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Miscibility of poly(2,6-dimethyl-1,4-phenylene oxide)/poly(vinyl pyrrolidone) blends

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ABSTRACT

The miscibility of blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(vinylpyrrolidone) (PVP) was studied by differential scanning calorimetry (DSC) through the analysis of the glass transition temperature Tg. The dependence of Tg with the annealing temperature was determined for PPO and PVP samples of different molecular weights. The phase diagrams for blends containing three different PVP samples were established. Blends of PPO and PVP were found to be miscible for composition lower than 30% and higher than 65% of PVP. A inmiscibility window between 30 and 65% of PVP is also described.

Introduction

Polymer blends are a class of polymeric systems which can achieve important purposes, namely, to obtain materials with a good range of properties with a low cost/price ratio. Unfortunately, most polymers, having chemical structures strongly different, are incompatible and their properties are very modest and frecuently worse than those of the parent polymers (1,2). When two high molecular weight polymers are blended the gain in combinatorial entropy upon mixing is negligible, then miscibility of polymer pairs is the result of exothermic heat of mixing (3).

It is well known that poly(2,6-dimethyl-1,4-phenylene oxide) (poly-[oxy(2,6-dimethyl-1,4-phenylene)]) (PPO) is miscible with poly(styrene) (PS) over the whole composition range and accessible temperatures (4-8). However, small modifications of the chemical structure of either polymer, influence appreciably the miscibility behaviour of the blend. In fact, PPO is miscible with poly(α-methylstyrene) (7) and poly(p-methylstyrene) (9) but immiscible with halogenated polystyrene such as poly(o-chlorostyrene), poly(p-chlorostyrene), poly(p-fluorostyrene) (10-12). The presence of interacting groups on one of the polymers seems to play an important rol in

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*To whom offprint requests should be sent the compatibility behaviour of polymer blends. Miscibility has been attributed to the formation of specific interactions between both polymers which lead to favorable heats of mixing. The miscibility of PPO/PS blends has been attributed to dispersive interaction between the phenyl groups of the polymers (13). On the other hand, miscibility of PPO with sterically hindered amines has been studied in order to obtain blends with good thermal and photostability (14) and the miscibility depend on the composition, being miscible when the percentage of PPO in the blend is $\geq 40\%$.

In this paper we report the miscibility behaviour of PPO with poly(vinyl pyrrolidone) (PVP) samples of three different molecular weights. Both are polar polymers and therefore there exist the possibility of specific interactions favouring the miscibility. Therefore, it would be possible to expect miscibility due to their similar affinities and blends could give rise to very interesting materials where polarity of the structures is needed.

Experimental

Materials.

PPO was obtained from Polyscience; its viscosity average molecular weight (Mv) was 35.000 by intrinsic viscosity measurements in toluene at 298 K and using the equation $[\eta](ml/g) = 2.85 \times 10^{-3} Mv^{0.68}$. The PVP samples used for this study were from Aldrich and the average molecular weights were 10.000, 24.000 and 40.000 respectively and labelled as PVP_{10}, PVP_{24} and PVP_{40} respectively.

Preparation of the blends.

All the blends were prepared by dissolving the polymers in chloroform and blending the solutions in the desired proportions and the total concentration of polymers was always 2% (w/w). The blend in solution was precipitated with petroleum ether under vigorous stirring. Blends were dried in vacuum at room temperature following the experimental procedure described by Kim et al. (15).

Calorimetric measurements.

The glass Transition Temperature (Tg) of the different samples were measured with a Mettler TA-3000 system equipped with a TC-A10 processor and a DSC-20 cell. Polymer samples were dried under reduced pressure in a vacuum oven prior to measurements. Samples were weighed into de DSC aluminium pans. Dry nitrogen were used as purge gas and thermograms were measured in the range 308-513, 323-513 and 323-533 K for samples containing PVP_{10}, PVP_{24} and PVP_{40} respectively at a scan rate of 20 K min^{-1}. Regular calibration of the instrument were carried out using metal standards.

Before measuring the glass transition all samples were first heated to the annealing temperature previously determined for the corresponding homopolymers. The glass transition was located as baseline shift on the thermogram and Tg was estimated from the point of intersection of the sloping portion of the curve resulting from the baseline shift. Each blend was scanned several times between the temperature range described above.

Annealing experiments were performed by heating the polymer sample to the selected annealing temperature and maintaining it at this temperature for 20 min. This period was found by experiment to be long enough to attain a distinct phase separation in these samples in the temperature range of interest but not long enough to produce degradation of the polymers.

FTIR Spectroscopy.

FTIR results were obtained with a Bruker IFS-25 spectrometer. The films were cast into a KBr window. The samples were stored under vacuum to minimize water absorption.

Results and Discussion

The most common procedure to analyze the miscibility of polymer blends is to examine its glass transition behaviour. The criterion for compatibility or incompatibility in polymer blends is the presence of a single glass transition temperature Tg for the material, which is intermediate between the Tg of the pure components and the existence of two Tg's in the DSC thermograms for incompatible polymer blends. The phase behaviour of blends of PPO with PVP of different molecular weights was studied by DSC. The glass transition temperature Tg of the three PVP samples, labelled as PVP_{10}, PVP_{24} and PVP_{40} and for PPO were found 138.5°C, 151.7°C, 161.4°C and 207°C respectively. The annealing temperatures for the parent polymers were previously determined in order to establish the appropriate annealing temperature for blends. Table 1 summarizes the annealing temperatures (Ta) and the corresponding Tg values for the samples of PPO, PVP_{10}, PVP_{24} and PVP_{40} considered in this study. In all cases for annealing temperatures upper than ~200 °C a constant Tg value is obtained. Therefore, all the polymer blends studied were heated for 20 min at temperatures above the annealing temperature of the parent polymers.

The calorimetric behaviour of PPO/PVP blends, is illustrated in Figure 1. This Figure shows the most representative DSC thermograms in the Tg region for blends of different compositions of PPO and PVP_{40}. As can be seen in Figure 1, for compositions between 30 and 65% of PVP, two Tg values are observed and for compositions lower than 30% and higher than 65% of PVP only a single Tg value is found. A similar behaviour is observed for blends containing PVP_{10}, and PVP_{24} namely, phase separation takes place between 30 and 65% of PVP what can be considered as a window of

Table 1. Annealing temperatures (Ta) for PPO, PVP$_{40}$, PVP$_{24}$ and PVP$_{10}$ and the correspondig glass transition temperatures (Tg).

	Tg °C			
Ta °C	PPO	PVP$_{10}$	PVP$_{24}$	PVP$_{40}$
150	-	107.3	-	-
160	-	112	-	-
170	198.6	113	130	129.5
175	-	-	134.4	-
180	201.3	112.7	140.7	131.3
185	-	-	141.2	-
190	202	114.4	146.6	148.3
195	202.5	-	-	56.7
200	203.7	-	-	159.3
210	205	117.4	148.4	158.0
220	205.7	-	-	158.5
225	-	-	149.9	158.7
230	205.3	121	-	-
240	206.2	-	150.1	159.9
250	206.7	124.4	151.7	162.7
270	206.9	-	149.7	161.7

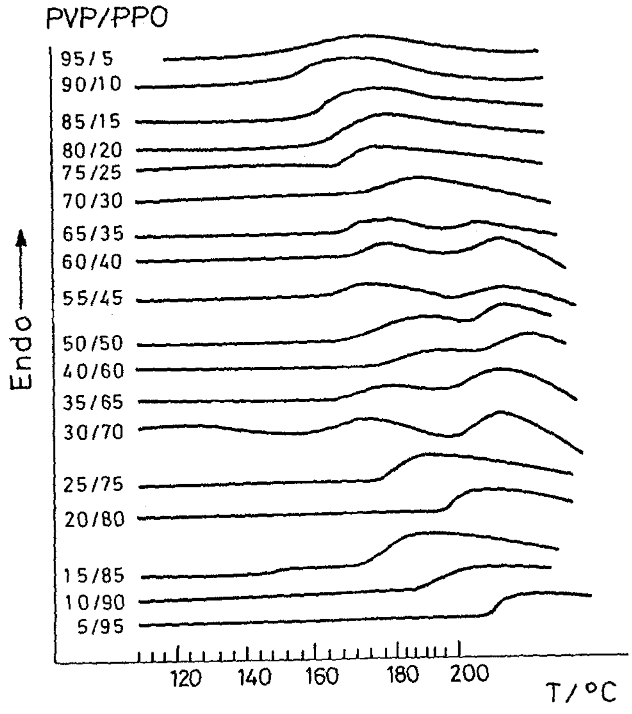

Figure 1. Thermograms for blends containing PPO/PVP$_{40}$.

inmiscibility. Blends less than 30% and more than 65% of PVP were transparent as prepared indicating that they might be miscible. They remained transparent upon heating to 300°C. On the other hand, blends of PPO/PVP with composition ranging between 30% and 65% were cloudy at room temperature.

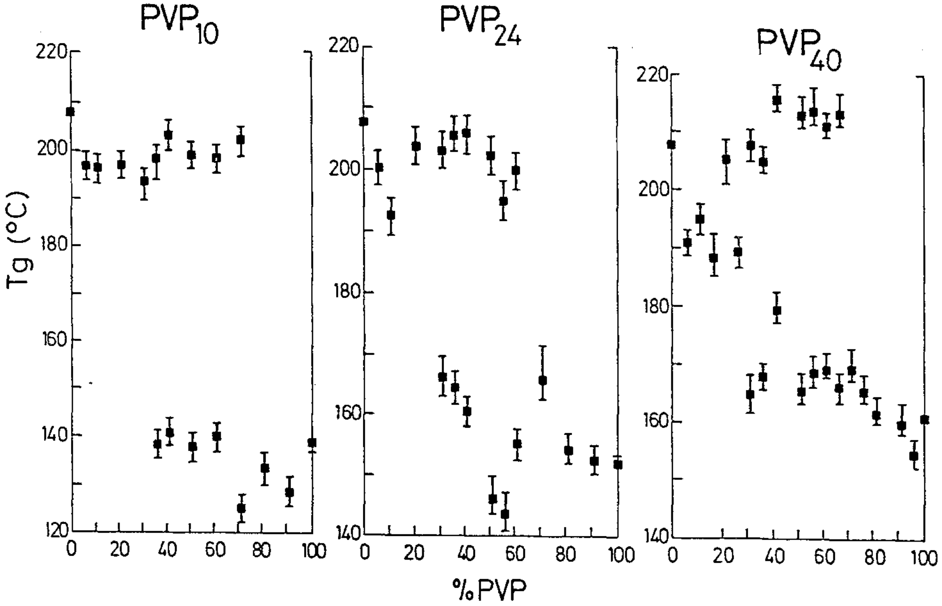

Figure 2. Phase diagrams for blends containing PVP$_{10}$, PVP$_{24}$ and PVP$_{40}$.

Figure 2 represents the phase diagrams of blends of PPO with PVP$_{10}$, PVP$_{24}$ and PVP$_{40}$ respectively. Two regions can be clearly identified: the first, for compositions lower than 30% and higher than 65% of PVP where only one Tg value of the blend, which is intermediate between the glass transition temperature of PPO and PVP can be observed and the second where blends show two glass transition temperatures located at nearly the same temperature as those corresponding to the Tg values of the pure components. The last region can be associated with blends of two-phase nature. Thus, we can consider that blends of PPO with PVP in the midcomposition region show a window of inmiscibility and both polymers can be considered as incompatible while they give rise to compatible polymer blends at either extreme. It is interesting to note that this behaviour is the same for the different PVP samples irrespective of the molecular weight in the range of molecular weight studied. This result seems to indicate that the Flory-Huggings interaction parameter χ_{12} for the blend should be negative. Nevertheless this interaction parameter should be small in magnitude due to the different nature of the forces involved in this kind of blend. This effect could be attributed to attractive forces between the negatively charged oxygen atoms of PPO and positively charged carbonyl carbon atoms of PVP. But on the other hand the attractive interaction is weakned by the repulsive forces offered by the negatively charged nitrogen atoms of PVP. A similar behaviour has been found in the blend PEO/atactic PMMA (16-18) using different experimental techniques. For a blend at the point of phase separation

$$\chi_{crit} = 1/2(X_1^{-1/2} + X_2^{-1/2})^2 \qquad (1)$$

where X_1 and X_2 are the degrees of polymerization of the two polymers. For a blend of two polymers of different degrees of polymerization χ_{crit} depends mainly on the polymer with lower degree of polymerization. In this case for the blend containing PVP_{40} the degree of polymerization is the same for both polymers which is about 360 and χ_{crit} is 0.0055. For blends containing PVP_{24} and PVP_{10} the degree of polymerization are 216 and 90 and χ_{crit} are 0.05 and 0.07 respectively. A linear dependence of χ_{crit} with the inverse of the molecular weight of PVP is observed for the samples studied. The FTIR spectra for the samples show a shift in the carbonyl signal of PVP for compositions where the blend is considered as compatible.

Finally we can conclude that partial miscibility of PVP/PPO blends can be considered for compositions higher than 65% and lower than 30% of PVP.

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