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Phase behaviour and thermodynamics of poly(1,4-phenylene ether sulphone) and poly(ethylene oxide)/alkali-metal salt complex blends: a thermal analysis study

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Abstract

The phase behaviour and thermodynamics of poly(1,4-phenylene ether sulfone) (PES) and poly(ethylene oxide) (PEO)/alkali-metal salt complex blends were investigated by means of differential scanning calorimetry (DSC) and modulated DSC (MDSC). Experimental results show that the blend systems remain miscible after incorporating various alkali-metal salts: CF_3SO_3Li, CF_3SO_3Na and CF_3SO_3K. The cloud point temperature strongly depended on the Li (Na or K)/O ratio in the PES-PEO/alkali-metal salt complex blends. With increasing the Li^+ (Na^+ or K^+)/O ratio, the phase diagram of the PES-PEO/alkali-metal salt complex blends tended to be symmetrical. When $Li^+/O = 0.02$, the lower critical solution temperature (LCST) of the PES-PEO/CF_3SO_3Li complex blends was located at the 30/70 PES/PEO composition. The mixing enthalpy decreased in the PES-PEO/alkali-metal salt complex blends with increasing Li^+ (Na^+ or K^+)/O ratio. The radius of ion has significant influence on the phase behaviour of PES/PEO blends. MDSC results showed that the change of heat capacity at the temperature of the binodal phase separation is similar to that of a melt transition in semi-crystalline polymers, which confirms the mechanism of binodal phase separation: nucleation and growth.

Keywords: Phase separation; Polymer blends; Thermal analysis.

1. Introduction

The blend of PEO with alkali-metal salts can form PEO electrolyte complexes. However, the mechanical properties of the PEO electrolyte complexes are poor. The mechanical properties of the PEO electrolyte complexes could be improved by blending with high-glass-transition polymers, such as poly(1,4-phenylene ether sulphone) (PES), with good mechanical properties. One has attempted to develop new electrolytes by means of PES/PEO-CF_3SO_3Li complexes [1]. In publications it has been suggested that PES is miscible with PEO [2–5]. At high temperature, PES/PEO blends go to spinodal decomposition. [4,5]. Bi-continue phase structure will be created by the spinodal decomposition. The feature could be used to develop new PEO-based electrolytes with good mechanical properties. It is because mechanical properties can be improved by PES phase and the electrolyte properties cannot also be affected. First of all, it is necessary to know the effects of alkali-metal salts on the phase behaviour of PES/PEO blends, because phase behaviour of polymer blends influences their physical properties. In this communication, we report the phase behaviour of PES-PEO/alkali-metal salt complex blends and the effect of different kinds and concentrations of alkali-metal salts on the phase behaviour of PES/PEO blends.

2. Experimental

2.1. Materials

The materials used in this study, poly(1,4-phenylene ether sulfone) (PES) with nominal melt index (380 °C/2.16 kg) of

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75 g/10 min and density of 1.370 g/cm^3, poly(ethylene oxide) (PEO) with nominal molecular weights of 10,000 g/mol, lithium trifluoromethanesulfonate (CF_3SO_3Li), sodium trifluoromethanesulfonate (CF_3SO_3Na) and potassium trifluoromethanesulfonate (CF_3SO_3K) were all purchased from Aldrich (UK).

2.2. *Sample preparation*

Blends of PES and PEO, and PES and PEO/alkali-metal salt complex blends were prepared by solution process. PES, PEO, CF_3SO_3Li, CF_3SO_3Na and CF_3SO_3K were separately dissolved in *N,N*-dimethylformamide to form 5 wt.% solutions. These were centrifuged to remove particulate impurities. PEO/CF_3SO_3Li, PEO/CF_3SO_3Na and PEO/CF_3SO_3K solutions were prepared by mixing PEO, CF_3SO_3Li, CF_3SO_3Na, CF_3SO_3K solutions in appropriate proportions, respectively. PES and PEO, PES and PEO/alkali-metal salt complex solutions were then mixed in appropriate proportions and cast on glass plates to form films 100–200 μm thick. The films were dried in a vacuum oven at 68 °C for at least 2 weeks to remove the solvent. The films were kept in the vacuum oven at 68 °C before use.

3. Instrumentation

3.1. *Differential scanning calorimetry (DSC)*

The temperature of binodal phase separation and heat of mixing of the blends were determined by DSC and modulated-temperature DSC (MDSC). A TA Instruments DSC2920 calorimeter was used. All measurements were run in nitrogen atmosphere and the temperature ramp was set at 10 °C/min for DSC measurements. An oscillation amplitude of ±1.0 °C, an oscillation period of 60 s and a heating rate of 3 °C/min were used for MDSC experiments. The calorimeter was calibrated with a standard indium sample.

3.2. *Measurement of cloud points and heat of mixing*

Cloud points and heats of demixing for PES/PEO and PES/PEO-alkali-metal salt complex blends were determined by means of DSC and MDSC. The weight of samples was 7–8 mg for all experiments. All samples were heated at a rate of 30 °C/min from room temperature to 70 °C and held there for 60 min. Afterward, these samples were heated to 200 °C at a rate of 10 °C/min for DSC experiments and at a rate of 3 °C/min for MDSC experiments.

4. Results and discussion

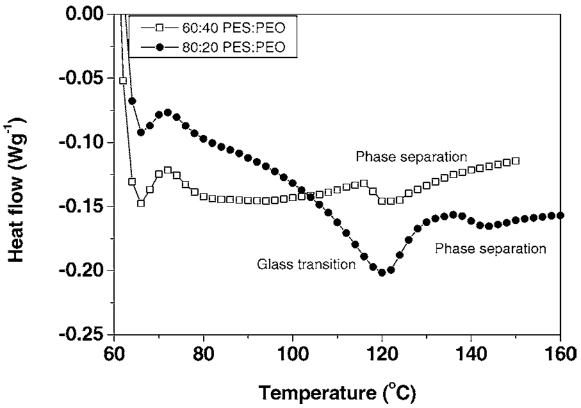

Fig. 1. DSC curves at a heating rate 10 °C/min for 60/40 and 80/20 PES/PEO blends, respectively.

Fig. 1 shows thermograms for the blends with PES/PEO = 60/40 and 20/80. The results clearly indicate that phase separation occurred. According to the explanation [6], the endothermic peaks shown in Fig. 1 corresponds to the heat (enthalpy) of demixing of this blend. For 80/20 PES/PEO blend, the temperature of phase separation just is 20 °C higher than the glass transition temperature of the system. It was suggested that PES/PEO blends exhibit lower critical solution temperature [4,5].

Figs. 2 and 3 show the typical relationship of the phase separation temperature (onset point of the curve of heat of demixing) and enthalpy of demixing versus heating rates, respectively. The phase separation temperature (cloud point) and the enthalpy of mixing increased with the heating rate at the beginning and reached a constant value when the heating rate was 40 °C/min. By extrapolation of the curve of the phase separation temperature, the enthalpy of mixing versus heating rates to zero one, the equilibrium phase separation temperature and the enthalpy of mixing could be obtained for the corresponding blend system. The data of the phase separation temperature and the enthalpy of demixing at the heating rate of zero were given.

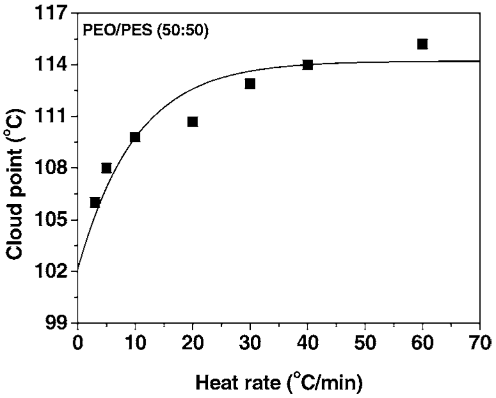

Fig. 2. Temperature of phase separation dependence on the heating rate (PES:PEO = 50:50).

It is clear that there are interactions between Li$^+$ and oxygen atoms of PEO. It is expected that Li$^+$ will have

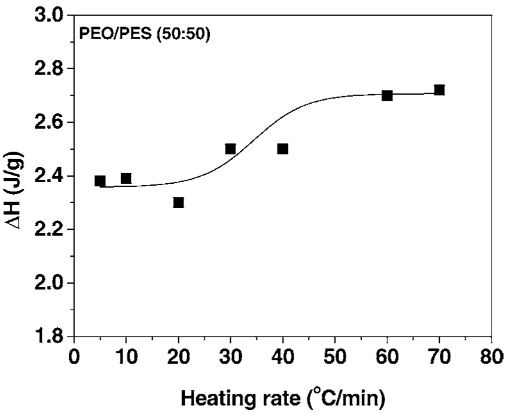

Fig. 3. Enthalpy of mixing dependence on the heating rate (PES:PEO = 50:50).

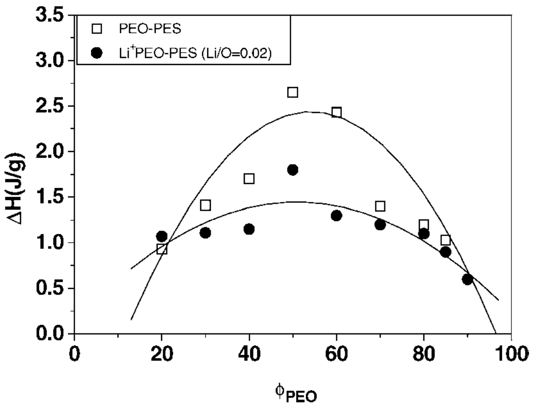

Fig. 5. Enthalpy of mixing of PES-PEO/CF_3SO_3Li complex blends.

influences on the phase behaviour of PES/PEO-CF_3SO_3Li complex blends. Fig. 4 shows the phase behaviour for PES/PEO-CF_3SO_3Li complex blends at different Li^+/O ratios. It was found that with increasing Li^+/O ratio, the temperature of phase separation increased and phase diagram of PES/PEO-CF_3SO_3Li complex blends became symmetrical. When $Li^+/O = 0.02$, the lower critical solution temperature of the PES/PEO-CF_3SO_3Li complex blends was located at the 30/70 PES/PEO composition. It is well known [2] that the lower critical solution temperature of the PES/PEO blends was located at the 10/90 PES/PEO composition.

Generally, pure PEO chain is in the trans-trans-gauche (ttg) conformation, which is very close to the 7_2 helical conformation [7]. When PEO blends with the alkali-metal salt, CF_3SO_3Li, to form complexes, the conformation of PEO chain will change to $(\text{ttg ttg tt-g})_2$ ‘helix’ conformation [7]. Adding salt of CF_3SO_3Li could affect the conformation of PEO chain, which will results in the change of the enthalpy of mixing of PES/PEO. Fig. 5 shows the enthalpy of mixing for PES/PEO and PES/PEO-CF_3SO_3Li ($Li^+/O = 0.02$) complex blends. Results indicated, indeed, that the addition of alkali-metal salt has an influence on the enthalpy of mixing of PES-PEO/CF_3SO_3Li complex blend system.

Fig. 6 gives a comparison for the effect of Li^+, Na^+ and K^+ on the phase behaviour of PES-PEO/CF_3SO_3Li, /CF_3SO_3Na and /CF_3SO_3K complex blends. Li^+ (or Na^+ or K^+)/O = 0.02. The K^+-blend systems have the highest temperature of phase separation. The symmetrization of phase diagram for the PES/PEO-CF_3SO_3Li ($Li^+/O = 0.02$) complex blends is greater than that for the PES/PEO-CF_3SO_3Na and -CF_3SO_3K (Na^+ or K^+)/O = 0.02) blends. It is known that K^+ has the biggest ionic radius among them. The results indicate that ionic radius exerts an effect on the phase behaviour. With increasing ionic radius, the temperature of phase separation of PES/PEO-alkali-metal salt complex blends increased.

Fig. 7 shows the enthalpy of mixing for PES-PEO/CF_3SO_3Li, /CF_3SO_3Na and /CF_3SO_3K complex blends. Li^+ (or Na^+ or K^+)/O = 0.02. It was also found that the ionic radius has an influence on the enthalpy of mixing slightly. Generally, experimental results indicate with increasing the ionic radius, the value of the enthalpy of mixing increases.

Fig. 8 shows the effect of the ratio of Li^+ (or Na^+ or K^+)/O on the cloud points of PES-PEO/CF_3SO_3Li (or /CF_3SO_3Na

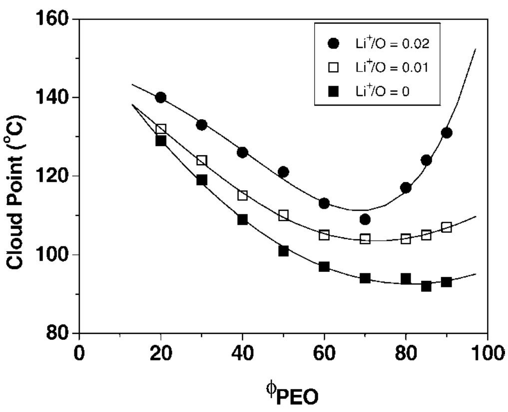

Fig. 4. Phase diagram of PES/PEO-CF_3SO_3Li complex blends with different Li^+/O ratios.

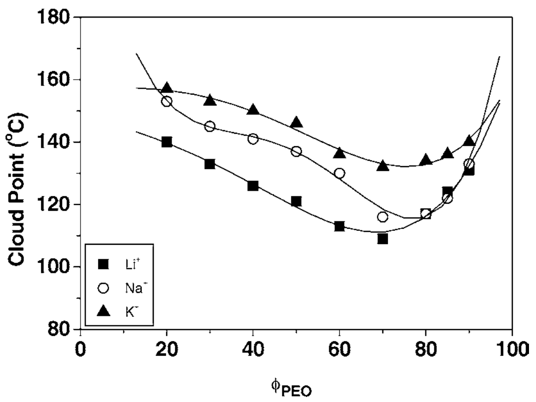

Fig. 6. Phase diagram of PES/PEO-CF_3SO_3Li, /CF_3SO_3Na and /CF_3SO_3K complex blends. Li^+ (or Na^+ or K^+)/O = 0.02.

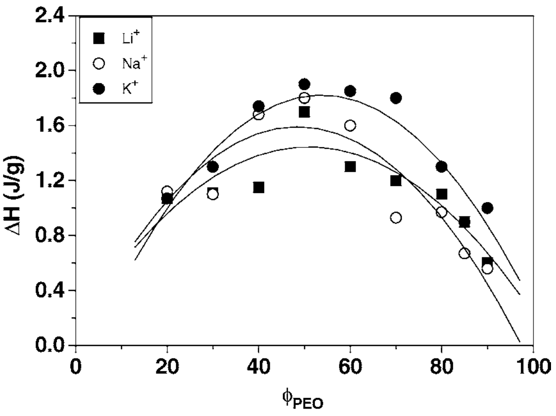

Fig. 7. Enthalpy of mixing for PES/PEO-CF_3SO_3Li, /CF_3SO_3Na and /CF_3SO_3K complex blends. Li^+ (or Na^+ or K^+)/O = 0.02.

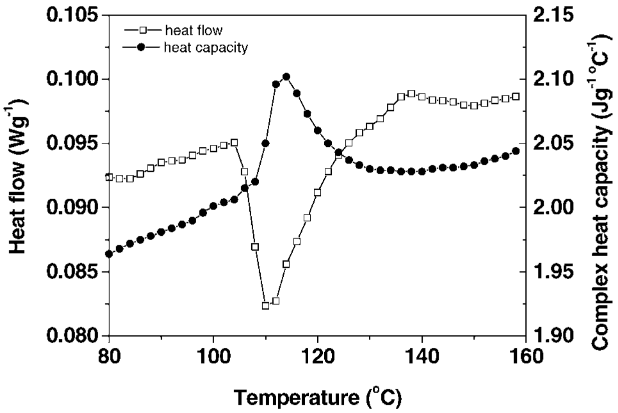

Fig. 10. Change of heat capacity at the temperature of the binodal phase separation for the 40:60 PES/PEO-CF_3SO_3Li complex blend (Li^+/O = 0.02).

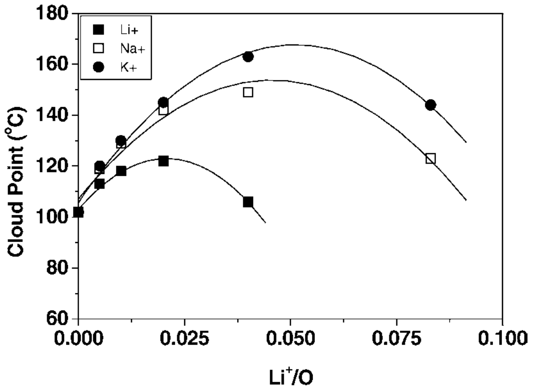

Fig. 8. Effect of ionic concentration on temperature of phase separation for PES/PEO-CF_3SO_3Li, /CF_3SO_3Na and /CF_3SO_3K complex blends.

or /CF_3SO_3K) complex blends. With increasing Li^+(Na^+ or K^+)/O ratio, the phase separation temperature increased upto a highest point, then decreased. This indicates that with increasing Li^+(Na^+ or K^+)/O ratio upto a value, stability of the complex of PES and PEO-alkali-metal salt increased. Beyond this point, the stability between them decreased. It can be imaged that beyond some Li^+(Na^+ or K^+)/O ratio, PES/PEO-alkali-metal salt complex blends could be immiscible.

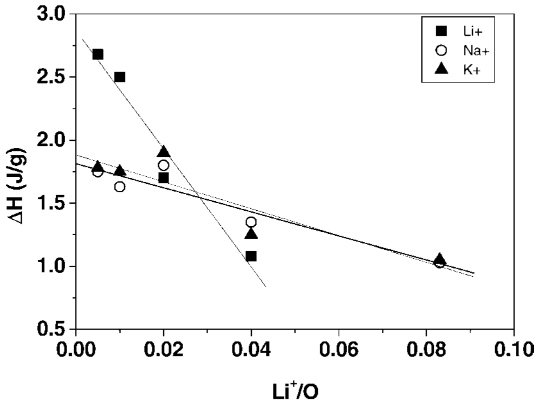

Fig. 9. Enthalpy of mixing vs. ionic concentration for PES/PEO-CF_3SO_3Li, /CF_3SO_3Na and /CF_3SO_3K complex blends.

Fig. 9 shows the effect of the ratio of Li^+ (or Na^+ or K^+)/O on the enthalpy of mixing for PES (50)-PEO (50)/CF_3SO_3Li (or /CF_3SO_3Na or /CF_3SO_3K) complex blends. With increasing the ionic concentration, the value of the enthalpy of mixing decreases. PES(50)/PEO(50)-CF_3SO_3Na and /CF_3SO_3K blend systems almost have the same values of the enthalpy of mixing. At the ratio of ionic concentration/O = 0.03, it was found that the three blend systems have the same value of the enthalpy of mixing. Below the point, the enthalpy of mixing for PES(50)-PEO(50)/CF_3SO_3Li blend is higher than that for both PES(50)/PEO(50)-CF_3SO_3Na and /CF_3SO_3K blends.

A new phenomena has been revealed by MDSC study for PES-PEO/alkali-metal salt complex blends, i.e., The change of heat capacity at the temperature of the binodal phase separation is similar to that of a melt transition in semi-crystalline polymers. Fig. 10 gives the result for the 40:60 PES/PEO-CF_3SO_3Li complex blend (Li^+/O = 0.02), which confirms the mechanism of binodal phase separation: nucleation and growth.

5. Conclusions

Experimental results show that the poly(1,4-phenylene ether sulfone) and poly(ethylene oxide) blends remain miscible after incorporating various alkali-metal salts: CF_3SO_3Li, CF_3SO_3Na and CF_3SO_3K. The cloud point temperature strongly depended on the Li (Na or K)/O ratio in the PES-PEO/alkali-metal salt complex blends. With increasing the Li^+ (Na^+ or K^+)/O ratio, the phase diagram of the PES-PEO/alkali-metal salt complex blends tended to be symmetrical. When Li^+/O = 0.02, the lower critical solution temperature (LCST) of the PES-PEO/CF_3SO_3Li complex blends was located at the 30/70 PES/PEO composition. The mixing enthalpy decreased in the PES-PEO/alkali-metal salt complex blends with increasing Li^+ (Na^+ or K^+)/O ratio. The radius of ion has significant influence on the phase behaviour of PES/PEO blends, i.e. with increasing the radius of ions, the phase separation temperature and enthalpy of mixing increase. MDSC results showed that the change of heat capacity at the temperature of the binodal phase separation is similar to that of a melt transition in semi-crystalline polymers.

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