Macromolecules **1992,** *25,* 1427–1432

Blends of Poly(enamino nitrile)

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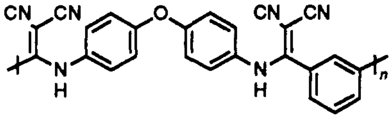
Received August 5, 1991

ABSTRACT: Poly(enamino nitrile) (PEAN) forms miscible blends with several commercial polymers including poly(ethylene oxide) (PEO), poly(4-vinylpyridine) (P4VP), and tertiary amide polymers such as poly(ethyloxazoline) (PEOX), poly(*N*-vinylpyrrolidine) (PNVP), and poly(*N*,*N*-dimethylacrylamide) (PDMA) as determined by the transparency of blend films and the observation of a single glass transition temperature which changes smoothly with composition. Binary blends containing more than 50 wt % of PEO showed PEO melting endotherms indicating the development of PEO crystallites in the homogeneous amorphous mixture. At higher temperatures PEO/PEAN blends undergo phase separation which signals the existence of a lower critical solution temperature. An endothermic transition associated with phase separation was clearly discernible by calorimetry, as was an exothermic transition associated with redissolution. These reversible phase separation and redissolution processes were observed by hot-stage optical microscopy. Strong hydrogen-bonding interaction between enamine hydrogen atoms and electronegative oxygen or nitrogen atoms on the other component polymers was evidenced by FT-IR and is suggested as a specific interaction which favors miscibilities in these blends.

Introduction

Poly(enamino nitriles) (PEANs) are novel, high molecular weight, film-forming polymers which have excellent thermal stability and good mechanical properties.[1]



These polymers are soluble in many organic solvents. The PEAN used in this work is soluble in acetone, THF, glymes, and pyridine as well as typical polar, aprotic solvents including DMF, NMP, DMAc, and DMSO. The good solubility of PEAN is in contrast to the very limited solubility of analogous aromatic polyamides (aramids). Introduction of the rather bulky and polarizable dicyanomethylidene group in place of oxygen atoms seems to result in the good solubility of this aromatic polymer by preventing crystallization and/or very strong hydrogen-bonding interactions as are expected in the amide structure. Compared to the very strongly associated amide NH proton, enamine hydrogen atoms may be less self-associated and able to form strong hydrogen bonds with molecules which contain good proton-accepting functional groups.

A homogeneous polymer blend consists of two (or more) polymers that are compatible at the molecular level, thus combining the properties of the polymeric components to yield a distinct new material. It has been well established that miscible blends of polymer materials result when exothermic physical interactions, such as hydrogen bonding, occur between unlike blend components.[2-5] Particularly, hydrogen bonding is of central importance in many polymer blend systems, and it is readily measured by spectroscopic methods.[3-5]

As pointed out by Coleman et al.,[6] polymers that are relatively weakly self-associated but contain sites, the oxygen or nitrogen atoms, which are capable of strong interaction (hydrogen bonding in this case) will be potential candidates expected to form miscible blends with PEAN. Polyethers and polypyridines are excellent examples of this class of polymer. Poly(4-vinylpyridine) (P4AVP) is one of the strongest proton acceptors known which has a nitrogen atom with a lone pair of electrons at the 4-position of the pyridine ring. The good solubility of PEAN in a series of polyether solvents and the existence of lower critical solution temperatures (LCST) for these solutions also suggest favorable mixing between poly(ethylene oxide) (PEO) and PEAN.[7] Polymers which have a tertiary amide structure such as poly(ethyloxazoline) (PEOX), poly(*N*-vinylpyrrolidone) (PNVP), and poly(*N*,*N*-dimethylacrylamide) (PDMA) are considered to be good hydrogen-bonding acceptors because of the slightly basic nature of this functional group. Many miscible blend systems involving these tertiary amide polymers and hydroxyl-containing polymers have been reported. It was expected, therefore, that these polymers would form miscible blends with poly(enamino nitrile). The attempted blends with poly(vinyl methyl ether), poly(vinyl acetate), and poly(methyl methacrylate) (PMMA) were found to be immiscible.

In this work, we studied the miscibility of PEAN with several good proton-acceptor polymers and the interesting phase behavior which is observed in PEO/PEAN blends. Differential scanning calorimetry (DSC) and optical microscopy were used to investigate miscibility and phase separation. FT-IR and NMR were used to study the specific interactions involved in these blend systems.

Experimental Section

Materials. Poly(enamino nitrile) with an intrinsic viscosity of 0.47 dL/g in DMF at 25 °C was prepared through condensation polymerization of 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene with oxydianiline (ODA) using the procedure we have developed.[1] The viscosity value corresponds to a weight-average molecular weight of 34 000 as measured by low-angle laser light scattering.

A model compound, 1,3-bis[2,2-dicyano-1-((4-phenoxyphenyl)-amino)vinyl]benzene, was prepared by treating 2 equiv of 4-phenoxyaniline with 1 equiv of 1,3-bis(1-chloro-2,2-dicyanovinyl)-benzene using the modified procedure reported.[1]

PEO with an average molecular weight of 100 000 was purchased from Aldrich Chemical Co. and used without purification. Poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) (P2VP) were obtained from Polysciences, Inc., with molecular weights of 50 000 and 40 000, respectively, and were used without purification. PEOX with a molecular weight of 200 000 was generously provided by Dow Chemical Co. and was purified by precipitation of a solution of the polymer in methyl ethyl ketone into a large volume of *n*-hexane and dried under vacuum at 80

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°C for 2 days. PNVP with an average molecular weight of 40 000 was purchased from Aldrich Chemical Co. and used without purification. Poly(*N*,*N*-dimethylacrylamide) was purchased from Polysciences, Inc., and was purified by precipitation of a polymer solution in methyl ethyl ketone into a large volume of ethyl ether and dried under vacuum at 100 °C for 2 days.

Blend Preparation. Blends were prepared by solution casting from DMF. A mixture (0.1 g) of the blend components in the desired ratio was stirred in 3–4 mL of DMF for several hours at 50 °C to give a homogeneous solution. The solution was filtered through a 0.45-mm microfilter and spread onto an aluminum pan. The solvent was evaporated slowly under N_2 flow at 60 °C. The resulting films were further dried in vacuo (<1 Torr) at 120 °C for 72 h and then slowly cooled to room temperature and stored in a desiccator over $CaCl_2$ prior to measurement. Despite the extensive drying in vacuum, a small amount of DMF seems to remain in relatively high T_g mixtures. The contents of residual solvents were determined from TGA weight-loss curves. In the case of PEO/PEAN blends, blend films containing more than 50 wt % of PEO did not show any evidence of remaining residual solvent. However, a 30 wt % PEO blend showed about 0.5 wt % of residual solvent remaining in the film, and a 20 wt % PEO blend and pure PEAN showed about 1.5–2.0 wt % of residual solvent remaining in the films. In the other blend systems, about 1.0–2.0 wt % of residual solvent was observed for the blend samples with high PEAN contents (>50 wt %) after drying.

The samples for FT-IR analysis were cast on NaCl plates using the same procedure as was used in the DSC measurements. However, the much thinner films used in this case should facilitate solvent removal, and the influences of residual solvents are expected to be very small or negligible in FT-IR analysis. No noticeable DMF absorption bands were observed in the IR of blend samples.

Calorimetric Measurements. Thermal analysis studies were performed on a Perkin-Elmer System 7 differential scanning calorimeter and thermogravimeter interfaced with a Perkin-Elmer Model 7500 computer under a nitrogen atmosphere. A heating rate of 20 K/min was used in all measurements if it is not specified otherwise. Sample sizes ranged from 5 to 10 mg. The glass transition temperature was taken as the midpoint of the heat capacity change. The T_g values from the second heating cycle are reported.

The cloud point curve in PEO/PEAN blends was established by DSC and microscopic observations of the onset of phase separation. The morphology of the phase-separated structure was observed on a hot-stage optical microscope. FT-IR spectra were recorded on a Perkin-Elmer Model 1800 spectrometer at a resolution of 2 cm^{-1}. At least 32 scans were signal-averaged. NMR spectra were recorded on a Varian Model XL-200 spectrometer.

Results and Discussion

1. PEO/PEAN Blends. Films containing 10, 20, 30, 40, 50, 60, 70, 80, and 90 wt % of PEO were prepared as described above. Films containing up to 50 wt % of PEO were transparent, but films containing more than 50 wt % of PEO became increasingly less transparent with increasing PEO content. Careful microscopic observations revealed that the turbidity is caused by the growth of crystallites of PEO which has exceeded its solubility limit in PEAN under the conditions at hand. Indeed, the calorimogram began to show the melting endotherm of PEO with growing peak intensity as the PEO content increased beyond 60 wt %. Thus these blends containing more than 50 wt % PEO may be viewed in terms of crystallites of PEO coexisting with a mixed amorphous matrix of PEAN and PEO, to a first approximation.

The crystallinity of PEO as a function of blend composition was calculated from the equation

$$X_c = (\Delta H_{fus}/\Delta H^\circ_{fus}) \times 100$$

where X_c is percent crystallinity and ΔH°_{fus}, the heat of fusion of perfectly crystalline PEO, has been reported to be 51 cal/g.[8] The results are plotted in Figure 1. Earlier studies on blends between PEO and amorphous polymers, e.g., PMMA, reported that the degree of crystallization, melting temperature, crystallization rate, and microstructure of PEO are perturbed strongly by the presence of the amorphous polymer because of specific interactions between the two.[9] As shown in Figure 1, the crystallinity of PEO in the blend containing 10 and 20 wt % PEAN does not deviate much from the dashed line, which represents the crystallinity of PEO in the blends when the crystallization process is not influenced by the presence of PEAN. The deviation becomes significant above 20 wt % PEAN, which suggests a pronounced inhibition of crystallization by the presence of PEAN. This result is more evident from the rescan of a quenched sample. Compared to the small drop in the crystallinity up to 20 wt % PEAN, almost complete repression in the crystallization of PEO was observed for the 30 wt % PEAN blend.

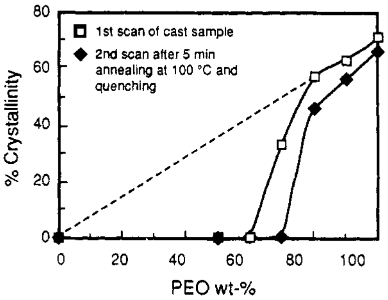


Figure 1. Percent crystallinity of PEO in PEAN/PEO blends.

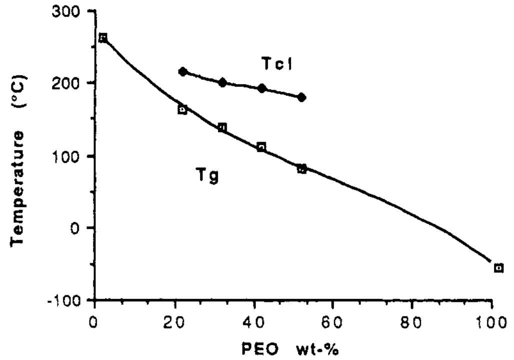


Figure 2. Cloud point (T_{cl}) and T_g vs composition curves of PEO/PEAN blend.

The T_g vs composition curve up to 50 wt % PEO is shown in Figure 2 (lower curve). A single glass transition changing smoothly between the limiting values of T_g for the pure polymers suggests miscibility between these two polymers. Besides the glass transition, another composition-dependent endothermic transition was observed at higher temperatures during heating. A typical DSC trace for the 50/50 PEAN/PEO blend is shown in Figure 3 (upper curve). Hot-stage microscopy showed that the phase separation process occurs at the same temperature as the exotherm observed by DSC. The initially clear film became opaque upon heating beyond 175 °C and became clear again when the sample was cooled; i.e., the process was reversible. The kinetic aspects of phase separation and redissolution are an interesting subject, but it is beyond the scope of this paper. A partial cloud point curve was obtained from DSC and microscopic observations of the onset of phase separation as shown in Figure 2 (upper line). This lower consolute type of phase behavior further substantiates miscibility at temperatures below the cloud point and suggests that these polymers are miscible as a result of an exothermic interaction. A highly interconnected two-phase morphology with uniform domain size, which are some of the familiar characteristics of spinodal

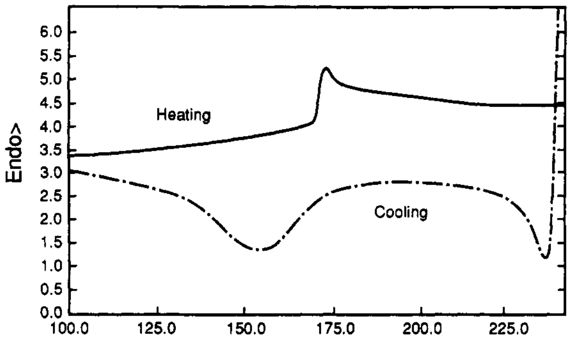


Figure 3. Calorimetry of phase separation and redissolution for a 50/50 PEO/PEAN blend.

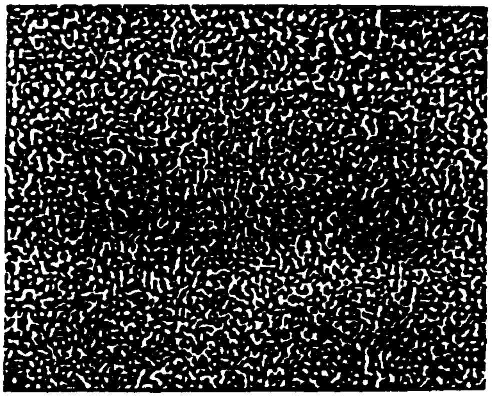


Figure 4. Optical micrograph of the phase-separated structure for 50/50 PEO/PEAN blend taken on a hot-stage microscope at 200 °C (original magnification 600×; the micrograph has been reduced to 70% of its original size for publication).

decomposition,[10] is seen in the micrograph of a 50/50 PEAN/PEO blend (Figure 4) which had been heated to 200 °C. In this system, phase redissolution occurred relatively rapidly, and reheating the sample reproduced the original separation process.

Recently, several authors[11-13] have studied the heat of demixing associated with LCST phase behavior by DSC. From the DSC of a 50/50 PEAN/PEO blend at different heating rates (5–40 K/min), the onset temperature of the endothermic peak was found to shift slightly to higher temperature with increasing rate, as has been observed by other authors.[11,13] Heats of demixing were determined from the area under the endothermic peaks. At lower heating rates, the area spreads out dramatically and precise measurement becomes difficult. Within the heating rate range from 5 to 40 K/min, $\Delta H_{\mathrm{demix}}$ was found to be approximately 5.0 ± 0.5 J/g (corresponding to 4.26 ± 0.4 kJ/mol of PEAN). This value is comparable to 0.48 cal/g (2.0 J/g) reported by Uriarte et al. recently for the 50/50 poly(vinyl methyl ether)/poly(Bisphenol A hydroxy ether) blend.[11] It seems that the heat of demixing does not change much depending on the heating rate in the PEO/PEAN blend system. The value of this heat of demixing gives an approximation of the heat of mixing of a particular blend, as was proposed by Evert et al.[13] Of course, this approximation presumes that the phases are composed mainly of the pure components. Figure 5 (upper curve) represents the heat of demixing vs blend composition. The heat of demixing increases, showing a maximum value at around 50 wt %, and then decreases as the PEO concentration increases.

As discussed earlier, the phase separation in PEO/PEAN blends is associated with an endothermic process which was observed by DSC, and the phase redissolution seems to occur quite rapidly in this blend system as observed by optical microscopy and a rescan of the calorimetry after quenching. From the above results, it is expected that the corresponding exothermic transition associated with the phase redissolution should be observed in the subsequent cooling scan on the calorimeter. Indeed, the expected exothermic transition was observed in the DSC cooling scan of 50/50 PEAN/PEO blend as shown in Figure 3 (lower curve). These data provide direct evidence of the negative enthalpy of mixing and the reversible nature of phase separation involved in these blends. Even though the base line was not perfect and the transitions were rather broad, it was possible to calculate the approximate enthalpy values associated with this phase mixing from the exothermic peaks of subsequent cooling scans after some corrections because of curvature. The results are plotted in Figure 5 (lower curve). The transitions below 20 and above 80 wt % PEO were so broad that the calculation was difficult. For blends between 30 and 70 wt % PEO, however, very close values from both heating and cooling scans were obtained within experimental error, which indicates the truly equilibrium nature of the phase changes in this blend system. These values provide an approximate range of interaction energy which is involved in stabilizing intermixing between the two component polymers.

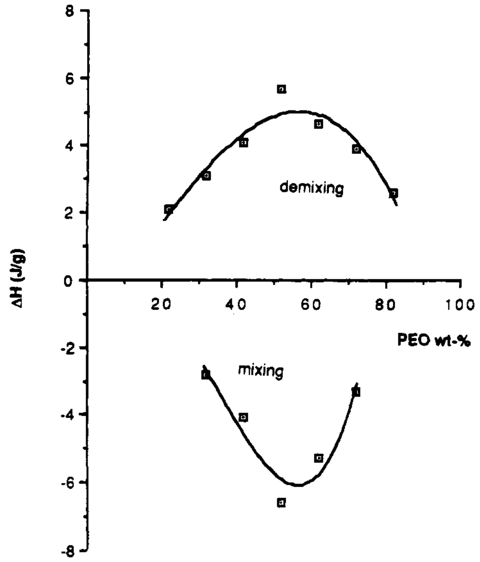


Figure 5. Heat of demixing and mixing (phase redissolution) as a function of composition.

FT-IR spectrometry was used to study the hydrogen-bonding interaction involved in this blend. The FT-IR spectra of the NH stretching region of PEAN are shown in Figure 6. As the concentration of PEO is increased in the blend, the infrared band at 3360 cm^{-1}, attributed to relatively "free" NH groups, decreases and the broad band originally centered at 3250 cm^{-1}, attributed to the whole range of the weakly associated NH, is shifted to lower frequency. This result indicates a strong hydrogen-bonding interaction between the enamine hydrogen atoms on the PEAN backbone and the oxygen atoms in PEO. Thermogravimograms of the blends are shown in Figure 7. It is interesting to notice that the onset of decomposition of PEO shifts slightly to higher temperatures as the PEAN content increases. This improvement in the thermal stabilities of the blends also suggests intimate mixing between the component polymers.

2. P4VP/PEAN Blends. Films cast from mixtures of the two polymers in DMF are completely transparent, and each blend exhibits a single T_g which varies smoothly with composition between the T_g values of the two

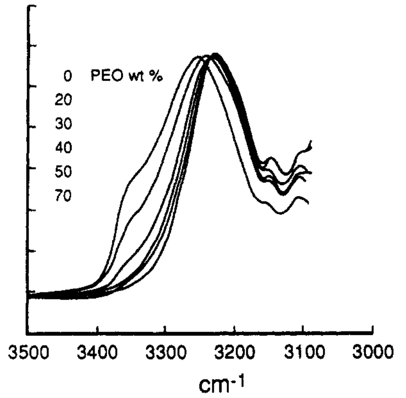


Figure 6. FT-IR spectra of the N–H stretching region of the PEO/PEAN blends.

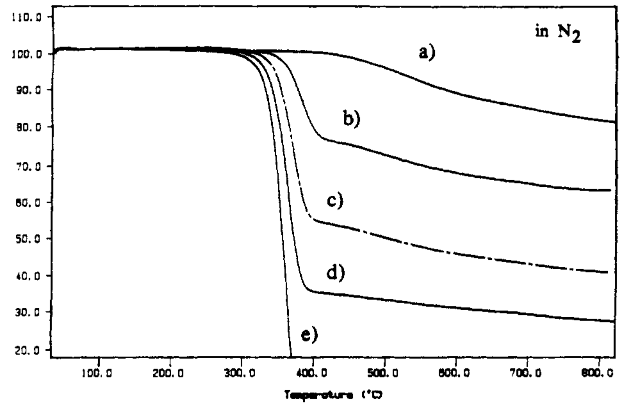


Figure 7. Thermogravimograms of PEO/PEAN blends: (a) 1,3-ODA-PEAN; (b) 70/30 PEAN/PEO; (c) 50/50 PEAN/PEO; (d) 30/70 PEAN/PEO; (e) pure PEO.

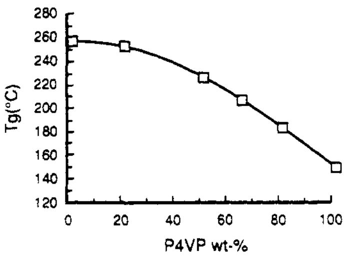


Figure 8. T_g vs composition curve of P4VP/PEAN blend.

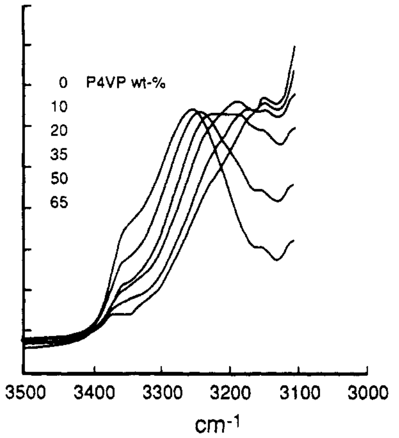


Figure 9. FT-IR spectra of the N–H stretching region of the P4VP/PEAN blends.

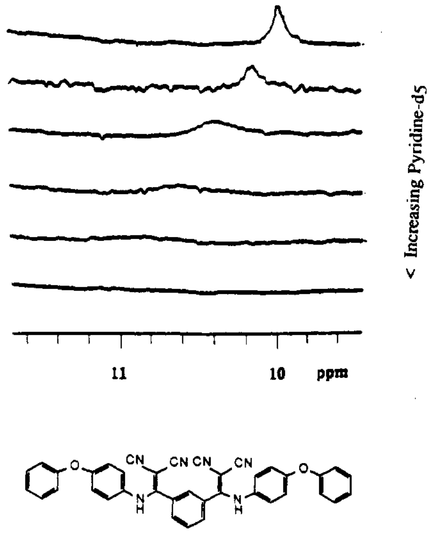


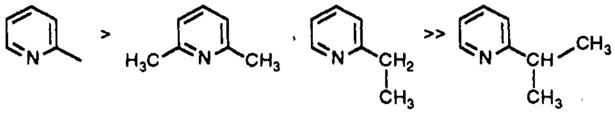
Figure 10. Chemical shift of the enamine protons in NMR by addition of pyridine-d_6 (NMR solvent, acetone-d_6).

component polymers. The T_g vs composition curves are shown in Figure 8.

The FT-IR spectra of the blends suggest that hydrogen-bonding interactions are involved in stabilizing these blends. Figure 9 shows representative scale-expanded infrared spectra of the N–H stretching region of pure PEAN and its blends. As the concentration of P4VP is increased, the N–H band originally centered at 3250 cm^{-1} shifts to lower frequency around 3190 cm^{-1} and the absorption band around 3360 cm^{-1} decreases. An NMR study of a model compound, 1,3-bis[2,2-dicyano-1-((4-phenoxyphenyl)amino)vinyl]benzene, also suggests strong interaction of the enamine hydrogen atom with pyridine. The NH proton peak originally at 9.96 ppm in acetone shifts downfield more and more and undergoes peak broadening as pyridine-d_5 is added to the solution in an NMR tube (Figure 10).

In contrast to the complete miscibility between PEAN and P4VP, P2VP was found to form immiscible blends under the same conditions. DSC traces of P2VP/PEAN blends exhibited two clearly separated T_g values, indicating the overall immiscibility of this system. Only the film containing 10 wt % P2VP appeared clear to the naked eye. From 20 wt % P2VP on, the films became translucent and then completely opaque at higher concentrations of P2VP. Apart from their obvious opaque appearance and the gross multiphase character observed from DSC, infrared spectroscopic studies disclose that there are very few, if any, intermolecular hydrogen-bonding interactions occurring between the components of the blends, revealing an insignificant degree of mixing at the molecular level. The N–H stretching region of the FT-IR spectrum of this immiscible system is shown in Figure 11.

In relation to this result, it seemed useful to check the solubility of 1,3-ODA-PEAN in several pyridine derivatives. It was observed that solubility of the polymer decreases as follows:



1,3-ODA-PEAN was almost insoluble in 2-isopropylpyridine. Interestingly, dilute solutions (0.4–0.5%) in 2,6-lutidine or in 2-ethylpyridine showed cloud points around 60 °C, and this process was totally reversible. A solution of 1,3-ODA-PEAN in 2-picoline did not show any phase separation up to the boiling temperature of the solvent. We believe that this solubility behavior suggests the existence of specific interactions between solvents and solutes which favor mutual solubility, and the reduced

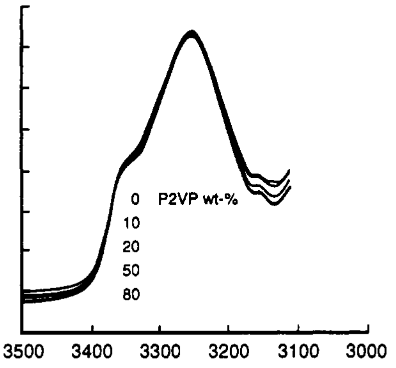
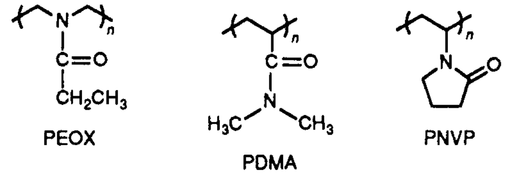


Figure 11. FT-IR spectra of the N–H stretching region of the immiscible P2VP/PEAN blends.

interaction caused by steric hindrance is responsible for the overall immiscibility observed for PEAN/P2VP blends. Steric limitations on the interaction ability of P2VP in comparison to P4VP have been noted previously. Abe et al.[14] observed that poly(methacrylic acid) formed stronger complexes with P4VP than with P2VP and concluded that the closeness of the pyridine nitrogen atom to the main chain in P2VP made complexation difficult. Similarly, P4VP was considered to be a "sterically unhindered amine" in comparison with P2VP in regard to the binding of copper salts by these polymers.[15] It is worthwhile to note that the PEANs used in this study show cloud points in a series of glyme solvents which are considered to be relatively weaker hydrogen-bonding acceptors compared to pyridine as described previously.[7]

3. PEAN Blends with Tertiary Amide Polymers. Three different tertiary amide polymers were used to investigate their miscibility behavior with PEAN. Poly(ethyl oxazoline) is a commercially important material which is soluble in water and in many organic solvents. This polymer is known to form miscible blends with many homopolymers and copolymers. Several miscible blends with polymers containing hydroxyl or carboxylic acid groups have been reported,[16] suggesting that hydrogen-bonding interaction plays an important role in these blends. Poly(*N*,*N*-dimethylacrylamide) (PDMA), which has a structure isomeric with PEOX as shown below, is expected to have similar solubility and miscibility behavior.

Poly(*N*-vinylpyrrolidone) (PNVP), which contains a substituted amide group similar in structure to PEOX and PDMA, is also known to form homogeneous blends or complex via hydrogen-bonding with several polymers containing proton-donating groups.[17]



All blend films of these polymers (PEOX, PNVP, and PDMA) with PEAN were transparent over the whole composition range, and each blend showed a single T_g which varies smoothly between the T_g values of the component polymers to meet one criterion for miscibility. The T_g vs composition curves of these three different blend systems are shown in Figures 12–14, respectively.

Direct evidence of hydrogen-bonding interactions between enamine hydrogen atoms of the PEAN and carbonyl groups of these tertiary amide polymers was obtained from infrared spectroscopy. Figure 15 shows FT-IR spectra in the N–H stretching region of PEAN/PEOX blends of varying compositions. As the concentration of PEOX is increased in the blend, the absorption band around 3360 cm^{-1} attributed to relatively "free" NH groups decreases and the major broad band originally centered at 3240 cm^{-1}, which is attributed to the whole range of a weakly associated NH, is shifted to lower frequency to 3190 cm^{-1}. Similar trends were also observed from the other blend systems.

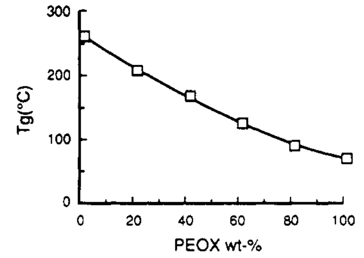


Figure 12. T_g vs composition curve of PEOX/PEAN blend.

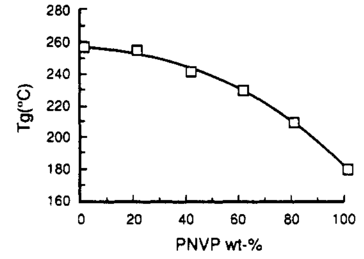


Figure 13. T_g vs composition curve of PNVP/PEAN blend.

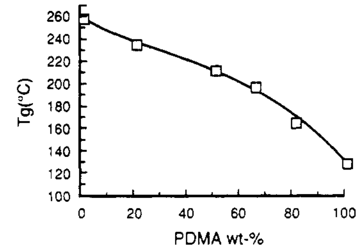


Figure 14. T_g vs composition curve of PDMA/PEAN blend.

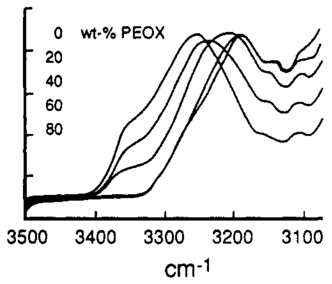


Figure 15. FT-IR spectra of the N–H stretching region of the PEOX/PEAN blends.

Figure 16 shows the corresponding carbonyl stretching region of PEOX/PEAN blends. Pure PEOX is characterized by a rather broad band centered at 1645 cm^{-1} attributed to the carbonyl stretching vibration. Upon increasing the PEAN content in the blend, this band shifts to lower frequency, which indicates an increase in the proportion of hydrogen-bonded carbonyl groups. Similar changes in IR spectra were observed from the other two blend systems (not shown). Relatively small shifts in the carbonyl stretching band were observed from the PDMA/PEAN system.

In homogeneous polymer blends, the hydrogen-bonding interaction between the two polymer chains may act as quasi-cross-linking. Hence, the solubility characteristics

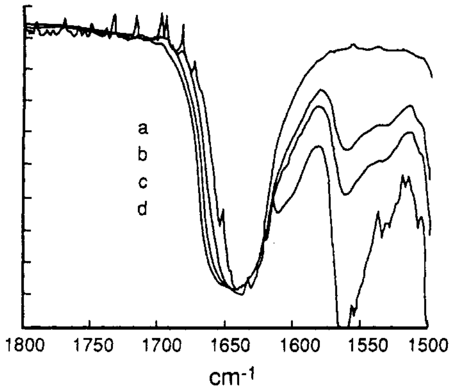


Figure 16. FT-IR spectra of the carbonyl stretching region of the PEOX/PEAN blends: (a) pure PEOX, (b) 80/20, (c) 60/40, (d) 40/60 (PEOX/1,3-PEAN blend).

may be very different from those of the individual components. By soaking several selected blend samples (50/50 PEOX/PEAN, 40/60 PDMA/PEAN, 30/70 PNVP/PEAN) in water, it was found that the water-soluble components were not leached from the blends, indicating the intimate mixing of the components. No appreciable weight loss was observed after soaking in stirred water for 48 h. Even after longer periods (up to 1 month) at room temperature the films remained transparent. This result again suggests that strong intermolecular interaction exists between the blend components.

Conclusions

PEAN forms miscible blends with good hydrogen-bonding acceptors such as PEO, P4VP, and three different tertiary amide polymers including PEOX, PNVP, and PDMA. The miscibility was determined by optical clarity and the observation of a single glass transition temperature changing smoothly with composition. PEO/PEAN blends exhibit LCST type phase behavior, and the phase separation is associated with an endothermic process. A broad exothermic transition associated with phase redissolution was also observed in the subsequent cooling scans. The heat exchanges involved in these reversible separation processes were calculated from the peak areas. The cloud point curve was obtained by means of DSC and microscopic observation of the onset of phase separation. Hydrogen bonding evidenced by FT-IR and NMR is suggested as a specific interaction responsible for the miscibility between the blend components.

Acknowledgment. This work was supported partially by a grant from the Office of Naval Research and an IBM graduate fellowship. Molecular weight measurements by light scattering were performed by Dr. T. Mourey, Eastman Kodak. Helpful discussions with Prof. S. Krause and Prof. K. Levon are gratefully acknowledged.

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Registry No. PEAN (copolymer), 108090-24-0; PEAN (SRU), 117371-55-8; PEO, 25322-68-3; P4VP, 25232-41-1; P2VP, 25014-15-7; PEOX, 25805-17-8; PNVP, 9003-39-8; 1,3-bis[2,2-dicyano-1-((4-phenoxyphenyl)amino)vinyl]benzene, 117371-52-5; poly(*N,N*-dimethylacrylamide), 26793-34-0.