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Miscibility of poly(1-vinylimidazole)/ poly(p-vinylphenol) blends

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Summary

Blends of poly(1-vinylimidazole) (PVI) and poly(p-vinylphenol) (PVPh) were cast from ethanol or N,N-dimethylformamide (DMF). All the blends are miscible based on the single glass transition temperature (T_g) criterion. The T_g values of the blends are higher than those calculated from linear additivity rule. Blends cast from ethanol show a larger positive deviation than those cast from DMF. The T_g-composition curves can be fitted by the Kwei equation. FTIR studies show the existence of a strong hydrogen-bonding interaction between PVI and PVPh.

Introduction

The formation of a miscible polymer blend generally arises from a favorable intermolecular interaction between the two component polymers. Therefore, it is not surprising that poly(vinylpyridines) are miscible with a large number of proton-donating polymers through hydrogen-bonding interactions. For example, poly(4-vinylpyridine) (P4VPy) is miscible with poly(p-vinylphenol) (PVPh) (1,2), poly(acrylic acid) (PAA) (3,4), poly(methacrylic acid) (PMAA) (4), poly(monoalkyl itaconates) (5-7) and poly(hydroxyether of bisphenol-A) (8).

It is also well known that when the intermolecular interaction is strong enough, the two polymers may form interpolymer complexes by co-precipitating from their common solvent in which both component polymers are initially soluble. P4VPy forms interpolymer complexes with PVPh, PAA, PMAA and poly(monoalkyl itaconates). However, the occurrence of complexation depends on the nature of solvent. Complexation does not occur if the solvent interacts strongly with one or both of the component polymers. For example, P4VPy forms interpolymer complexes with PVPh in ethanol but not in N,N-dimethylformamide (DMF) (2).

Poly(1-vinylimidazole) (PVI) has been used as a corrosion inhibitor for copper (9,10) and as a compatibilizer for polyethylene/polystyrene blends (11). Since imidazole (pK_b = 7.05) is a stronger base than pyridine (pK_b = 8.75), it is envisaged that PVI may also be miscible with proton-donating polymers. In this communication, we report the miscibility of PVI with PVPh.

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Experimental

Materials

PVPh with a reported molecular weight range of 1500-7000 was obtained from Polysciences. 1-Vinylimidazole (from Fluka) was distilled at 78-79°C/13 mmHg. PVI was prepared by solution polymerization in absolute ethanol at 70°C for 40 hours. 20 mL of the monomer was mixed with 50 mL of solvent and initiated by 0.040 g of 2,2-azobis(isobutyronitrile). PVI was obtained by precipitating the ethanol solution in excess of THF/n-hexane (3:8) solution. The polymer was washed repeatedly with the non-solvent mixture and dried in vacuo at 80°C for a week.

The molecular weight of PVI was determined by intrinsic viscosity measurements in ethanol using the Mark-Houwink equations (12):

$$[\eta] = 9.83 \times 10^{-4} M_n^{0.54} \quad \text{and} \quad [\eta] = 7.90 \times 10^{-4} M_w^{0.54}$$

The number- and weight-average molecular weights of PVI are 60000 and 89000, respectively.

Preparation of blends

Our previous study has shown that PVPh forms complexes with P4VPy in ethanol but not in DMF (2). The mixing of ethanol solutions of PVPh and P4VPy led to the formation of precipitates. To study a possible solvent effect on PVI/PVPh system, both ethanol and DMF were used as solvents. Appropriate amounts of PVI and PVPh were separately dissolved in ethanol or DMF to give a 1% (w/v) solution. The two polymer solutions were then mixed. In all cases, the mixing of the two polymer solutions led to a cloudy solution. This is an indication that PVI and PVPh interact strongly with each other with a tendency of precipitating out from the solution. However, the particles were so fine that neither filtration nor centrifugation was able to separate out the precipitates. As a result, the solution was allowed to evaporate slowly to dryness at room temperature. Blends with PVI:PVPh mole ratios of 1:3, 1:1 and 3:1 were prepared. All the blends as cast from ethanol or DMF were transparent. The blends were subsequently dried in vacuo at 80°C for at least one week.

T_g measurements

The glass transition temperatures (T_gs) of various samples were measured with a TA Instruments 2920 differential scanning calorimeter using a heating rate of 20°C/min. Each sample was subjected to several heating/cooling cycles to obtain reproducible T_g values. The initial onset of the change of slope in the DSC curve is taken to be the T_g.

FTIR studies

Samples for Fourier-transform infrared (FTIR) analysis were prepared by casting the ethanol or DMF solution onto KBr discs and then dried in vacuo at 80°C for a week. FTIR spectra were acquired on a Perkin-Elmer 1600 FTIR spectrophotometer at a resolution of 2 cm^{-1}. Spectra were recorded at 120°C using a SPECAC high-temeprature cell.

Results and Discussion

Each of the PVI/PVPh blends shows a single T_g, indicating miscibility. The T_g-composition curves for PVI/PVPh blends cast from ethanol and DMF are shown in Fig. 1. In both cases, the T_g value of the blend is larger than that calculated from additivity rule. Such a large positive deviation in T_g value indicates a very strong intermolecular interaction between the two polymers (13). The two T_g-composition curves can be fitted by the Kwei equation (13,14):

$$T_g(\text{blend}) = [(w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)] + qw_1w_2$$

where w_i and T_{gi} are the weight fraction and T_g of polymer i in the blend respectively, and K and q are fitting constants. The curves in Fig. 1 were drawn using k and q values of 1 and 156, and 1 and 81 for blends cast from ethanol and DMF, respectively. Similarly, the T_g values of P4VPy/PVPh blends also show large positive deviations from linear additivity rule (1,2).

Kwei (13) pointed out that the quadratic term qw_1w_2 is proportional to the number of specific interactions in the blends. In this respect, there are a larger number of interactions in blends obtained from ethanol as inferred by the larger q value. The aprotic nature of DMF enables it to interact strongly with hydroxyl groups, preventing to a certain extent the hydrogen-bonding interaction between PVI and PVPh. The hydrogen-bonding breaking ability of DMF is well documented (2,5,15-17)

FTIR is widely used to study hydrogen-bonding interactions in polymer blends. The frequency shifts of the hydroxyl bands of hydroxyl-containing polymers are commonly used to measure the strength of hydrogen-bonding interactions. In many miscible blends of PVPh such as those with poly(methyl methacrylate) (18-20), poly(ε-caprolactone) (21), poly(vinyl acetate) (22) and poly(dialkyl itaconates) (23), the self-association of PVPh is stronger than intermolecular hydrogen-bonding interactions. In other miscible PVPh blend systems such as those with poly(N-vinyl-2-pyrrolidone) (21), poly(N,N-dimethylacrylamide) (18) and P4VPy (2), the intermolecular hydrogen-bonding interactions are stronger than the self-association of PVPh.

In view of the hygroscopic nature of both PVI and PVPh, FTIR measurements were carried out at 120°C. The FTIR spectra in the hydroxyl region of PVPh and PVI/PVPh (1:3) blends cast from ethanol and from DMF are shown in Fig. 2. For pure PVPh, the band at 3518 cm^{-1} is ascribed to the free hydroxyl groups and the broad band centered at 3366 cm^{-1} is attributed to a wide distribution of hydrogen-bonded hydroxyl groups (self-association). For the PVI/PVPh (1:3) blend cast from DMF, there is no significant change in the position of the hydrogen-bonded hydroxyl band. The result indicates that the hydrogen-bonding interaction is of the same magnitude as the self-association of PVPh. However, for the PVI/PVPh (1:3) blend cast from ethanol, the center of the hydrogen-bonded hydroxyl band shifts to 3265 cm^{-1}. Such a low-frequency shift shows that the hydrogen-bonding interaction is stronger than the self-association of PVPh. Therefore, PVI and PVPh interact more strongly in blends cast from ethanol than in blends cast from DMF. The indication is consistent with the larger positive deviation of T_g values and also the larger q value for blends cast from ethanol as mentioned earlier.

In conclusion, PVI is miscible with PVPh arising from a strong hydrogen-bonding interaction. The nature of solvent has a significant effect on the hydrogen-bonding interaction between the two polymers.

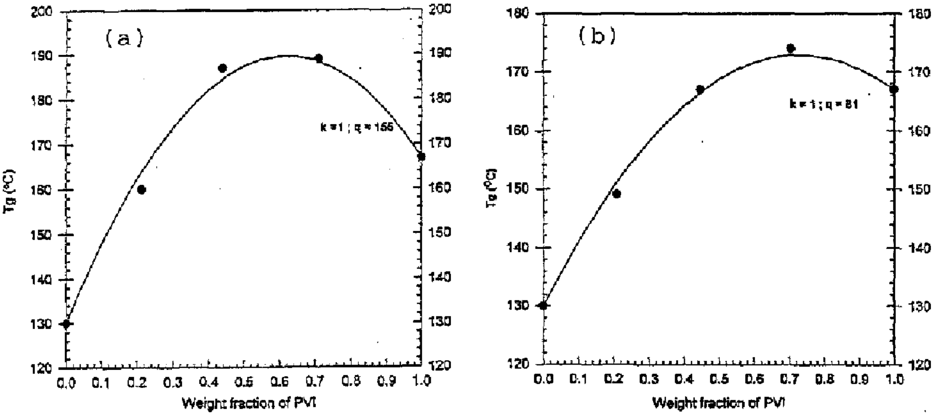

Fig. 1. T_g-composition curves of PVI/PVPh blends cast from (a) ethanol and (b) DMF.

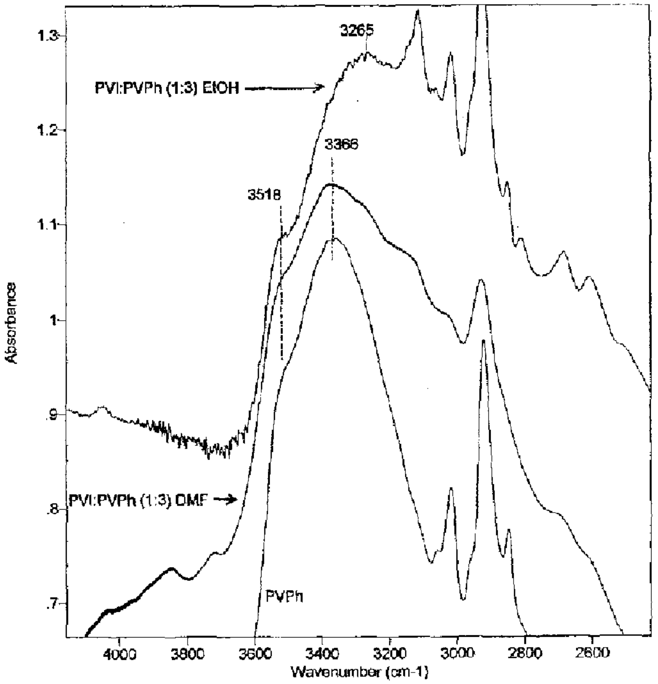

Fig. 2. FTIR spectra in the hydroxyl region of PVPh, ethanol-cast PVI/PVPh (1:3) blend and DMF-cast PVI/PVPh (1:3) blend recorded at 120°C.

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