

Water Extraction of Polyethyloxazoline from Miscible and Immiscible Polymer Blends

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Synopsis

Blends of water-soluble polyethyloxazoline (PEOx) with a series of hydrophobic styrene-acrylonitrile copolymers (SAN) of varying AN contents were immersed in water to determine the kinetics of water swelling and the extent of PEOx extraction. Copolymers containing 25 and 40% by weight of AN form miscible blends with PEOx; those containing higher and lower amounts of AN form immiscible mixtures with PEOx. A high degree of PEOx extraction was observed for the immiscible blends as expected, whereas surprisingly little PEOx was extracted from the miscible blends over periods up to 2 years in spite of a high degree of water swelling. Similar behavior has been noted for other blends of hydrophobic and hydrophilic polymers. In the present system, thermal analysis revealed that the sorption of large amounts of water induces a microphase separation of the two miscible polymers to form microdomains of SAN in which, evidently, segments of PEOx are entrapped to form physical cross-links that preclude disintegration of the sample and extraction of the PEOx whose phase is highly swollen by the sorbed water. It is proposed that a similar situation probably occurs for other blend systems exhibiting such behavior.

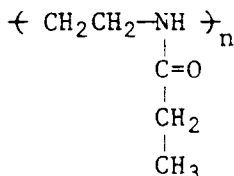
INTRODUCTION

Recent studies on blends of water-soluble polymers with hydrophobic polymers have suggested important differences in the swelling and extraction behavior of these blends by water based on the state of miscibility of the two polymers. Robeson et al.^{1,2} have reported briefly on miscible blends of the poly(hydroxy ether) of bisphenol A, a water-insoluble polymer, with two water-soluble polymers, poly(*N*-vinylpyrrolidone) and poly(ethylene oxide). Both systems are swollen by water to an extent that increases dramatically as the content of the water-soluble component increases; however, in both cases, surprisingly small amounts of the water-soluble polymer is extractable even when the blends are highly swollen by water. Both swelling and extraction levels are higher for blends containing poly(ethylene oxide) than those containing poly(*N*-vinylpyrrolidone). The latter is said to reflect a fair degree of association of the two polymers forming the blend.¹ Walsh and Singh³ have reported that poly(ether sulfone) and poly(ethylene oxide) form miscible blends that phase separate on heating; that is, lower critical solution temperature (LCST) behavior exists. By combining their findings with observations reported in two patents,^{4,5} Walsh and Singh conclude that poly(ethylene oxide) cannot be extracted by water from the miscible blends but it can from blends that have been phase separated by heating. Related observations have been noted for blends of partially hydrolyzed poly(styrene-

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co-maleic anhydride) with polymers like poly(vinyl acetate), which are reported to be miscible,^{6,7} and they apparently have a number of applications related to their readily tailored water-sorbing capacity. Some of these materials also show LCST behavior.

In a recent paper,⁸ we reported that polyethyloxazoline (PEOx) is miscible



with styrene-acrylonitrile copolymers (SAN) over a certain range of acrylonitrile contents. This type of copolymer miscibility window in blends with other polymers seems to be a relatively common phenomenon, as other discussions have pointed out.⁹⁻¹² The range of miscibility of PEOx with SAN is shown schematically in Fig. 1. These blends are interesting with respect to the observations noted above, for two reasons. First, PEOx is a water-soluble polymer, whereas, of course, the various SAN are not. The water solubility of PEOx is not based on ionizable functional groups, and it is also soluble in certain organic solvents. PEOx has good thermal stability,¹³ and its miscible blends with SAN do not show LCST behavior⁸ up to 300°C, permitting the use of standard thermoplastic fabricating procedures for making film, sheets, and moldings. Second, by varying the AN content of the SAN, the state of SAN miscibility with PEOx can be varied. Thus, PEOx-SAN blends provide interesting systems for more elaborate study of water swelling and extraction along the lines mentioned above.

EXPERIMENTAL

The polymers used in this work are identified by source and composition in Table I. Thin sheets about 0.2 mm thick were prepared from melt-processed blends and the pure components by a compression molding technique

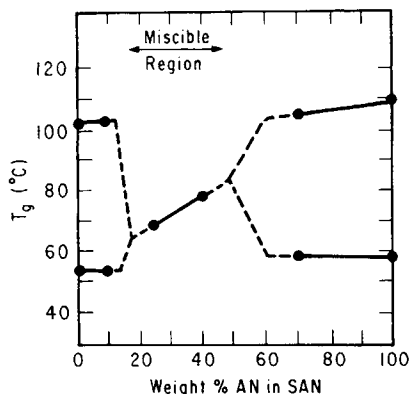


Fig. 1. Glass transition of blends containing 40% PEOx with styrene-acrylonitrile copolymers to illustrate miscibility region for PEOx-SAN mixtures.

TABLE I
Polymers Used in This Study

Polymer	Designation used here	Description	Source
Polyethyloxazaline	PEO _x	$M_w = 439,000$ $M_w/M_n = 3.9$	Dow
Polystyrene	PS	Styron 685D	Dow
Poly(styrene-co-acrylonitrile)	SAN 8	8% by weight AN	Dow
Poly(styrene-co-acrylonitrile)	SAN 25	25% by weight AN Tyril 867	Dow
Poly(styrene-co-acrylonitrile)	SAN 40	40% by weight AN EX 2020	Dow
Rubber-modified SAN	SAN 70	15% by weight rubber, particles ~0.1 μ m, matrix SAN contains 70% by weight AN Vico-bar 301	ICI

using procedures described earlier.⁸ Specimens, about 1 × 2 cm, were immersed in 20 cm³ of distilled water at room temperature without agitation. After various times, specimens were removed from the water, wiped free of surface moisture, and weighed. This quantity is called the *wet weight*. Next, the sorbed water was removed by evaporation in a vacuum oven at 80°C for 2 days. Normally constant weight was reached within 1 day. This quantity is termed the *final dry weight* and in general is less than the *initial weight* (dry) for the specimen owing to PEO_x extraction during the immersion period. A fresh sample was employed for each determination.

WATER SWELLING AND EXTRACTION

After only brief immersion in water, the immiscible blends, that is, those prepared from SAN containing 0, 8, and 70% AN, became sticky to the touch. In contrast, the miscible blends prepared from SAN containing 25 and 40% AN did not become sticky even after immersion times of months. The latter become swollen and more flexible, depending on composition, and remained transparent. Quantitative results on swelling and PEO_x extraction for these various blends are described in detail below.

Figure 2 shows the wet weight relative to the final dry weight as a function of time of immersion in water for various blends of PEO_x with polystyrene. This is a complex experiment since PEO_x is being extracted simultaneously with the process of water sorption, as shown in Fig. 3. The choice of the final dry weight rather than initial dry weight as the reference state is useful since this reveals the relative amount of water in the sample at any time. As seen in Fig. 2, there is an initial rapid uptake of water that is greater the higher the PEO_x content of the blend. This is followed by a similarly rapid *decrease* in water content, and eventually a more or less stable water content is reached. This response is clearly related to the extraction of PEO_x shown in Fig. 3. The rapid water uptake is related to the strong affinity of PEO_x for water and the rapid diffusion of the small water

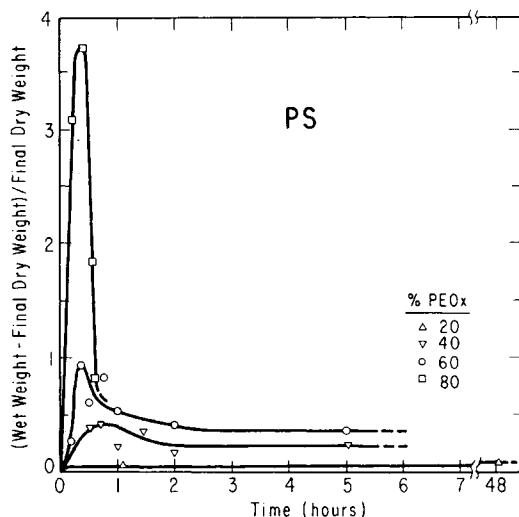


Fig. 2. Swelling dynamics of immiscible PEOx-PS blends.

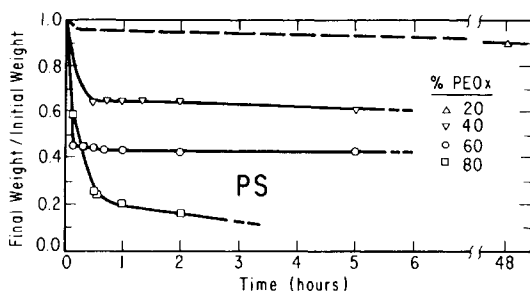


Fig. 3. PEOx extraction from PEOx-PS blends.

molecules through this component of the two-phase blend. Once plasticized by water, PEOx molecules are able to diffuse from the film, most likely by a reptation mechanism. The magnitude of the water sorption peak and plateau and the amount of PEOx extracted must be related to the initial amount of PEOx in the blend and the morphology of the two-phase blend as initially prepared.

Qualitatively, the responses shown in Figs. 4 and 5 for PEOx blends with the SAN containing 8% AN are quite similar to those noted above for blends with polystyrene. Any quantitative differences may relate to morphology and preparation protocols, so no detailed discussion of them is warranted at this point. For the 80% PEOx blend, some of the SAN component is also removed by the macroscopic loss of sample integrity. The significant point is that SAN 8 is immiscible with PEOx just as polystyrene is.

Next, we describe swelling and extraction for the blends of PEOx with SAN 25 and SAN 40, both of which form miscible systems. The results shown in Figs. 6 through 9, are given on a scale of many days rather than a few hours as used in Figs. 2 through 5. As seen in Figs. 6 and 8, there is no large peak in water swelling like that in Figs. 2 and 4; although the final "equilibrium" water contents are generally higher for the former compared with the latter. We believe this is related to the drastically reduced

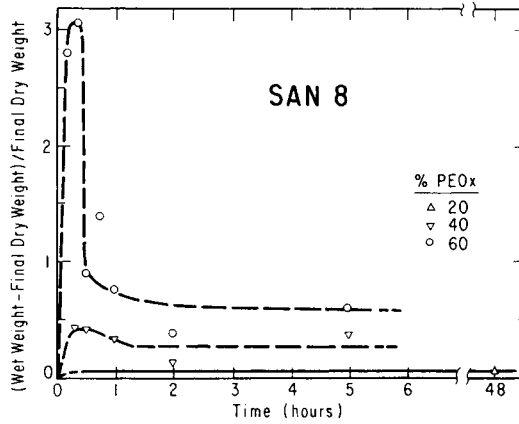


Fig. 4. Swelling dynamics of immiscible PEO_x-SAN 8 blends.

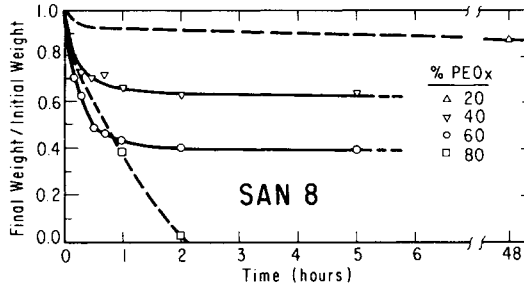


Fig. 5. PEO_x extraction from PEO_x-SAN 8 blends.

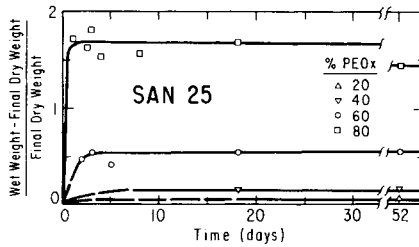


Fig. 6. Swelling dynamics of miscible PEO_x-SAN 25 blends.

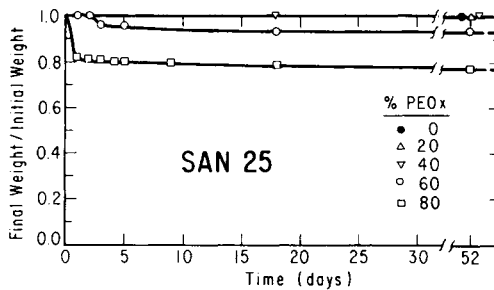


Fig. 7. PEO_x extraction from PEO_x-SAN 25 blends.

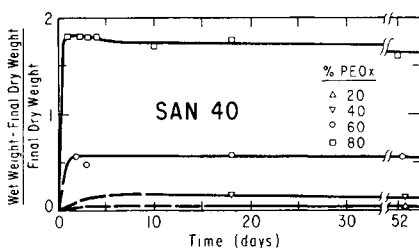


Fig. 8. Swelling dynamics of miscible PEOx-SAN 40 blends.

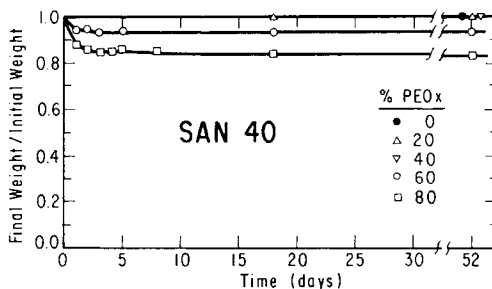


Fig. 9. PEOx extraction from PEOx-SAN 40 blends.

amount of PEOx extraction from the miscible blends (see Figs. 7 and 9) compared with the previous immiscible blends (see Figs. 3 and 5). This difference in extractability of PEOx is quite significant and will be discussed further.

Finally, we examine the effect of water on PEOx blends with SAN 70. Note that the latter is actually a rubber-modified composition whose matrix phase contains 70% AN and 30% styrene. The matrix is immiscible⁸ with PEOx, and we assume that the rubber phase plays no significant role in the present observations. Figure 10 shows no observable peak in water sorption as noted in Figs. 2 and 4; however, the extent of PEOx extraction by water (Fig. 11) is more typical of blends with polystyrene and SAN 8 (immiscible with PEOx) than blends of PEOx with SAN 25 and SAN 40 (miscible with PEOx).

Some alternate methods of presentation of these data give a clearer picture of the effect of water on these blends. Here we concentrate on the maximum or peak water sorption values and the plateau PEOx extraction values at long immersion times defined in terms of hours or days for immiscible blends and weeks or months for miscible ones. It is not possible to claim the latter to be "equilibrium" states, as further changes may occur over very long time scales. However, samples stored in water for 2 years following this experimental program do not appear to have changed significantly from those reported here. Figure 12 shows the peak wet weight and the maximum amount of PEOx extracted relative to the initial PEOx in the blends versus the initial PEOx content of the blend with composition of the SAN as a parameter. The maximum water sorption for the three immiscible blends

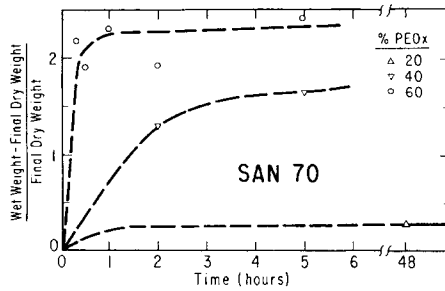


Fig. 10. Swelling dynamics of immiscible PEO_x-SAN 70 blends.

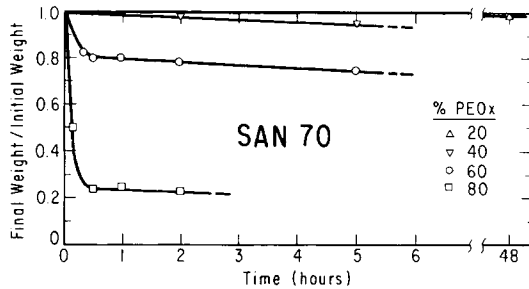


Fig. 11. PEO_x extraction from PEO_x-SAN 70 blends.

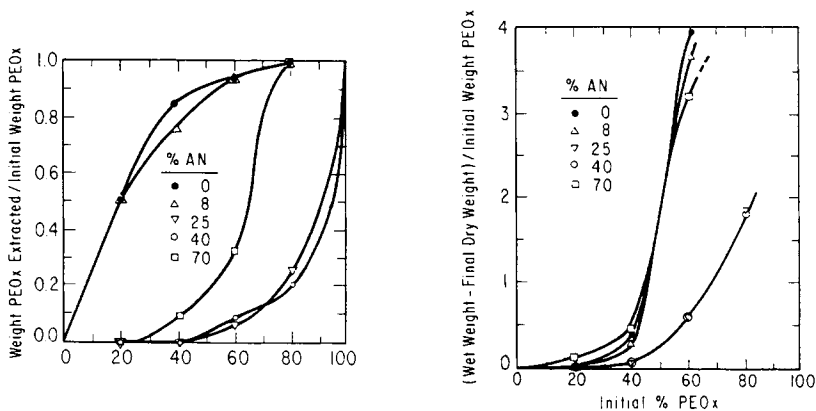


Fig. 12. Effect of initial PEO_x content of blends on amount of PEO_x extracted (top) and peak swelling (bottom) relative to initial PEO_x content of blends with various SAN.

form one curve; the two miscible blends fall on another curve lying below the former. Both curves increase with the original amount of PEO_x in the blend. The relative amount of PEO_x extracted increases with the PEO_x content of the blend; however, the curves for blends with polystyrene and SAN 8 are about the same and rise much more steeply than those for SAN 25 and SAN 40, also about the same; SAN 70 shows intermediate behavior.

The top part of Fig. 13 shows the peak water sorption referenced to the final dry weight. Again the miscible blends form one curve, but the three

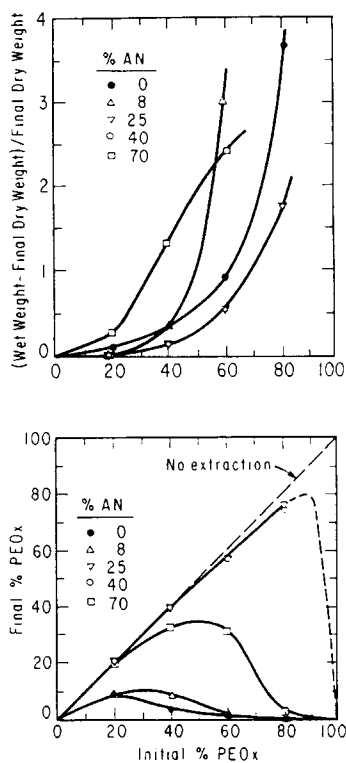


Fig. 13. Effect of initial PEOx content of blends on peak water sorption (top) and remaining PEOx after extraction (bottom) relative to final dry weight of blends with various SAN.

immiscible blends show separate curves that are all higher than the miscible blend curve. The lower part of Fig. 13 gives the PEOx composition of the extracted blend versus the initial PEOx content. The diagonal line represents no extraction. The miscible blends follow this line very closely over the entire range of initial PEOx concentrations examined. These curves must go to zero at 100% PEOx for all SAN since the neat PEOx is readily soluble in water.

Finally, it is useful to show the same information as a function of the acrylonitrile content of the SAN with the fraction of PEOx in the blend as a parameter. This presentation in Fig. 14 demonstrates that peak water sorption and PEOx extraction goes through a minimum versus the percentage of AN corresponding to the miscible range (see Fig. 1), with both quantities smaller with decreasing PEOx in the blend.

DIFFERENTIAL SCANNING CALORIMETRY

In this section, thermal analysis techniques are employed to gain information about the state of the water in highly swollen blends of PEOx and SAN 25 and the state of mixing between the two polymers.

The literature contains several reports on the use of thermal analysis to obtain information about the nature of water contained in hydrogels and

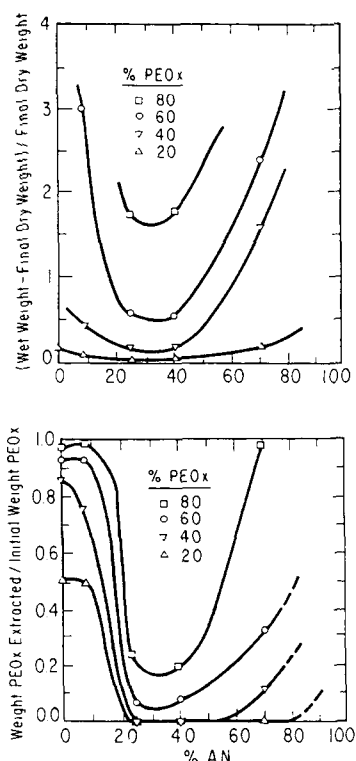


Fig. 14. Peak swelling (top) and fraction of PEO_x extracted (bottom) as a function of AN content of SAN for various initial PEO_x contents of blends.

cellulose acetate membranes.¹⁴⁻¹⁶ These studies make distinctions between water contained in these hydrophilic materials, which freezes, and that which does not freeze. The melting point of water that freezes may or may not be depressed below its normal value, depending on the degree of interaction with the polymer. A cursory examination of the freezing behavior of water in SAN-PEO_x blends was made using differential scanning calorimetry (DSC), and the most informative results are described here.

Figure 15 shows thermograms for a series of miscible blends prepared from SAN 25 with varying amounts of PEO_x that had been stored in water for approximately 2 years. Care was taken to avoid the loss of water while loading samples in the DSC. The sample initially containing 40% PEO_x shows no evidence of a melting endotherm for water that might have frozen on cooling in the DSC. Based on results from the previous section, this sample contained about 17% water and virtually all of the original PEO_x. On the other hand, the blend initially containing 60% PEO_x exhibits two melting endotherms. One occurs near the normal melting point for water, and a somewhat larger peak occurs about 10°C lower than this. This sample contained about 37% water, and the PEO_x content was reduced to about 56% on a dry basis by extraction. An 80% PEO_x blend also exhibits two melting endotherms, both of which are considerably larger than those ob-

served for the 60% PEOx blend. Curiously, the lower peak is only about 4°C below the normal melting point for water. This blend contained about 64% water, and the PEOx content was reduced to about 74% on a dry basis by extraction. Even for these two blends all of the water present does not freeze since quantitative integration of the peak areas fails to account for all of the water known to be present. By this approach it has been estimated that only 13% of the water present in the 60% PEOx blend freezes but 40% of the water in the 80% PEOx blend freezes.

Figure 16 compares thermograms for blends initially containing 80% PEOx

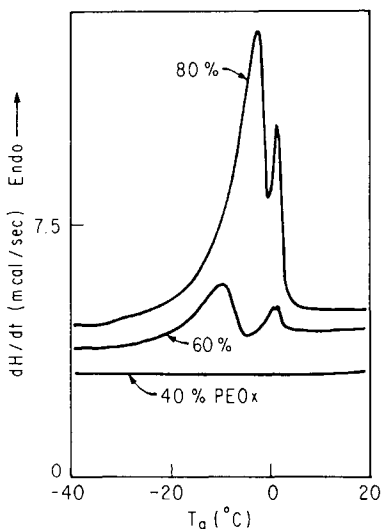


Fig. 15. DSC thermograms for blends with SAN 25 containing various initial PEOx levels after storage in water for 2 years.

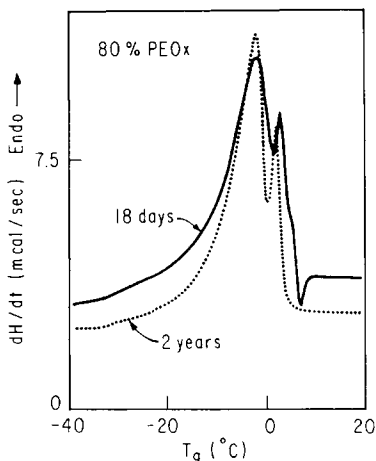


Fig. 16. DSC thermograms for SAN 25 blends containing 80% PEOx initially as a function of time stored in water.

with SAN 25 that had been immersed in water for 18 days and for approximately 2 years. The two are remarkably similar except for slight differences in the height and breadth of the peaks, indicating little difference in the amount and nature of the water in the two samples. The peak areas indicate that 44% of the water present in the sample stored in water for 18 days froze on cooling in the DSC and 40% of that in the sample stored in water for 2 years did so. However, a similar comparison, shown in Fig. 17, leads to a different conclusion for samples initially containing 60% PEO_x. In this case, the sample exposed to water for 18 days shows only an endotherm near the normal melting point for ice, which is somewhat smaller than the corresponding peak for the sample that had been immersed in water for 2 years. The lower temperature endotherm peak does not appear at all for the former. This suggests that, on prolonged storage in water, some change in nature does occur, although based on these results it is not possible to define the exact character of these changes.

For the 80% PEO_x blend stored in water for 2 years, successive scans were run up to 87°C, which allowed some water to evaporate as indicated by the reduction in the melting peak areas in Fig. 18. Interestingly, on the third heating the peak at the normal melting point of ice had disappeared completely, indicating that this form of water evaporates more readily than that associated with the lower melting peak.

To examine the state of mixing of the PEO_x and the SAN 25 in a blend after swelling in water, hydrated samples were dried at 80°C in vacuo for 4 days, stored at room temperature in a desiccator, and then heated in the DSC. Figure 19 shows typical results for a blend initially containing 60% PEO_x that had been stored in water for 2 years. The first heat in the DSC reveals two well-defined glass transitions corresponding closely to the pure component polymers. The heat capacity overshoots at each of the two transitions are a result of the sub- T_g annealing¹⁷ induced by the thermal history mentioned above. In this first heat, the sample was heated to about 150°C

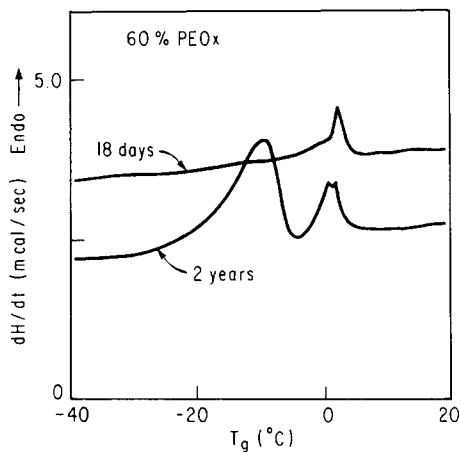


Fig. 17. DSC thermograms for SAN 25 blends containing 60% PEO_x initially as a function of time stored in water.

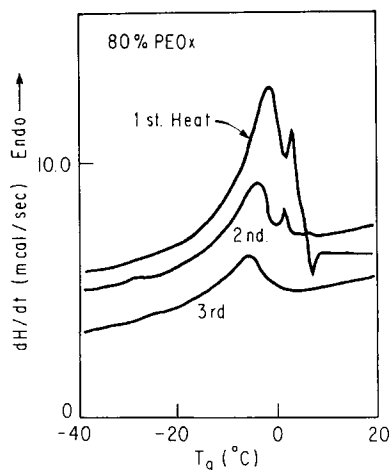


Fig. 18. Sequential heats in the DSC of SAN 25 blends initially containing 80% PEOx after storage in water for 2 years.

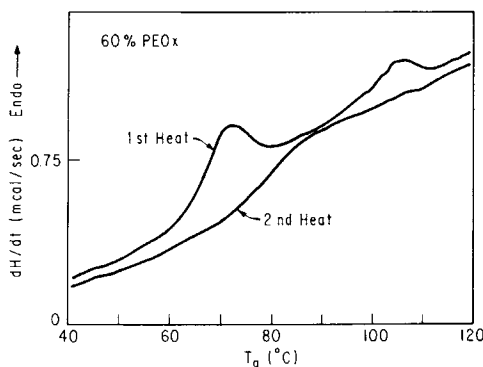


Fig. 19. First and second DSC heats for blends of SAN 25 initially containing 60% PEOx after 2 years in water and then dried as described in the text.

and then rapidly quenched. A second heat, also included in Fig. 19, showed a single glass transition at a temperature expected for a miscible blend of this composition.⁸ These results, which are typical of many similar experiments, may be interpreted as follows.

Water is imbibed into an initially homogeneous PEOx-SAN 25 blend because of its affinity for PEOx. At some point in this swelling process, the hydrophobic SAN component is forced to segregate into a separate phase that is not appreciably swollen by water and, therefore, is a rigid glass. Since the PEOx is also miscible in the SAN, it is reasonable that some PEOx segments will be trapped in the SAN phases that form. The resulting situation is pictorially represented in Fig. 20, which explains how a stable but highly swollen structure is developed from which the PEOx cannot be extracted even though the blend is now essentially phase segregated. The SAN microdomains containing portions of PEOx chains act as physical cross-

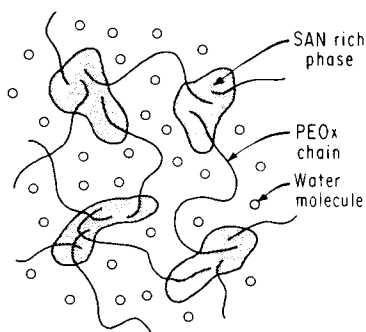


Fig. 20. Schematic of microphase-separated blends (initially miscible) swollen by water.

links preventing disintegration of the sample and extraction of the PEO_x. However, a high degree of macroscopic swelling can be obtained since most of the PEO_x is in the water phase, but the scale of the phase segregation is evidently sufficiently small that portions of most PEO_x chains are also associated with SAN microdomains. Physical entanglements of PEO_x chains in the aqueous phase are also likely to be part of this network topology. The thermal behavior of the water described above attests to its intimate mixing with PEO_x in the aqueous phase external to the SAN microdomains. On heating the dried blend to 150°C in the DSC, the PEO_x and SAN 25 rapidly diffuse together, owing to the small scale of the phase separation, to produce a homogeneous, single T_g mixture on the second heat, as illustrated in Fig. 19. Further evidence of the small size of the microdomains is the optical transparency of the phase-separated blends.

SCANNING ELECTRON MICROSCOPY

The surfaces of several blends that had been immersed in water for some time were examined by scanning electron microscopy to learn more about their morphology. Figure 21 shows the surfaces of immiscible blends of SAN 8 with varying initial amounts of PEO_x as identified in the figure. The duration of exposure to water is also indicated in the figure. The SAN 8 remaining at the surfaces of blends initially containing 40, 60, and 80% PEO_x has a fibrillar character that apparently was created by radial flow during melt blending and compression molding. This fibrillar structure for the SAN 8 phase permits easy removal of PEO_x by water extraction. The blend containing 20% PEO_x does not have this fibrillar morphology since apparently SAN 8 forms the matrix phase in this case, and for this reason it is more difficult to remove the PEO_x, as the extraction studies showed.

Figure 22 shows the surface of a miscible blend formed from 60% PEO_x and 40% SAN 40 that had been exposed to water for 2 days. There is no pitting of the surface or other indication of extraction. Isopropanol is a more effective solvent for PEO_x than is water. Figure 23 shows a series of photographs of SAN 40 blends containing varying amounts of PEO_x after exposure to isopropanol for the times indicated. The progressive dimpling of the surfaces with increasing PEO_x content is indicative of swelling by iso-

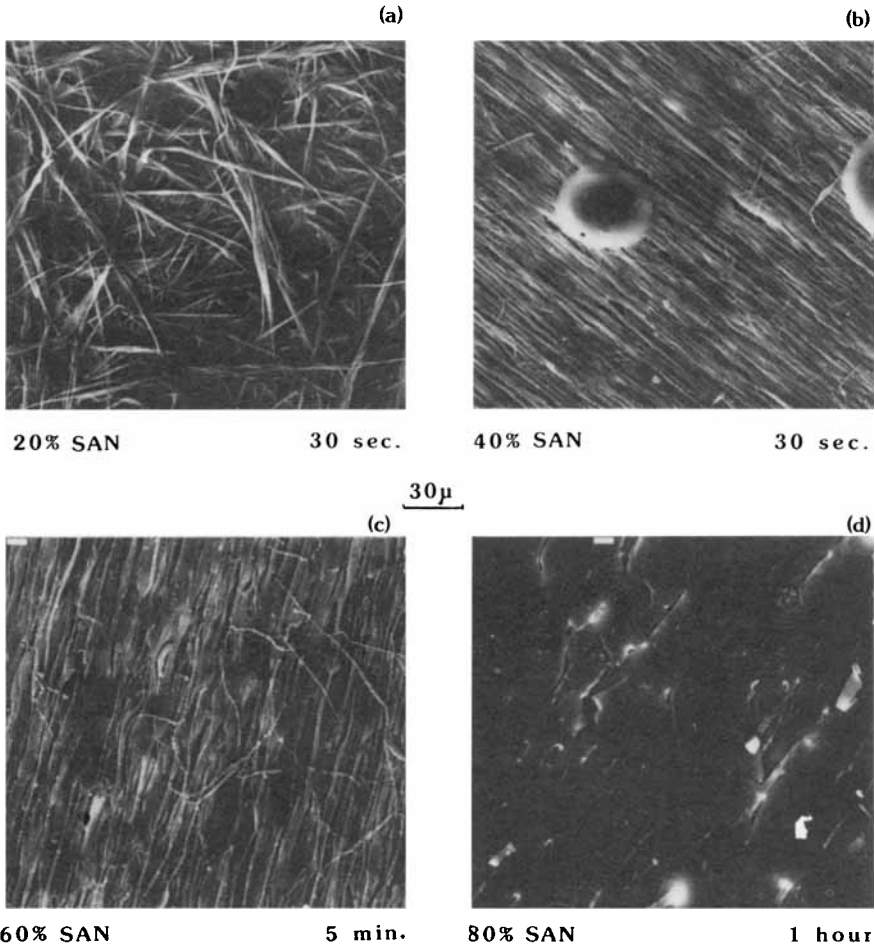


Fig. 21. Scanning electron micrographs of surfaces of PEOx-SAN 8 blends after water extraction.

propanol or, possibly, PEOx extraction. No quantitative swelling or extraction studies with isopropanol were done.

SUMMARY AND CONCLUSIONS

Several studies reported in the recent literature suggest that it is surprisingly difficult to extract a hydrophilic polymer from a miscible blend with a hydrophobic polymer by water. This observation has been confirmed and extended in this study through the use of blends of water-soluble polyethyl-oxazoline with a series of styrene-acrylonitrile copolymers of different acrylonitrile contents. Copolymers containing 25 and 40% AN are miscible with PEOx; copolymers containing more or less AN were immiscible with PEOx, which provides a novel opportunity to examine the role of blend miscibility on water swelling and extraction using a series of related materials.

The results conclusively demonstrate that, in general, miscible blends of

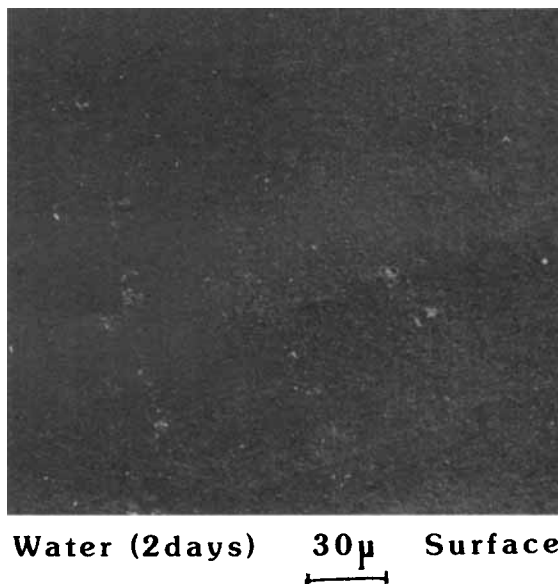


Fig. 22. Scanning electron micrograph of surface of miscible blend of SAN 40 containing 60% PEO_x after exposure to water for 2 days.

hydrophilic and hydrophobic polymers can swell extensively in water yet rather little of the hydrophilic component is extracted by water over months or years. On the other hand, similar blends that are not miscible usually experience extensive extraction of the hydrophilic component during relatively short periods of immersion in water. For either type of blend the extents of swelling and extraction depend on the proportions of the hydrophilic and hydrophobic polymers in the blend. Thermal analysis and scanning electron microscopy were used in the present study to gain further insights.

The behavior of immiscible blends in this regard is rather easy to understand as the two polymers exist in separate phases; however, the ability of miscible blends to undergo extensive swelling in water without extensive extraction of the hydrophilic component is not so obvious, and some further explanation is needed.

With respect to swelling, these miscible blends behave as if there are cross-links that prevent sample disintegration or complete dissolution of the PEO_x in the water. In analogy with the extensive literature on thermoreversible gels,¹⁸ which certain polymers form when dissolved in solvents, it is appropriate to think in terms of physical cross-links that may be rather stable in time. The most likely origin of such cross-links is a microphase segregation in which the hydrophobic polymer separates into very small domains as the water content becomes too high for it to remain intimately mixed with the hydrophilic polymer. Since the hydrophilic polymer is also miscible with the hydrophobic polymer, it is likely that segments of its chains will become entrapped to some degree in the hydrophobic microdo-

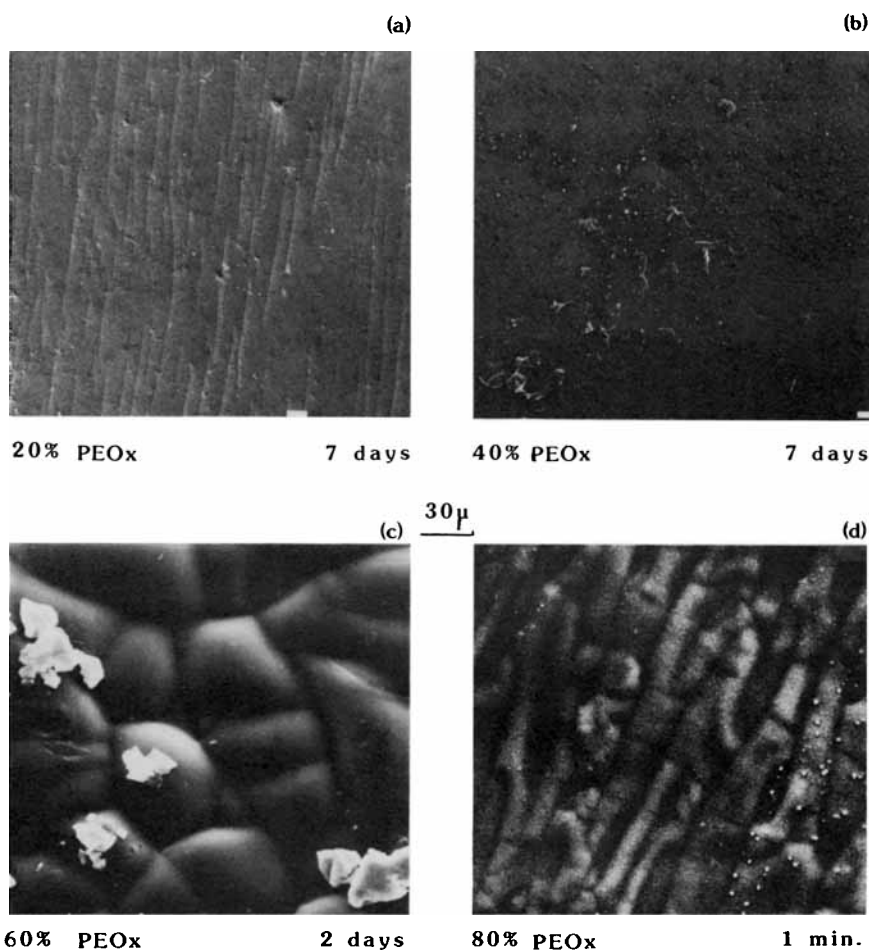


Fig. 23. Scanning electron micrographs of surface of various SAN 40 blends after exposure to isopropanol for times shown.

mains, which are envisioned to act like physical cross-links. This would explain the stable high level of swelling and the inability to extract the hydrophilic polymer. Thermal analysis of such systems that have been dried after being swollen by water reveal glass transitions corresponding closely to the original component polymers, thus supporting the notion of microphase separation on swelling and the explanation given above. This is believed to be a general mechanism for blend systems exhibiting this type of behavior.

The authors wish to express their appreciation to the Dow Chemical Co. for support of this research.

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