Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Yeo, Y. T. , Goh, S. H. and Lee, S. Y.(1997) 'Miscibility of Polyacrylonitrile with Tertiary Amide Polymers', Journal of Macromolecular Science, Part A, 34: 4, 597 — 603

To link to this Article: DOI: 10.1080/10601329708014987

URL: http://dx.doi.org/10.1080/10601329708014987

J.M.S.—PURE APPL. CHEM., A34(4), pp. 597–603 (1997)

MISCIBILITY OF POLYACRYLONITRILE WITH TERTIARY AMIDE POLYMERS

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ABSTRACT

The miscibility of polyacrylonitrile (PAN) with four tertiary amide polymers was studied. Each of the binary blends of PAN with poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(*N*-methyl-*N*-vinylacetamide) (PMVAc), or poly(*N*,*N*-dimethylacrylamide) (PDMA) showed a single glass transition temperature (T_g), indicating miscibility. However, PAN is immiscible with poly(2-ethyl-2-oxazoline) (PEOx) as shown by the appearance of two T_gs in each of the blends. Based on the frequency shifts of the carbonyl band of the tertiary amide polymer and the cyano band of PAN, the intensity of intermolecular interaction between PAN and tertiary amide polymer is in the order PVP > PMVAc > PDMA > PEOx.

INTRODUCTION

Tertiary amide polymers such as poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(*N*,*N*-dimethylacrylamide) (PDMA), poly(*N*-methyl-*N*-vinylacetamide) (PMVAc), and poly(2-ethyl-2-oxazoline) (PEOx) are miscible with a large variety of polymers including poly(*p*-vinylphenol) [1, 2], poly(vinyl alcohol) [3, 4], hydroxyl-containing polymethacrylates [5, 6], poly(dialkyl itaconates) [7], poly(monoalkyl itaconates) [8], poly(vinylidene fluoride) [9], halogen-containing polymethacrylates [7, 10], and poly(enamino nitrile) [11]. The miscibility of these blends arises from specific intermolecular interactions involving the carbonyl groups of tertiary amide polymers.

When the intermolecular interactions are particularly strong, tertiary amide polymers can even form interpolymer complexes with some polymers.

We have recently studied the miscibility and complexation behavior of tertiary amide polymers [12–14]. The ability of tertiary amide polymers to form miscible blends or complexes with hydroxyl-containing polymers is in the order PVP > PMVAc > PDMA > PEOx. We have also studied the miscibility of tertiary amide polymers with cyano-containing polymethacrylates [15]. PVP, PMVAc, and PDMA are miscible with poly(cyanomethyl methacrylate) (PCYMMA) and with poly(2-cyanoethyl methacrylate) (PCYEMA). However, PEOx is miscible with PCYMMA and PCYEMA when the blend contains more than 60 wt% PCYMMA or more than 80 wt% PCYEMA.

In contrast, there have been few studies on the miscibility of polyacrylonitrile (PAN) blends. It was believed that the large solubility parameter value of PAN is unfavorable for miscibility with other polymers [16]. Nevertheless, the miscibility of PAN with cellulose has been studied extensively [17–20]. Dynamic mechanical measurements showed the existence of a single glass transition temperature for each of the PAN/cellulose blends, indicating miscibility [17]. Guo et al. [21] recently reported PAN is miscible with PVP based on the glass transition behavior. In view of the miscibility of cyano-containing polymethacrylates with tertiary amide polymers and that of PAN/PVP blends, we have studied the miscibility of various PAN/tertiary amide polymer blends using differential scanning calorimetry and Fourier-transform infrared (FT-IR) spectroscopy. It will be shown in this communication that PAN is miscible with PVP, PMVAc, and PDMA but immiscible with PEOx.

EXPERIMENTAL

Materials

PAN and PVP were obtained from Scientific Polymer Products, Inc.; the nominal molecular weights of PAN and PVP are 150 and 40 kg/mol, respectively. PEOx with a nominal molecular weight of 200 kg/mol was obtained from Dow Chemicals. PDMA and PMVAc were prepared by solution polymerization in 1,4-dioxane at 80°C for 4 hours using azobisisobutyronitrile as initiator. The polymers were recovered from the dioxane solution by precipitation in *n*-hexane. The number- and weight-average molecular weights of PMVAc are 3.3 and 3.7 kg/mol, respectively, and those of PDMA are 12 and 20 kg/mol, respectively, as determined by GPC.

Various PAN/tertiary amide polymer blends containing 10, 25, 50, and 75 wt% PAN were prepared by solution casting from *N*,*N*-dimethylformamide (DMF). Initial evaporation of DMF was done on a hot plate maintained at 100°C. The blends were further dried in vacuo at 90°C for 10 days.

Thermal Characterization

The glass transition temperatures (T_gs) of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C/min. Samples were subjected to heat treatment at 130°C for 15 minutes prior to DSC measurements to remove absorbed moisture and residual solvent. The T_g value was 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 T_g values.

FT-IR Studies

FT-IR spectra were recorded on a Perkin-Elmer 1725X spectrophotometer. A minimum of 64 scans at 2 cm^{-1} spectral resolution was averaged in all cases. Samples were prepared by casting 1% DMF solutions (w/v) of polymer blend onto KBr disks. The disks were dried at 90°C in vacuo for at least 4 days and then stored in a desiccator. Prior to FT-IR measurements, the disks were heated again at 130°C for 15 minutes to remove any absorbed moisture.

RESULTS AND DISCUSSION

Thermal Characterization

The appearance of a single composition-dependent T_g in a polymer blend is commonly used as the criterion of miscibility. Each of the binary blends of PAN with PVP, PMVAc, or PDMA showed a single T_g. It is therefore concluded that PAN is miscible with PVP, PMVAc, and PDMA. The T_g-composition curves of the three blend systems are shown in Fig. 1. Guo et al. [21] also found that each of the PAN/PVP blends showed a single T_g. In contrast, each of the PEOx/PAN blends showed two T_gs, indicating that PEOx is immiscible with PAN. The immiscibility of PEOx/PAN blends is consistent with an earlier study on PEOx/poly(styrene-*co*-acrylonitrile) (SAN) blends by Keskkula and Paul [22]. PEOx is miscible

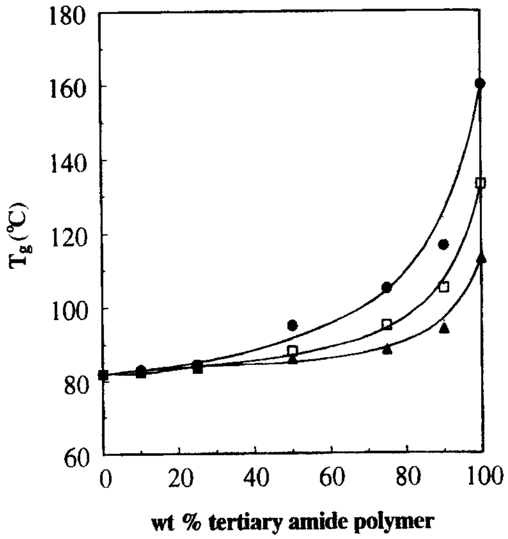

FIG. 1. T_g-composition curves for (●) PAN/PVP, (□) PAN/PMVAc, and (▲) PAN/PDMA blends.

with SAN when the acrylonitrile content of SAN is 23.5, 25, or 40%, but it is immiscible with a rubber-modified SAN containing 70% acrylonitrile.

The T_g-composition curves of many miscible blends can be fitted by the Gordon–Taylor equation:

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

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 blend; and k is an adjustable parameter. The curves in Fig. 1 were drawn using the Gordon–Taylor equation with k values of 0.13, 0.10, and 0.09 for PVP/PAN, PMVAc/PAN, and PDMA/PAN blends, respectively. The fitting is reasonably good. For blends of similar chemical structures, the Gordon–Taylor k parameter can be taken as a measure of the intensity of intermolecular interaction [23, 24]. The larger the k value, the more intense is the interaction. In this respect, the order of the intensity of interaction of PAN with the three tertiary amide polymers is then PVP > PMVAc > PDMA.

FT-IR Studies

FT-IR studies provide information on the nature and intensity of intermolecular interactions in polymer blends. For miscible blends of tertiary amide polymers, the amide carbonyl band of tertiary amide polymer either shifts to a lower freqency [6, 11, 15] or shows the development of a shoulder at a lower frequency [1, 13]. Figure 2 shows the FT-IR spectra in the amide carbonyl region of various PVP/

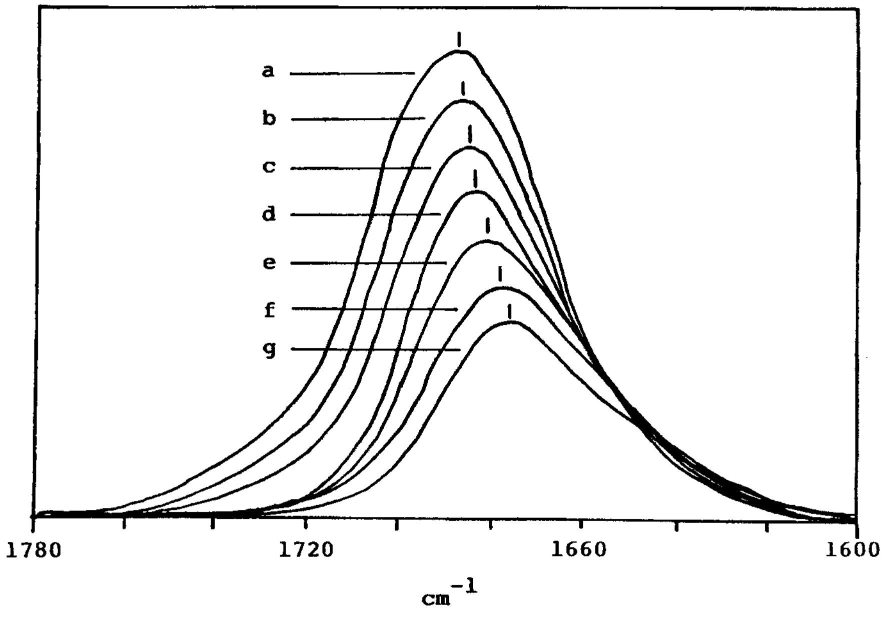

FIG. 2. Scale-expanded IR spectra of amide carbonyl bands of PVP in PAN/PVP blends of varying compositions: (a) pure PVP, (b) 10% PAN, (c) 25% PAN, (d) 50% PAN, (e) 75% PAN, (f) 83% PAN, and (g) 90% PAN.

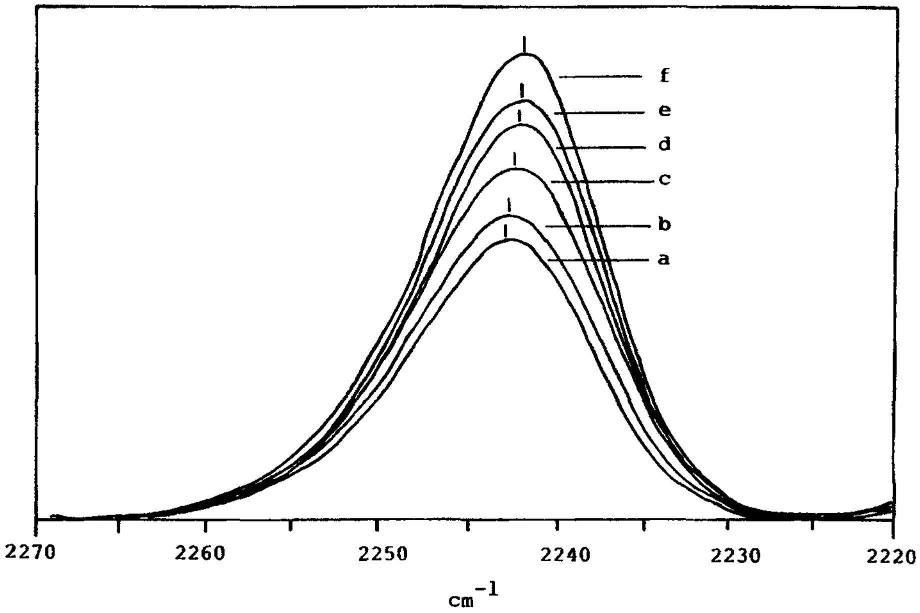

FIG. 3. Scale-expanded IR spectra of cyano bands of PAN in PAN/PVP blends of varying compositions: (a) pure PAN, (b) 10% PVP, (c) 25% PVP, (d) 50% PVP, (e) 75% PVP, and (f) 90% PVP.

PAN blends. Upon the addition of PAN, the center of the amide carbonyl band gradually shifts to a lower frequency. For a PAN/PVP blend containing 90 wt% PAN, the low-frequency shift is 10 cm^{-1}, which is of the same order of magnitude as that observed in PVP/cyano-containing polymethacrylate blends [15]. Guo et al. [21] did not characterize PVP/PAN blends by FT-IR. The amide carbonyl band spectra of PAN/PMVAc and PAN/PDMA blends show similar low-frequency shifts. However, the shift is negligible for PAN/PEOx blends, and this is consistent with the immiscibility of the blends as shown by T_g measurements. If the extent of low-frequency shift is taken as an indication of polymer-polymer interaction, the intensity of the interaction between PAN and the four tertiary amide polymers is then in the order PVP ($\Delta\nu = 10\ cm^{-1}$) > PMVAc ($\Delta\nu = 8.5\ cm^{-1}$) > PDMA ($\Delta\nu = 7.5\ cm^{-1}$) > PEOx ($\Delta\nu = 0\ cm^{-1}$). The order is in agreement with those observed for other blends of tertiary amide polymers [14, 15] and is consistent with that based on the Gordon-Taylor *k* parameter as mentioned earlier.

In our earlier studies on blends of tertiary amide polymers with cyano-containing polymethacrylates [15], the cyano band of poly(2-cyanoethyl methacrylate) (PCYEMA) was found to show a low-frequency shift. Figure 3 shows the cyano bands of PAN in various PAN/PVP blends. The cyano band of PAN at 2243 cm^{-1} shifts toward lower frequencies with increasing PVP content in the blends and is shifted to 2242 cm^{-1} for a blend containing 90 wt% PVP. The shift is quite small but is of similar magnitude as those of tertiary amide polymer/PCYEMA blends and liquid mixtures of *N*-methyl-2-pyrrolidone and benzonitrile [15]. The cyano bands of PAN in PAN/PMVAc and PAN/PDMA blends also show small low-frequency shifts but not in PEOx/PAN blends. The extent of frequency shift is in the order PVP ($\Delta\nu = 1\ \text{cm}^{-1}$) > PMVAc ($\Delta\nu = 0.9\ \text{cm}^{-1}$) > PDMA ($\Delta\nu = 0.8\ \text{cm}^{-1}$) > PEOx ($\Delta\nu = 0\ \text{cm}^{-1}$). The order is in agreement with that based on the frequency shift of the amide carbonyl band as shown earlier.

Miscibility arises from intermolecular interactions between the two component polymers. For the present blend systems, the involvement of amide carbonyl groups is obvious. For PAN, there are two possible sites of interaction: the α-hydrogen and the cyano group. For complexes of organic nitriles, a high-frequency shift of the cyano band is taken to indicate complex formation via the lone pair electrons of the nitrogen atom, while a low-frequency shift of the cyano band is taken to indicate complexation via the π-orbital of the C≡N bond [25, 26]. The observed low-frequency shift of the cyano band of PAN in the three miscible blend systems appears to suggest interaction involving the π-orbital. However, an alternative interaction mode involving the α-hydrogen is likely in view of a recent molecular modeling study on blends of PAN with poly(ethylene-*alt*-maleic anhydride) (PEMA) [27]. Quantum mechanical calculations were applied to search for the existence of attractive interactions between PAN and PEMA. The calculation results suggest that interactions mainly involve the oxygen atoms of PEMA and the α-hydrogens of PAN. It is likely that interactions involving the α-hydrogens of PAN and the amide carbonyl groups of PVP, PMVAc, and PDMA are responsible for the miscibility of these blend systems. Guo et al. [21] also suggested the miscibility of PVP/PAN blends could be due to hydrogen-bonding interactions involving the α-hydrogens of PAN.

In summary, the present study has shown that PAN is miscible with PVP, PMVAc, and PDMA but immiscible with PEOx. Our recent series of studies has also shown that for the three isomeric tertiary amide polymers, viz. PMVAc, PDMA, and PEOx, PEOx shows the poorest ability in forming miscible blends with other polymers. This has been attributed to the poorer accessibility of the amide carbonyl groups of PEOx since they are close to the polymer main chain and therefore are prevented from interacting with functional moieties of the other polymers [14].

CONCLUSION

PAN is miscible with PVP, PMVAc, and PDMA but is immiscible with PEOx. FT-IR studies show that the intensity of interaction between PAN and tertiary amide polymer is in the order PVP > PMVAc > PDMA > PEOx.

ACKNOWLEDGMENT

Financial support of this work by the National University of Singapore is gratefully acknowledged.

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Received May 15, 1996
Revision received August 1, 1996