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Miscible blends of poly(*n*-vinyl-2-pyrrolidone) with poly(3-chloropropyl methacrylate), poly(2-bromoethyl methacrylate) and poly(2-iodoethyl methacrylate)

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Summary

Poly(N-vinyl-2-pyrrolidone) is miscible with poly(3-chloropropyl methacrylate), poly(2-bromoethyl methacrylate) and poly(2-iodoethyl methacrylate) as shown by the optical clarity and the glass transition behaviour of the blends. The miscible blends degrade before phase separation could be induced by heating. The three T_g-composition curves can be fitted by the Gordon-Taylor equation. The implication of the Gordon-Taylor k parameters of the blends is discussed.

Introduction

Poly(N-vinyl-2-pyrrolidone) (PVP), a tertiary amide polymer, is miscible with many hydroxyl-containing polymers including poly(p-vinylphenol) (1), poly(hydroxyether of bisphenol-A) (2), poly(vinyl alcohol) (3-6), poly(2-hydroxyethyl methacrylate) (7), poly(2-hydroxypropyl methacrylate) (7), poly(styrene-co-allyl alcohol) (7), and copolymers of 2-hydroxyethyl methacrylate (8,9). Fourier-transform infrared spectroscopic studies have shown the existence of hydrogen-bonding interactions between the hydroxyl groups and the carbonyl groups of PVP (1,3,4).

PVP is also miscible with chlorine-containing polymers such as poly(vinyl chloride) and polyepichlorohydrin (10). We have previously reported that PVP is miscible with poly(chloromethyl methacrylate) (PCMMA) and poly(2-chloroethyl methacrylate) (PCEMA) but is immiscible with poly(methyl methacrylate) and poly(ethyl methacrylate) (11).

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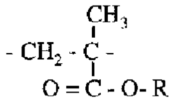
We have recently found that poly(N,N-dimethylacrylamide) (PDMA), also a tertiary amide polymer, is miscible with PCMMA, PCEMA, poly(2-bromoethyl methacrylate) (PBEMA), poly(2-iodoethyl methacrylate) (PIEMA) and poly(3-chloropropyl methacrylate) (PCPMA) (12). It is of interest to study if PVP is also miscible with PBEMA, PIEMA and PCPMA.



$$-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{O=C-O-R}{|}}{C}}-$$

R = $-CH_2CH_2Br$ (PBEMA)
$-CH_2CH_2I$ (PIEMA)
$-CH_2CH_2CH_2Cl$ (PCPMA)

Experimental

Materials

PVP, with a weight-average molecular weight (M_w) of 40,000 and a glass transition temperature (T_g) of 168°C, was obtained from Scientific Polymer Products. The preparation of PBEMA, PIEMA and PCPMA has been reported previously (12-14). The M_w and T_g values of PBEMA, PIEMA and PCPMA are 37,000 and 65°C, 100,000 and 55°C, and 138,000 and 52°C, respectively.

Preparation of blends

Binary blends of varying compositions were prepared by solution casting from dimethylformamide (DMF). Initial removal of solvent was done on a hot plate at 90°C and the blends were further dried in vacuo at 90°C for 4 days. The blends were stored in a desiccator to prevent absorption of moisture.

T_g measurements

The T_gs of various samples were measured with a Du Pont 910 differential scanning calorimeter using a heating rate of 20°C/min. The T_g value of PVP is sensitive to moisture caused by the hygroscopic nature of the polymer (16,17). Blends of PVP which have not been properly dried show anomalously low T_g values (5). Turner and Schwartz have shown that PVP can be dried in the course of DSC runs to give reproducible T_g values (17). Thus, the blends were first heated to 175°C and kept at that temperature for 5 min and subsequent scans were then made. The T_g is taken as the initial onset of the change of slope in the DSC curve. Each sample was scanned several times to check the reproducibility of the T_g values.

All the miscible blends were examined for the existence of lower critical solution temperature using the method as described previously (18).

Results and Discussion

All the binary blends were transparent and remained so upon heating to 260°C where discolouration began to develop. An amorphous immiscible blend can be transparent if the difference in the refractive indices of the two polymers is less than 0.01. The refractive indices of PVP is 1.53 (19) and those of the halogen-containing polymethacrylates are in the range of 1.49-1.50 as estimated by the Vogel method (20). Thus, the transparency of the blends might be an indication of miscibility.

Each of the blends showed one composition-dependent T_g indicating complete miscibility. The three T_g-composition curves are shown in Fig. 1. These curves can be fitted by the Gordon-Taylor equation:

$$T_g = (w_1T_{g1} + kw_2T_{g2}) / (w_1 + kw_2)$$

where T_g, T_{g1} and T_{g2} are the glass transition temperatures of the blend, polymer 1 and polymer 2, respectively, w_1 and w_2 are the weight fractions of polymer 1 and polymer 2 in the blends, and k is an adjustable parameter. The curves in Fig. 1 were drawn using the Gordon-Taylor equation with k values of 0.41, 0.32 and 0.20 for PVP/PBEMA, PVP/PIEMA and PVP/PCPMA blends, respectively. We have earlier shown that the k values for PVP/PCMMA and PVP/PCEMA blends are 0.62 and 0.48, respectively (11).

Prud'homme and co-worker (21,22) suggested that the Gordon-Taylor k parameter can be taken as a measure of the strength of the specific interaction. They observed that the k value for poly(ε-caprolactone) (PCL)/chlorinated polyethylene (CPE) blends decreased with decreasing chlorine content in CPE and PCL was immiscible with CPE having a sufficiently low chlorine content. They also pointed out that the k value cannot be used to compare two completely different series of blends. We have previously observed that for blends of PVP with poly(ethyl methacrylate-co-2-hydroxyethyl methacrylate), the k value increases with increasing 2-hydroxyethyl methacrylate (HEMA) in the copolymers (8). The variation of k value is consistent with the consideration that the higher the HEMA content, the more hydroxyl groups are there to interact with PVP. The present results can then be taken to indicate that the interaction between PVP and a halogen-containing polymethacrylate decreases in the order PCMMA > PCEMA > PBEMA > PIEMA > PCPMA.

The interactions between PVP and halogen-containing polymethacrylates may involve the carbonyl groups of PVP and the α-hydrogens of the $-CH_2X$ groups. We

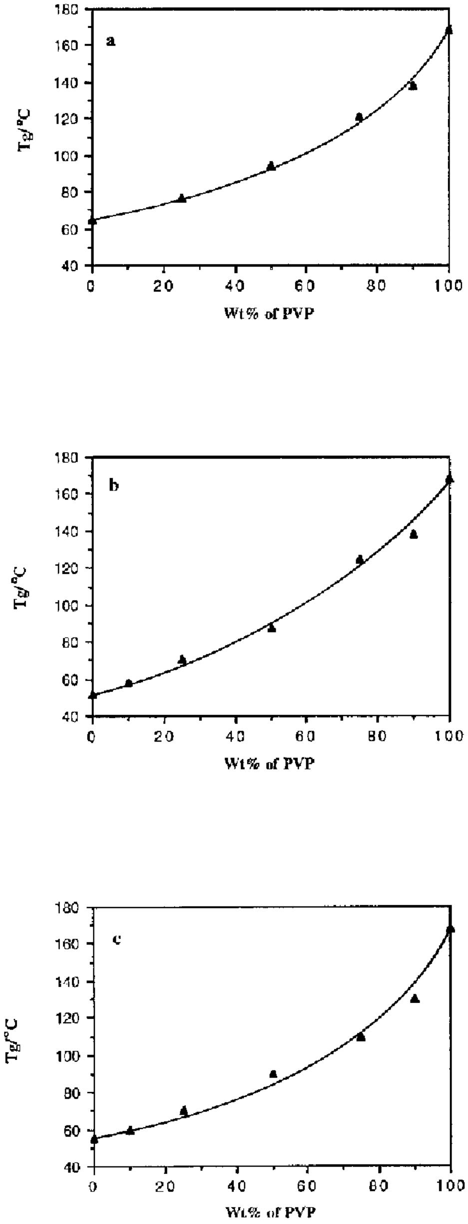


Figure 1 T_g-composition curves for (a) PBEMA/PVP (b) PCPMA/PVP (c) PIEMA/PVP blends have recently studied the miscibility of halogen-containing polymethacrylates with poly(alkyl methacrylate)s (13-15,18,23). The abilities of halogen-containing polymethacrylates to be miscible with poly(alkyl methacrylate)s are in the order PCMMA > PCEMA > PCPMA, and PCEMA > PBEMA > PIEMA. We suggested that the miscibility of halogen-containing polymethacrylates may arise from interactions involving the α-hydrogens of the pendant -CH_2X groups. The presence of electron-withdrawing halogen and the ester carboxyl group makes the hydrogens of the -CH_2X group acidic. The acidity of the hydrogens decreases in the order PCMMA > PCEMA > PCPMA because of the intervening methylene group, and PCEMA > PBEMA > PIEMA because of the decreasing electronegativity from chlorine to iodine. We have recently computed the atomic charge distributions of various halogen-containing polymethacrylate segments (24) using a self-consistent field molecular orbital calculations (25). The atomic charges of α-hydrogens, which indicate acidity, are 0.136, 0.127, 0.120, 0.118 and 0.107 for PCMMA, PCEMA, PBEMA, PIEMA and PCPMA, respectively. The variation of the Gordon-Taylor k values follows the same trend as the variation of the acidity of the -CH_2X group.

In summary, while PVP is immiscible with poly(alkyl methacrylate)s, it is readily miscible with the five halogen-containing polymethacrylates, indicating the important role of halogen in achieving miscibility. The blends degrade before phase separation could be induced by heating.

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