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MISCIBILITY OF POLY(HYDROXYETHER OF PHENOLPHTHALEIN) WITH POLY(ETHER SULPHONE)

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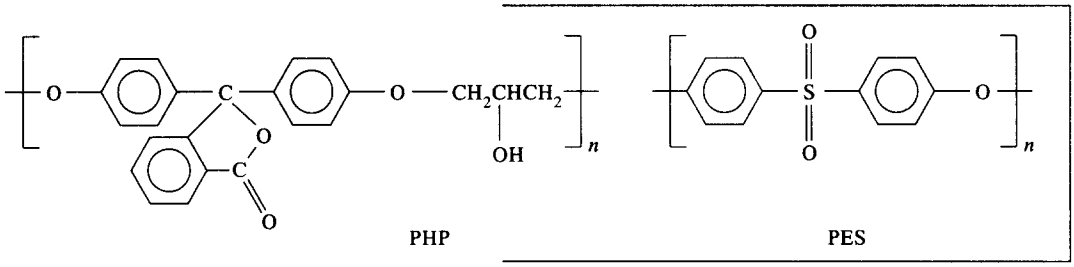
Abstract—Blends of poly(hydroxyether of phenolphthalein) (PHP) with poly(ether sulphone) (PES) were prepared by casting from a common solvent; they were found to be miscible and show a single, composition-dependent glass transition temperature. All the PHP/PES blends exhibited lower critical solution temperature behaviour, i.e. phase separation occurred at elevated temperatures. A F.T.-i.r. study revealed that a hydrogen-bonding interaction occurs between these polymers but it is weaker than in pure PHP. The observed miscibility is hence proposed to be the result of specific interactions betweeen the polymers.

INTRODUCTION

Poly(hydroxyether of phenolphthalein) (PHP), a novel polymer like other polyhydroxyethers such as poly(hydroxyether of bisphenol-A) (phenoxy) [1–8], has excellent potential for hydrogen-bonding as a proton-donor because of its pendant hydroxyl groups.



It has been proved that PHP is miscible with some proton-accepting polymers such as poly(ethylene oxide) [9], poly(butylene terephthalate) and polycarbonate [10].

In this communication, we describe the phase behaviour and miscibility of PHP with poly(ether sulphone) (PES). The techniques employed included differential scanning calorimetry (DSC) for glass transition behaviour and optical observations for phase separation on heating or lower critical solution temperature (LCST) behaviour. A brief FTIR study confirmed that the miscibility of the PHP/PES system is attributed to the existence of specific interactions between the blend components.

EXPERIMENTAL PROCEDURES

Materials and preparation of blends

PHP with a reduced viscosity of 0.34 dl/g when measured in 0.5 wt% solution in *N,N*-dimethylformamide (DMF) at 25° was kindly supplied by Professor T. Chen of this Institute. It was prepared by the direct reaction of phenolphthalein with epichlorohydrin in an alkaline medium [11]. The PES with a reduced viscosity of 0.35 dl/g as a 0.5 wt% solution in DMF at 25° was obtained from the Department of Polymer Chemistry, Jilin University, Changchun, People's Republic of China. DMF was A.R. grade and was used as received.

The PHP/PES blends were prepared by solution casting from DMF at 80°. To remove the residual solvent, the blends were dried in vacuum at 120° for one week.

Cloud point measurements

Blend clarity as a function of temperature was studied by placing a sample of the blend between two glass slides and heating it with a hot plate at about 10°/min [12, 13]. The temperature at which the first faint opalescence appeared on heating was designated as the cloud point. Observed melting points of several standard compounds using this method checked closely with published values.

Differential scanning calorimetry

The calorimetric measurements were made on a Perkin–Elmer DSC-7 differential scanning calorimeter at a heating rate of 20°/min. The midpoint of the slope change of the heat capacity plot of the second scan was taken as the glass transition temperature (T_g).

FTIR measurements

FTIR measurements were made with a Digilab FTS-20E spectrometer. Thin films were cast onto a NaCl window from 0.5% (w/v) DMF solutions. After evaporation of most of the solvent, the films were transferred to a vacuum oven and kept at 120° for 48 hr to remove the residual solvent, and then stored in a desiccator to avoid moisture absorption. All spectra were recorded at room temperature and

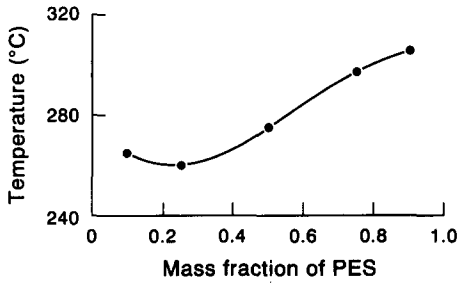


Fig. 1. Plot of cloud point temperature against composition for PHP/PES blends.

stored on a magnetic system. A minimum of 50 scans at a resolution of 2 cm^{-1}, were signal-averaged. The films used in this study were sufficiently thin to obey the Beer–Lambert law.

RESULTS AND DISCUSSION

All the PHP/PES blends were transparent at room temperature and were found to undergo phase separation at elevated temperature. The PHP/PES blend system exhibited LCST behaviour. The cloud point curve is shown in Fig. 1.

Figure 2 shows T_g data obtained by DSC. It can be seen that each blend has one composition-dependent T_g, indicating its single-phase nature. It is clear that PHP is miscible with PES over the entire composition range.

Several theoretical and empirical equations have been used to describe the T_g-composition of miscible blends. One of these, the Gordon–Taylor equation [14], can be written thus:

$$T_g = T_{g1} + (kW_2/W_1)(T_{g2} - T_g) \quad (1)$$

where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} are the glass transition temperatures of components 1 and 2, respectively, W is the weight fraction, and k is a constant. It has been suggested [12, 15–17] that the value of k relates to the strength of interaction between the components in the blend although no theoretical basis for such a relationship has been suggested. Figure 3 shows a plot of this relationship for the PHP/PES blend which gives $k = 0.57$. This value is moderate, implying that the interaction between PHP and PES is not strong.

Figure 4 shows FTIR spectra in the 2800 to 4000 cm^{-1} region of plain PHP and the PHP/PES

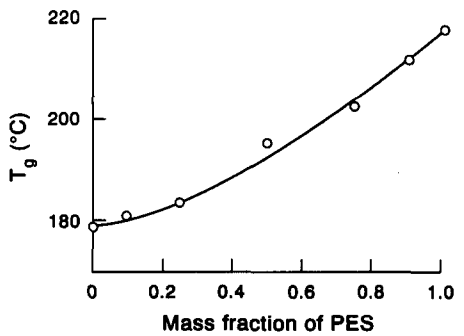


Fig. 2. Composition dependence of glass transition temperature of PHP/PES blends.

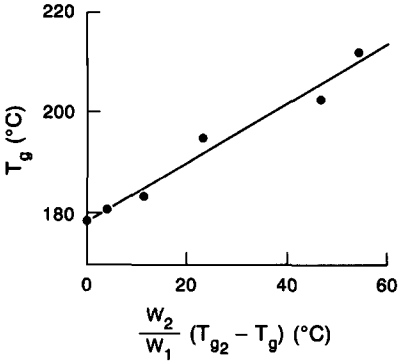


Fig. 3. Gordon–Taylor plot of T_g data for PHP/PES blends.

blends, all recorded at room temperature. The spectrum in this region for pure PHP may be considered to be composed of two components: a broad band centred at 3460 cm^{-1} attributed to hydrogen-bonded hydroxyl groups (self-associated) and a relatively narrow band at 3570 cm^{-1} assigned to free (non-associated) hydroxyl groups. Upon mixing with PES, the broad hydrogen-bonded hydroxyl band of PHP is observed to shift to higher frequencies as a function of increasing PES concentration, indicating that there is hydrogen-bonding interaction between PHP and PES. The frequency difference between the free hydroxyl absorbance and those of the hydrogen-bonded species ($\Delta\nu$) is a measure of the average strength of the intermolecular interactions [18]; the above results indicate that the average strength of the hydrogen bond between the PES ether oxygen and the PHP hydroxyl group ($\Delta\nu = 50\ cm^{-1}$ for 25/75 PHP/PES blend) is less than that between hydroxyl groups in pure PHP ($\Delta\nu = 110\ cm^{-1}$). This finding is entirely consistent with the results obtained in some phenoxy blend systems [3, 8] as well as with that implied by the

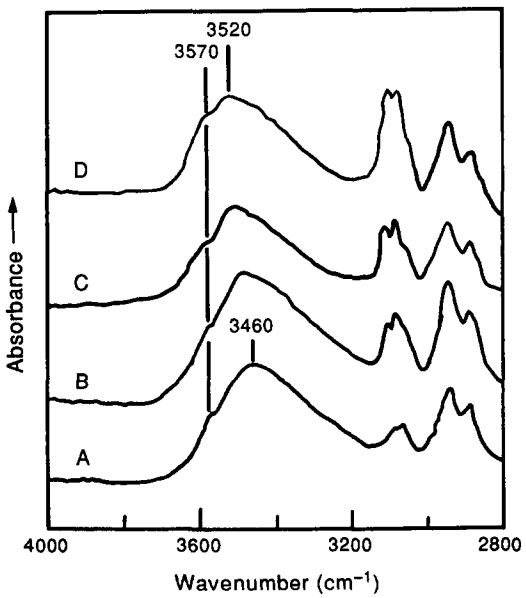


Fig. 4. FTIR spectra recorded at room temperature in the 2800–4000 cm^{-1} region for PHP/PES blends containing: (A) 0, (B) 25, (C) 50 and (D) 75 wt% PES.

moderate k value in the present PHP/PES system. Singh and Walsh [5] have been shown that PES and phenoxy are miscible and the favourable interaction between them is also weak.

CONCLUSIONS

In summary, PHP is miscible with PES. Homogeneous films were obtained for temperature below the cloud point curve. The existence of a single, composition-dependent T_g indicates that the blend forms a homogeneous single phase. FTIR study revealed that a hydrogen-bonding interaction occurs between these two components but it is weaker than that in pure PHP.

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