

Miscible blends of poly(*N*-vinyl-2-pyrrolidone) with polysulfone and carboxylated polysulfone

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Summary

The miscibility of poly(*N*-vinyl-2-pyrrolidone) (PVP) with polysulfone and carboxylated polysulfone was studied. Based on the optical appearance and the glass transition behavior of the blends, PVP was found to be miscible with polysulfone and four carboxylated polysulfone samples with degrees of carboxylation ranging between 0.43 and 1.93. All the miscible blends did not show lower critical solution temperature behavior. The T_g -composition curves of all the miscible blend systems can be described by the Gordon-Taylor equation.

Introduction

Polysulfone is a strong, rigid and tough materials with excellent dimensional stability. It is widely used for synthetic membranes in ultrafiltration processes (1). The hydrophilicity of polysulfone can be enhanced by sulfonation (2-4) or carboxylation (1,5). We have earlier studied the miscibility of polysulfone with a tertiary amide polymer poly(ethyl oxazoline) (PEOx) (6). While polysulfone is immiscible with PEOx, carboxylated polysulfone with a degree of carboxylation of 0.93 or more is miscible with PEOx.

Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a tertiary amide polymer readily miscible with many hydroxyl-containing polymers such as poly(vinyl phenol) (7), poly(hydroxy ether of bisphenol-A) (8), poly(vinyl alcohol) (9-11), poly(2-hydroxyethyl methacrylate) (12), poly(2-hydroxypropyl methacrylate) (12), and ethyl methacrylate/2-hydroxyethyl methacrylate copolymer (13). In some respects, the miscibility behavior of PVP is similar to that of polyoxazoline. For example, both PVP and PEOx are miscible with poly(vinylidene fluoride) (14,15); PVP (16) and poly(methyl oxazoline) (17) are miscible with poly(vinyl chloride). In this communication, we report the miscibility of PVP with polysulfone and carboxylated polysulfone (CPSf).

Experimental

The polysulfone used was Udel P-3500 supplied by Amoco Performance Products. It was dissolved in tetrahydrofuran,

precipitated in ethanol, followed by washing with distilled water and drying. Polysulfone was carboxylated to various extents following the procedures by Guiver and co-workers (1). Four CPSf samples with degrees of carboxylation of 0.43, 0.93, 1.38 and 1.93 were used in this study. The value refers to the average number of carboxylic groups per repeating unit of polysulfone. In the following discussion, the number after CPSf denotes the degree of carboxylation. PVP with a weight-average molecular weight of 40,000 was obtained from Scientific Polymer Products, Inc. It was dried in vacuo at 100°C overnight before blending with polysulfone and various CPSf samples.

All the blends were prepared by solution casting from dimethylformamide. Initial removal of solvent was done on a hot plate at 90°C and the blends were further dried in vacuo at 100°C for 4 days.

The glass transition temperatures (T_g) of various samples were measured with a Perkin-Elmer DSC-2 differential scanning calorimeter using a heating rate of 20°C/min. PVP is hygroscopic and its T_g value is sensitive to the moisture in the sample (18). Turner and Schwartz (19) have shown that reproducible T_g values can be obtained by prolonged heating the sample at 200°C in the DSC under nitrogen atmosphere. In the present study, the blends were first heated to 220°C and kept at that temperature for 45 min and subsequent runs were then made between 120-220°C. The T_g is taken as the initial onset of the change of slope in the DSC curve.

All the miscible blends were examined for the existence of lower critical solution temperature (LCST) behavior using the method as described previously (20).

Results and Discussion

All the PVP/polysulfone blends were transparent and did not show LCST upon heating to 250°C where they began to develop brown coloration. DSC measurements revealed the existence of a single T_g for each blend as shown in Fig. 1. Based on the optical clarity and the glass transition behavior, it is concluded that PVP is miscible with polysulfone. It is noted that polysulfone is miscible with PVP but not with PEOx. The formation of a miscible blend generally requires a favorable intermolecular interaction between the two component polymers (21). The miscibility of PVP/polysulfone blends may arise from dipole-dipole interactions between the amido groups of PVP and the sulfonyl groups of polysulfone. The present results also indicate that polysulfone interacts more intensely with PVP than with PEOx.

It has been observed that the T_g -composition curves of many PVP-containing blends (6,8,9,12,13,16) can be fitted by the Gordon-Taylor equation

$$T_g(\text{blend}) = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2)$$

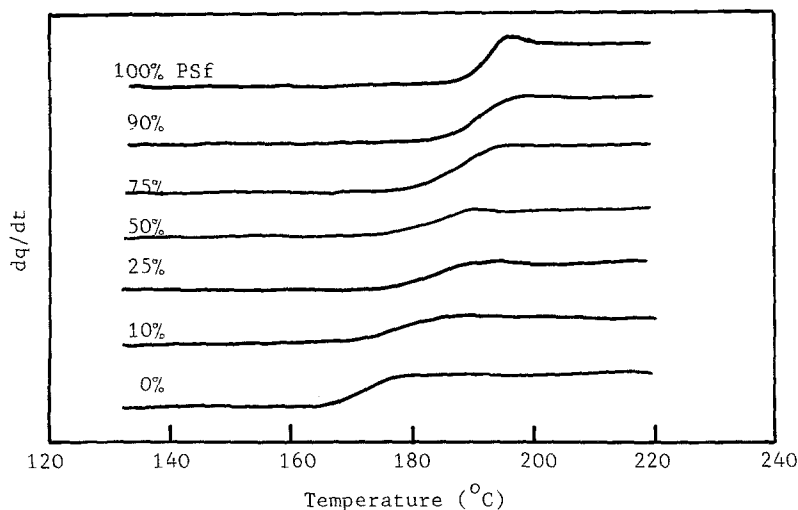


Fig. 1. DSC curves of PVP/polysulfone blends

where w_i and T_{g_i} are the weight fraction and T_g of polymer i in the blend, respectively, and k is an adjustable constant. The T_g -composition curve of PVP/polysulfone blends as shown in Fig. 2a is based on the Gordon-Taylor equation using a k value of 0.75.

All the blends of PVP with CPSf0.43, CPSf0.93, CPSf1.38 and CPSf1.93 were also transparent and did not show LCST behavior. In addition, each of the blends showed only one T_g , indicating its single-phase nature. Thus PVP is miscible with the four carboxylated polysulfone samples.

The T_g -composition curves of various PVP/CPSf blends can similarly be described by the Gordon-Taylor equation using k values of 0.60, 0.50, 0.40 and 0.25 for blends containing CPSf0.43, CPSf0.93, CPSf1.38 and CPSf1.93, respectively. The curves shown in Figs. 2b-2e were drawn using the appropriate k values. It has been suggested that the k value provides a semi-quantitative measurement of polymer-polymer interaction in the blend (22-25). A large k value indicates a stronger interaction. For the present blend systems, the k value becomes smaller as the degree of carboxylation increases, indicating a reduction in the intensity of interaction between the two polymers. The indication appears to be surprising as one would expect the incorporation of carboxylic groups would enhance interaction via hydrogen-bonding involving the carboxylic groups. However, the incorporation of carboxylic groups is likely to lead to self-association of carboxylated polysulfone. Thus, in addition to intermolecular interaction between PVP and CPSf, the self-association of CPSf and the accompanied entropy changes have to be considered as well. Coleman and co-workers have recently focused their attention on blends involving polymers which are strongly self-associated (26-29). Nevertheless, the present

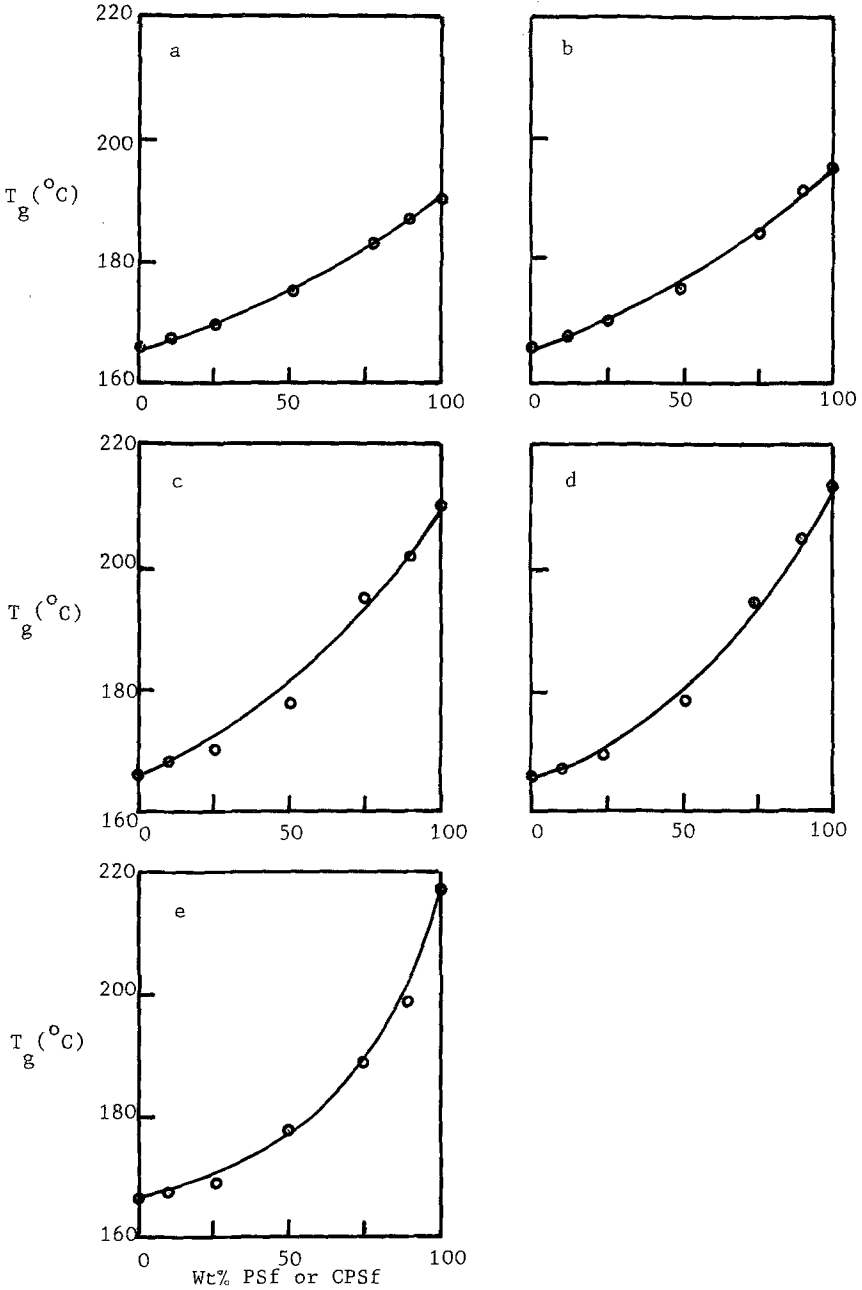


Fig. 2. T_g -composition curves of blends. (a) PVP/polysulfone; (b) PVP/CPSf0.43; (c) PVP/CPSf0.93; (d) PVP/CPSf1.38 and (e) PVP/CPSf1.93.

study has shown that PVP is miscible with polysulfone and carboxylated polysulfone.

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