

# Miscibility of Polyethyloxazoline with Thermoplastic Polymers

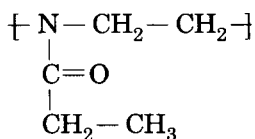
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## Synopsis

Polyethyloxazoline (PEOx) blends with several other thermoplastic polymers were examined by differential scanning calorimetry (DSC) for miscibility. Styrene/acrylonitrile (SAN) copolymers having compositions in the range of about 20–40% acrylonitrile (AN) by weight were found to be miscible with PEOx whereas SANs outside this range were not. The polyhydroxyl ether of bisphenol A (Phenoxy) was also found to be miscible with PEOx. A vinylidene chloride copolymer (Saran) was found to be partially miscible with PEOx, whereas poly(methyl methacrylate) and polycarbonate were not miscible at all.

## INTRODUCTION

Polyethyloxazoline (PEOx), whose structural formula is shown,



is a new and novel water-soluble tertiary amide polymer, which has excellent thermal stability and is easily melt fabricated.<sup>1,2</sup> Because of these versatile features, the miscibility of PEOx with other thermoplastic polymers was of interest.

In 1980, Olabisi and Robeson<sup>3</sup> reviewed water-soluble and miscible polymer systems, including poly(vinyl pyrrolidone) and poly(ethyleneimine). Their discussion, however, dealt mostly with complexes of water-soluble polymers as a function of composition and pH. Subsequently, they reported further on blends of the polyhydroxy ether of bisphenol A (Phenoxy) with water-soluble polyethers,<sup>4</sup> and additional systems were covered by Robeson.<sup>5</sup>

It has been frequently observed that random copolymers form miscible blends with other polymers, even though neither homopolymer formed from the individual comonomers is similarly miscible. One useful explanation of this behavior is a recently developed binary interaction model by Paul and Barlow.<sup>6</sup> It considers both intermolecular and intramolecular interactions, and appears to be broadly applicable. In the study of miscibility of polyethyloxazoline (PEOx) with other thermoplastic polymers, it was observed that styrene-acrylonitrile (SAN) copolymers and PEOx may provide another example of the applicability of this binary interaction model.

Differential scanning calorimetry (DSC) was used to study the glass transition behavior of blends with PEOx. This paper summarizes these results, showing the existence of a miscibility "window" of PEOx with SAN copolymers and its miscibility with Phenoxy and partial miscibility with Saran.

### EXPERIMENTAL

All polymers were received in granular form and used after an appropriate drying in a vacuum oven, usually at about 50–120°C. These polymers and pertinent information about them are listed in Table I.

Polymers were melt-blended in an oil-heated Brabender mixer at 190°C. A 10-min period was used for blending. The solidified blend was ground, and then compression moldings were prepared between two Mylar films. The ground polymer was first preheated in the compression mold at 190°C for 3 min, followed by 3 min under full ram pressure. The moldings were cooled under pressure. About 0.2-mm-thick moldings were used for visual observations as well as for thermal experiments.

Glass transition temperatures were determined using a Perkin-Elmer DSC-2 with a Thermal Analysis Data Station. Thermal data for the polymers and blends were obtained after storage of the test samples in a dessicator, followed by one heating cycle in the DSC to 460K. The sample was then quenched (at 320°/min) to 270°K, and the experimental thermogram was obtained at 20°/min.

### RESULTS AND DISCUSSION

The polymers used in this study all had glass transition temperatures sufficiently different from PEOx so that observation of  $T_g$  behavior by DSC provided a useful means of determining whether the blends were miscible or not. The DSC results were supplemented by other observations.

TABLE I  
Polymers Used in This Study

Polymer	Designation	Source and description
Polyethyloxazoline	PEOx	Dow Chemical, $\bar{M}_w = 439,000$ $\bar{M}_w/\bar{M}_n = 3.9$
Polystyrene	PS, Styron 658D	Dow Chemical
Poly(styrene-coacrylonitrile)	SAN-8	Dow Chemical, 8% AN by wt
Poly(styrene-coacrylonitrile)	SAN-25, Tyril 867	Dow Chemical, 25% AN by wt
Poly(styrene-coacrylonitrile)	SAN-40, EX2020	Dow Chemical, 40% AN by wt
Rubber-modified SAN	SAN-23.5, ABS 500	Dow Chemical, 13.5% rubber by wt, particles $\sim 0.5 \mu\text{m}$ , 23.5% AN by wt in matrix
Rubber-modified SAN	SAN-70, Vicobar 301	ICI, 15% rubber by wt, particles $\sim 0.1 \mu\text{m}$ , 70% AN by wt in matrix
Poly(methyl methacrylate)	PMMA, Lucite 140	Du Pont
Polycarbonate	PC, Lexan 131-111	General Electric, $\bar{M}_w = 29,200$
Polyhydroxy ether of bisphenol A	Phenoxy PKHH	Union Carbide
Poly(vinylidene chloride-covinyl chloride)	Saran	Dow Chemical, $\bar{M}_w = 101,000$ VC1 <sub>2</sub> /VC1 = 86.5/13.5 by wt

Compression-molded sheets of the polymer blends in this study were first inspected visually for clarity. It was noted that moldings of blends of PEO<sub>x</sub> with polystyrene (PS), poly(methyl methacrylate) (PMMA), and polycarbonate (PC) were distinctly hazy, indicating immiscibility. Figure 1 shows the presence of the two glass transition temperatures for blends of PEO<sub>x</sub> and PMMA, confirming immiscibility of this system. PC and PS blends with PEO<sub>x</sub> also showed two glass transition temperatures, corresponding to each of the component polymers.

### SAN/PEO<sub>x</sub> Blends

A series of SAN copolymers were blended with PEO<sub>x</sub>. SAN-8 produced hazy films, whereas SAN-25, SAN-40, and SAN-70 gave transparent moldings. Transparency of SAN films is a reasonable clue for miscibility with these copolymers because the refractive index (RI) of PEO<sub>x</sub> is 1.52<sup>2</sup>, whereas the styrenic copolymers have a significantly higher RI. PS has an RI of 1.59. The transparency of SAN-70 blends with PEO<sub>x</sub>, however, is misleading. In this case, apparently the RI of the two-component polymers is sufficiently close to give transparency due to an RI match, whereas their immiscibility was indicated by the thermal data (Figure 7). Also, the transparency of the blend with SAN-23.5 (ABS 500) requires further comment. In this case, thermal data indicate miscibility of the PEO<sub>x</sub> and the SAN matrix of the ABS (Fig. 4). The transparency is surprising, however, because of the presence of 0.5- $\mu$ m rubber particles. In this case, apparently the rubber phase and the mixed SAN-23.5/PEO<sub>x</sub> matrix produced a reasonable RI match to give transparency. With increasing PEO<sub>x</sub> content, transparency seemed to increase, and with only 20% PEO<sub>x</sub> in the blend, noticeably improved transparency was observed in comparison to ABS 500.

The existence of the lower critical solution temperature (LCST) is an expected phenomenon with miscible polymer blends. Paul and co-workers<sup>7</sup> have reported on the LCST behavior of a number of polymer blends. Their reported procedure for the determination of the LCST was followed with all of the transparent blends, and heating was carried out to 300°C. None of the SAN blends with PEO<sub>x</sub> showed any change of clarity during these experiments. ABS 500 blends were more clear after heating to 300°C than

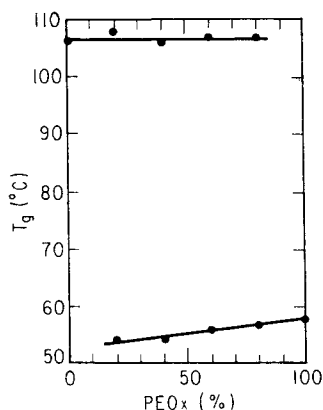


Fig. 1.  $T_g$  of PMMA/PEO<sub>x</sub> blends.

a corresponding sample of ABS 500. The existence of LCSTs of these blends is presumable at higher temperatures. Because of the possibility of thermal degradation at higher temperatures, no further experiments were carried out. Accordingly, it may be suggested that these blends can be molded or extruded without concern for developing opacity due to high fabrication temperatures.

Figure 2 shows the DSC data of the PEO<sub>x</sub> SAN-8 blend, which indicate immiscibility. The slight reduction in PEO<sub>x</sub>  $T_g$  on blending with SAN-8 is also observed with PMMA (Fig. 1). No ready explanation for this observation is apparent. Figures 3, 4, and 5 show the DSC data for PEO<sub>x</sub> blends with SAN-25, SAN-23.5 (ABS 500), and SAN-40, respectively. In every case, there is only one glass transition temperature for each composition, indicating miscibility of these copolymers with PEO<sub>x</sub>. In Figure 4, the blend of 80/20 PEO<sub>x</sub>/SAN-23.5 shows a higher than expected  $T_g$  at 63°C. No ready interpretation of this discrepancy is apparent.

The  $T_g$  data for the miscible blends was further analyzed by the use of Gordon-Taylor equation, which can be written in the following form:

$$T_g = T_{g1} + \frac{k w_2}{w_1} (T_{g2} - T_g)$$

Here,  $T_g$  is the glass transition temperature of the blend, whereas  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of the components 1 and 2, respectively,  $w$  is the weight fraction, and  $k$  is a constant. It has been suggested<sup>7</sup> that the value  $k$  relates to the strength of interaction between the components in the blend. However, no theoretical basis for such a relationship has been suggested. Figure 6 shows a plot of this relationship for the SAN-40/PEO<sub>x</sub> blend, and Table II shows the  $k$  values for the miscible blends.

Figure 7 shows the thermal data for the SAN-70/PEO<sub>x</sub> blends. Two distinct  $T_g$ 's are apparent for the intermediate compositions. The blend containing 20% PEO<sub>x</sub> did not show a  $T_g$  corresponding to PEO<sub>x</sub>, but the  $T_g$

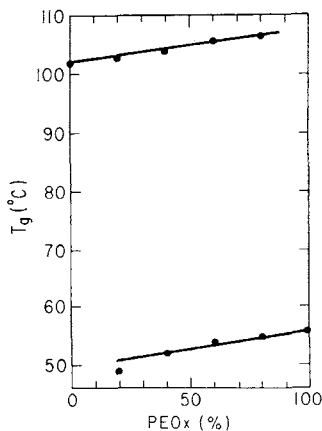


Fig. 2.  $T_g$  of SAN-8/PEO<sub>x</sub> blends.

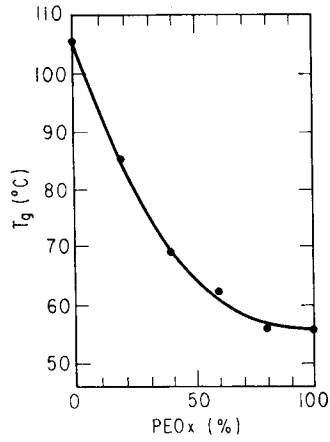


Fig. 3.  $T_g$  of SAN-25/PEO<sub>x</sub> blends.

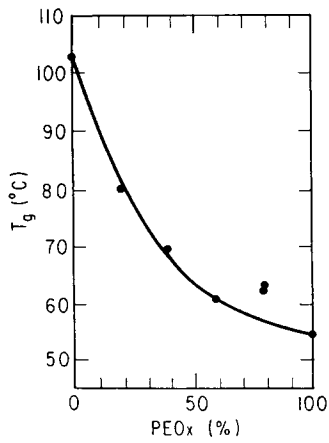


Fig. 4.  $T_g$  of SAN-23.5 (ABS 500)/PEO<sub>x</sub> blends.

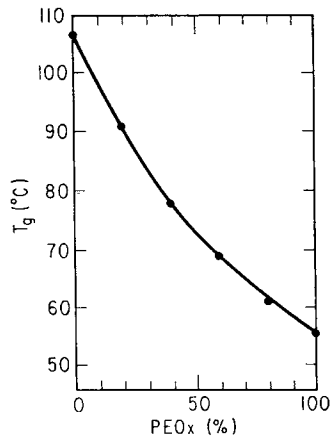


Fig. 5.  $T_g$  of SAN-40/PEO<sub>x</sub> blends.

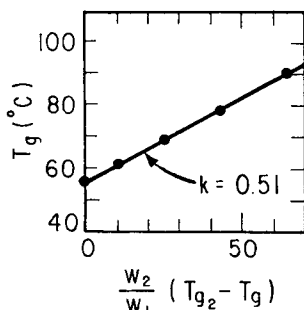


Fig. 6. Gordon-Taylor plot of  $T_g$  data from SAN-40/PEO $x$  blends.

of SAN-70 was not affected. For this series of blends, the  $T_g$  of SAN-70 showed more than normal scatter. Even though clear films were obtained with these blends for all compositions, the DSC data indicate immiscibility.

### Phenoxy/PEO $x$ Blends

Solution blends of Phenoxy and PEO $x$  were cast from tetrahydrofuran (THF) solution onto aluminum dishes. The films were dried slowly at room temperature for 2 days. This was followed by final drying in a vacuum oven at about 100°C. The resulting dried films were transparent. The DSC data for the blends are shown in Figure 8. All blends show only one intermediate  $T_g$ , indicating miscibility of the Phenoxy/PEO $x$  blends. The Gordon-Taylor analysis in Figure 9 gives  $k = 0.71$ , which is considerably higher than any of the  $k$ 's determined for the miscible SAN/PEO $x$  blends.

### Saran/PEO $x$ Blends

Solution blends of Saran and PEO $x$  were prepared in THF. In order to effect a complete dissolution of Saran, the mixtures were heated to 60°C and stirred magnetically for about 10 min. In the first experiment, the solutions were cast onto aluminum dishes. After drying at room temperature, they were dried in a vacuum oven at 60°C for several days. This drying procedure, however, was found to be inadequate. The DSC data for a Saran/PEO $x$  (80/20) blend showed a  $T_g$  for Saran of -11°C. The expected value is about 0°C.<sup>7</sup> Apparently, the plasticizing effect of the unremoved THF caused this reduction of  $T_g$ . Also, this experiment revealed that the crys-

TABLE II  
Miscibility of PEO $x$  and SAN

AN% in SAN	Miscibility	$k^a$
0	No	—
8	No	—
23.5	Yes	0.25
25	Yes	0.31
40	Yes	0.54
70	No	—

<sup>a</sup>  $k$  from Gordon-Taylor equation.

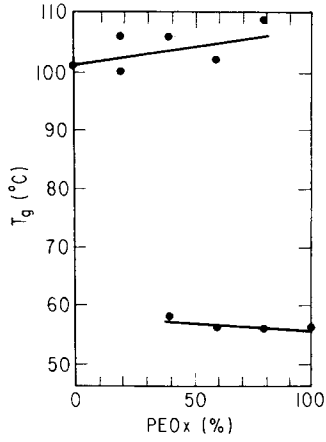


Fig. 7.  $T_g$  of SAN-70 (Vicobar 301)/PEO<sub>x</sub> blends.

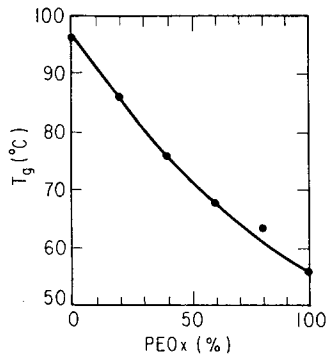


Fig. 8.  $T_g$  of Phenoxy/PEO<sub>x</sub> blends.

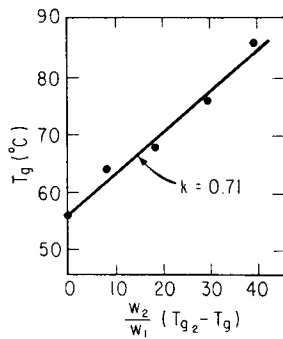


Fig. 9. Gordon-Taylor plot of  $T_g$  data from Phenoxy/PEO<sub>x</sub> blends.

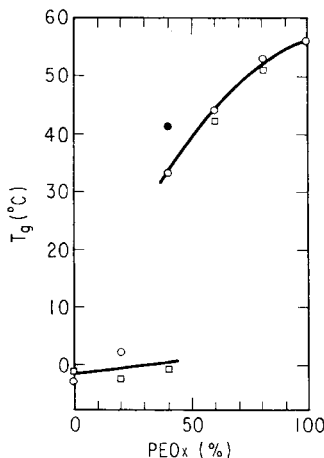


Fig. 10.  $T_g$  of Saran/PEOx blends. Sample annealed 15 min at 40°C (○); sample annealed 15 h at 40°C (◻); sample quenched from 187°C in DSC.

tallization exotherm for Saran is in the temperature range for the  $T_g$  of PEOx. Accordingly, another experiment was carried out in which the blend solutions in THF were first precipitated in an excess of *n*-heptane. The resulting precipitates were dried *in vacuo* for 5 days at 60°C. The DSC data for these blends are shown in Figure 10. Annealing the sample at 40°C for 15 min eliminated the crystallization exotherm for Saran. The data show that the  $T_g$  of Saran remains unaffected at a 20% PEOx concentration, whereas at 40% the quenched sample shows the  $T_g$  of Saran and also an intermediate  $T_g$  at 33°C. This composition shows the effect of physical aging as  $T_g$  increases to 41°C after 15 h at 40°C. At 60% and 80% PEOx, there is a single  $T_g$ , intermediate to those for PEOx and Saran. It is concluded from these data that there is a partial miscibility between Saran and PEOx, particularly in compositions containing a major proportion of PEOx.

## CONCLUSIONS

Thermal analysis of SAN/PEOx blends has shown that SAN copolymers containing from about 20% to over 40% AN are miscible with PEOx over the whole blend composition range. The existence of such "miscibility" windows has been treated recently by Paul and Barlow.<sup>6</sup> These blends do not show LCST behavior up to 300°C.

Phenoxy was also found to be miscible with PEOx over the whole composition range. The interaction between these polymers was particularly strong, as judged by the large  $k$  value from the Gordon-Taylor treatment. Saran was only partially miscible with PEOx, whereas PS, PMMA, and PC were immiscible with PEOx.

Melt blending work was carried out by J. C. Pawloski. The support and the supply of samples by The Dow Chemical Company are gratefully acknowledged.



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Received April 11, 1985

Accepted June 5, 1985