

Styrene / Maleimide Copolymer / / Poly(2-ethyl-2-oxazoline) Miscible Blends

Recent studies¹⁻³ on blends of various thermoplastic resins with poly(2-ethyl-2-oxazoline) (PEOx) have shown PEOx resin to be miscible with styrene/acrylonitrile copolymers (of controlled AN content), phenoxy resin and styrene/acrylic acid copolymers.

In this paper the miscibility of styrene/maleimide copolymers with PEOx resin is discussed along with some of the salient features of the blends.

The poly(2-ethyl-2-oxazoline) polymer used in this study was PEOx(XAS-10874) resin from Dow Chemical Company. The PEOx polymer exhibited a glass transition temperature of 332 K as measured by differential scanning calorimetry (DSC). The number average molecular weight as measured by gel permeation chromatography was 118,600 with a polydispersity of 3.7.

The styrene/maleimide copolymers were prepared by free radical chemistry in *N,N*-dimethylacetamide. S/MI 1-7 copolymers were prepared as 50–54% solids solutions in *N,N*-DMAc with a continuous addition of maleimide monomer solution to a solution of styrene monomer and free radical initiator. The alternating S/MI copolymer-8 was prepared by reacting equimolar quantities of styrene monomer and maleimide monomer in *N,N*-DMAc in the presence of a free radical initiator. Styrene monomer and maleimide monomer exhibit a propensity toward alternating copolymerization similar to that of styrene and maleic anhydride. The random maleimide monomer incorporation was judged based on (1) elemental analysis (maleimide content) and (2) a single, well-defined glass transition temperature. The S/MI 1-8 copolymers were fully characterized as shown in Table I.

Polymer blending was accomplished in a Brabender mixing apparatus for five minutes at 63 rpm at the specified temperature (Table II).

Glass transition temperature measurements were made by differential scanning calorimetry. The criteria for assigning a miscible polymer blend was the observance of a single T_g intermediate to the T_g 's of the blend components.

Solubility measurements of various blends and blend components were made by immersing a molded specimen (1/16" thickness) in the specific chemical environment with agitation for 24 h and then determining if the specimen dissolved (soluble) or retained physical form (insoluble).

The miscibility of styrene/maleimide copolymers with PEOx resin is highly dependent on the maleimide content of the styrenic copolymer. The miscibility window exists when the maleimide content of the styrene copolymer is greater than or equal to 9.5 mol% (Table II). At the minimum maleimide content of 9.5 mol% up to 48 mol% miscibility of styrene/maleimide copolymers with PEOx polymer encompasses the full range of blend compositions (Fig. 1) and all blend compositions are transparent.

The phenomena responsible for the miscibility of the two polymer systems appears to be hydrogen bonding between the imide hydrogen of the S/MI copolymers and the amide nitrogen of the PEOx polymer. Infrared spectroscopic analysis showed significant shifts in the imide hydrogen absorption frequencies (Table III). The possibility of absorption frequency shifts in the infrared spectra (IR) being due to changes brought about by degradation (via heat history) was eliminated from consideration when both styrene/maleimide copolymer and poly(2-ethyl-2-oxazoline) polymer showed no discernible differences in their respective IR spectra before and after the thermal processing step (Fig. 2). The possibility of interchange reaction (i.e. covalent bond formation between the S/MI and PEOx polymers) is considered not to be a contributing factor to the observed phase behavior of the blends, as the S/MI//PEOx blends having been subjected to a thermal heat history can be dissolved in dimethylacetamide and the PEOx extracted from the solution with water (> 99% PEOx recovered); and the S/MI copolymer component recovered unchanged. Nitrogen-15 nuclear magnetic resonance (NMR) indicates a

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TABLE I
Styrene/Maleimide Copolymers

S/MI	Mol% MI ^a	Inh (dl/g) ^b	Mn ^c	Mw/Mn ^c	T _g (K)
1	5.1	2.02	107,800	2.6	393
2	8.8	2.07	109,600	2.5	401
3	9.5	2.08	107,800	2.8	404
4	10.5	2.12	108,100	1.9	407
5	16.3	1.41	122,200	2.7	419
6	23.1	2.63	132,700	2.4	441
7	34.2	2.78	154,300	2.4	491
8	48.2	3.54	175,400	2.6	532

^a% MI determined via elemental nitrogen analysis.

^bInherent viscosity determined in dimethylacetamide.

^cGel permeation chromatography.

TABLE II
S/MI//PEOx Blends (50 : 50 Wt%)

S/MI	Brabender melt temp. (K)	Blend T _g (K)
1	443	322, 392
2	451	335, 392
3	454	363
4	457	365
4	469	370
6	491	384
7	541	420
8	572	456

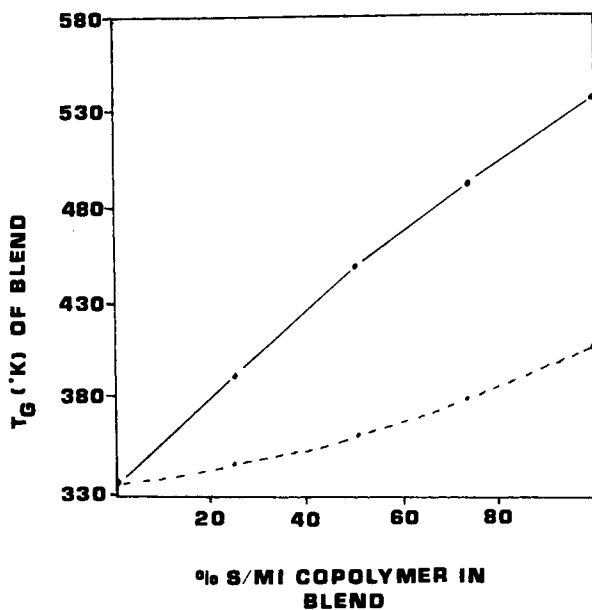


Fig. 1. S/MI//PEOx Blend Miscibility: (—) S/MI-8; (---) S/MI-3.

TABLE III
Spectroscopic Characterization of S/MI//PEOx Miscible Blends

S/MI-3	100	50	—	—	—
S/MI-8	—	—	100	50	—
PEOx	—	50	—	50	100
Imide hydrogen Frequency (cm^{-1})	3094, 3177	2859, 2994	3096, 3175	2857, 2996	—
N^{15} NMR (δ)					
Imide N	171.3	180.2	171.1	180.1	—
Amide N	—	122.7	—	122.5	130.2

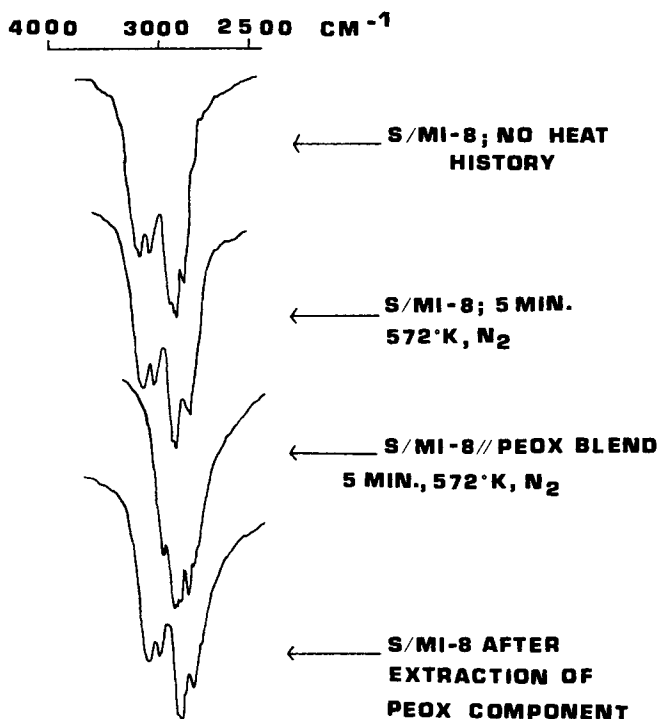


Fig. 2. IR Spectra: S/MI-8.

downfield shift of the imide nitrogen coupled with an upfield shift of the amide nitrogen (Table III). Thus, the spectroscopic data support the existence of hydrogen bonding exclusive of any degradative or amide-imide interchange effects (Fig. 2). There are numerous reports in the literature which discuss the enhancement of miscibility through hydrogen bonding.⁴⁻¹⁰

The effect of the hydrogen bonding on certain performance properties of the miscible blends is quite pronounced. For example, the solvent resistance of the blends is dramatically improved over that of the individual components (Table IV). Solubilization of S/MI/PEOx blends requires a polar, aprotic solvent; while none of the PEOx component of the S/MI-8//PEOx blend dissolved into the aqueous environment after 24 h of exposure (as determined by pre- and postimmersion weighings). Similar observations were made relative to miscible blends of styrene/acrylonitrile (25-40% AN content) and PEOx polymer.³ The hydrogen bonding appears to be responsible for the synergistic behavior observed for the tensile strength of the S/MI//PEOx blends (Table V).

Thus, styrene/maleimide copolymers are miscible with poly(2-ethyl-2-oxazoline) polymer and improved properties can be obtained through blending of the two materials.

TABLE IV
Solubility of S/MI//PEOx Miscible Blends

S/MI-3	100	50	—	—	—
S/MI-8	—	—	100	50	—
PEOx	—	50	—	50	100
Tetrahydrofuran	S	I	S	I	S
Chloroform	S	I	S	I	S
Dimethylacetamide	S	S	S	S	S
Boiling water	—	—	I	I	S

Abbreviations: I = insoluble; S = soluble.

TABLE V
Tensile Strength of S/MI//PEOx Miscible Blends

S/MI-3	100	50	—	—	—
S/MI-8	—	—	100	50	—
PEOx	—	50	—	50	100
Tensile strength (10^6 N/m ²)	48.9	56.8	46.9	61.4	28.9

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