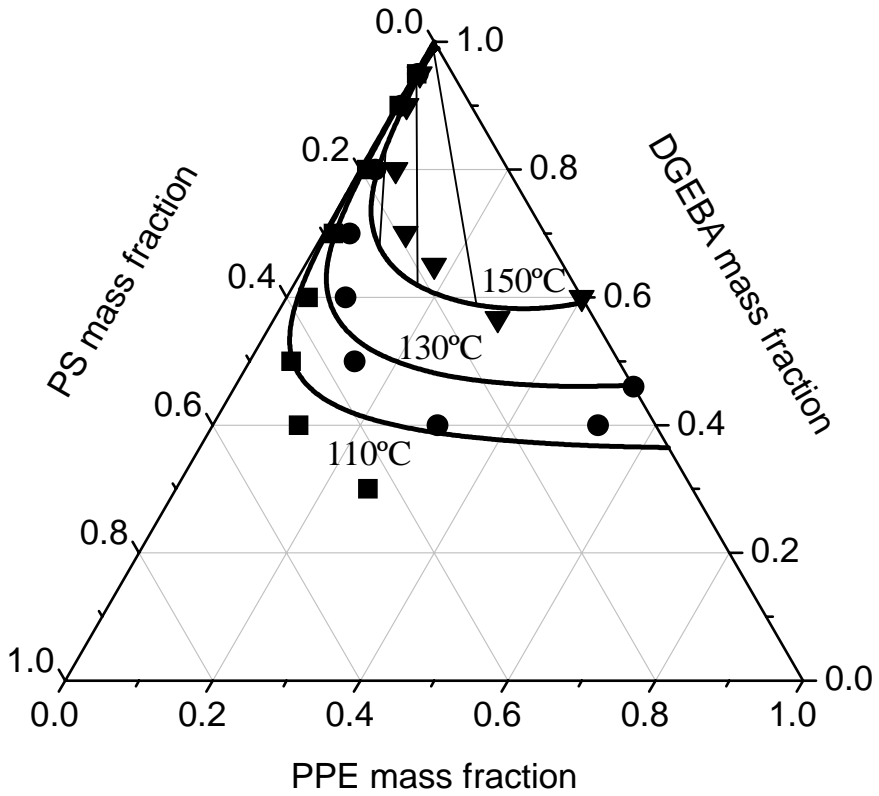


Figure 4



(a)



(b)

Figure 5

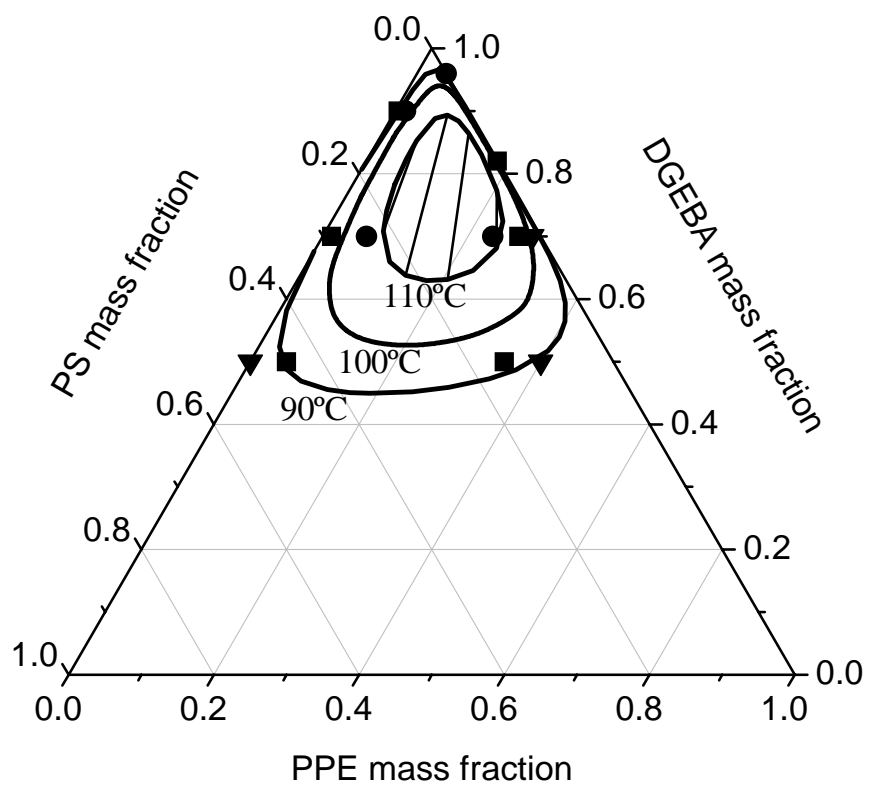


Figure 6

