

Styrene / *N*-Phenylmaleimide Copolymer Miscible Blends

Poly(styrene-co-acrylonitrile) has been blended with a variety of polymers and found to exhibit miscibility (partial to full) with poly(methyl methacrylate),¹⁻³ poly(methyl methacrylate-co-*N*-phenylmaleimide),⁴ polycarbonate,⁵ poly(ϵ -caprolactone),^{6,7} styrene/maleic anhydride copolymers,^{8,9} and terpolymers¹⁰ and poly(styrene-co-*N*-phenylmaleimide).¹¹ In all cases the extent of miscibility is related to the acrylonitrile content of the styrene/acrylonitrile copolymer.

This paper reports the miscibility of poly(styrene-co-cyanostyrene) with poly(styrene-alt-*N*-phenylmaleimide) and the utility of miscible polymer pair as a thermoplastic resin system with the capability of tailoring practical heat properties via blend composition.

The 2-cyanostyrene and 4-cyanostyrene monomers were prepared by the palladium-catalyzed coupling of ethylene with 2-bromobenzonitrile and 4-bromobenzonitrile,¹² respectively.

The styrene/isomeric cyanostyrene copolymers used in this study were prepared in the following manner. A citrate bottle was charged with 100 g of water; 1.2 g tricalcium phosphate; 0.002 g sodium bisulfite; 50 g of total monomer selected to achieve the desired composition from styrene, 2-cyanostyrene and/or 4-cyanostyrene (Table I); 0.04 g benzoyl peroxide and 0.095 g *t*-butylperbenzoate. The bottle was capped and tumbled in an oil bath at 95°C for 1.5 h and at 125°C for 6 h.

The styrene/*N*-phenylmaleimide copolymer used in this study was prepared by charging a citrate bottle with 100 g of water, 1.4 g of tricalcium phosphate, 0.002 g sodium bisulfite, 18.5 g of styrene monomer, 31.5 g of *N*-phenylmaleimide monomer, 0.03 g of benzoyl peroxide, and 0.07 g of *t*-butylperbenzoate. The bottle was capped and tumbled in an oil bath at 90°C for 1.5 h and at 140°C for 2.5 h. The styrene/*N*-phenylmaleimide copolymer analyzed for 5.1% nitrogen content (63 wt% *N*-PMI) and exhibited a glass transition temperature (T_g) of 496 K as measured by differential scanning calorimetry. The molecular weight (M_w) of the S/*N*-PMI copolymer was measured at 324,300 with a polydispersity of 2.2 by gel permeation chromatography versus a monodisperse polystyrene standard. The weight-average molecular weight as measured by light scattering was 239,000.

Glass transition temperature measurements were made by differential scanning calorimetry (20°C/min).

Polymer blends were prepared by melt mixing in a Brabender plastograph at 270°C for 6 minutes at a rotor speed of 63 rpm.

Infrared spectroscopy measurements were carried out with a Nicolet Fourier transform spectrometer.

The blends of the styrene/*N*-phenylmaleimide copolymer with the styrene/cyanostyrene copolymers prepared in the melt phase were transparent with a yellow color. All blends with the exception of the styrene/2-cyanostyrene copolymer exhibited complete miscibility with the S/*N*-PMI copolymer over the full range of polymer blend compositions as evidenced by a single glass transition temperature (Table II) related to blend composition by the Gordon-Taylor equation ($T_g = w_1 T_{g1} + W_2 T_{g2}$). The styrene/2-cyanostyrene copolymer exhibits a limited degree of mixing (i.e., partial miscibility) with the S/*N*-PMI copolymer based on the appearance of two glass transition temperatures in the DSC experiment which have shifted toward coalescence. The transparent nature of the blends is a result of formation of a single phase and not simply a matching of refractive indices ($n_D = 1.62$ for S/*N*-PMI and $n_D = 1.56 - 1.57$ for S/CNS copolymers).

Infrared spectroscopic analysis of the blend from S/*N*-PMI copolymer and the styrene/cyanostyrene copolymers showed no obvious shift in the imide carbonyl frequency (1701 cm^{-1}) but did exhibit a shift (2228 cm^{-1} , $\Delta = +7 \text{ cm}^{-1}$) of the nitrile stretching frequency relative to the base cyanostyrene copolymers (2221 cm^{-1}).

The blends were evaluated for the existence of lower critical solution temperature (LCST) behavior.^{3,13} The S/*N*-PMI copolymer blends with cyanostyrene copolymers derived from 4-cyanostyrene or mixtures of 2- and 4-cyanostyrene do not exhibit LCST behavior up to temperatures of 588°K.

TABLE I
Styrene/Cyanostyrene Copolymers

Designation	Copolymer ^a	Wt% N	Mole % Cyanostyrene	M_w	M_w/M_n	T_g (°K)
CNS-A	S/4-CNS	1.4	16.9	202,300	1.9	391
CNS-B	S/4-CNS	3.0	23.5	197,600 ^d	1.9	395
CNS-C	S/4-CNS	5.1	41.5	183,300 ^d	1.8	398
CNS-D	S/2,4-CNS ^b	3.0	23.5	192,000 ^d	1.8	396
CNS-E	S/2,4-CNS ^c	2.9	22.7	187,200 ^d	1.9	400
CNS-F	S/2-CNS	2.9	22.7	199,200	1.8	405

^aS = styrene, CNS = cyanostyrene, 2,4 = mixture of 2-cyanostyrene and 4-cyanostyrene.

^bIsomer ratio = 25% 2-CNS: 75% 4-CNS.

^cIsomer ratio = 78% 2-CNS: 22% 4-CNS.

^dWeight average molecular weight (M_w) by light scattering technique; CNS-B M_w = 186,400; CNS-C M_w = 180,200; CNS-E M_w = 182,400.

TABLE II
S/N-PMI//S/CNS Blend Miscibility

S/N-PMI	100	75	25	50	75	25	50	75	25	50
CNS-A	—	25	75	—	—	—	—	—	—	—
CNS-B	—	—	—	50	—	—	—	—	—	—
CNS-C	—	—	—	—	25	75	—	—	—	—
CNS-D	—	—	—	—	—	—	50	—	—	—
CNS-E	—	—	—	—	—	—	—	25	75	—
CNS-F	—	—	—	—	—	—	—	—	—	50
T_g (°K)	496	463	411	444	471	423	447	472	423	437, 475

The FTIR analysis indicates an interaction between the imide copolymer and the cyanostyrene copolymers(s), however whether the indicated negative heat of mixing can be solely attributed to this interaction remains in question. A more encompassing rationalization would involve applying the binary interaction model of Paul and Barlow¹⁴ and assuming the case for blends of two copolymers having a common monomer, in this case styrene monomer, where the interactions between the different monomer units in the copolymers as well as in the blends of both copolymers are taken into account.

The practical utility of the miscible polymer pair is the linear property relationships attainable according to blend ratio (Table III). In this series, the increased values of deflection temperature under load relative to the base styrene/4-cyanostyrene copolymer (CNS-B, Table I) correlate to the proportion of S/N-PMI copolymer present in the blend. Impact strength is controlled by the presence of an EPDM-g-poly(styrene-co-4-cyanostyrene) modifier¹⁵ where the composition of the

TABLE III
Physical Properties of S/N-PMI// S/CNS Polymer Blends

CNS-B	100	65	35	40	15	—
EPDM-g-S/4-CNS	—	—	—	30	30	—
S/N-PMI	—	35	65	30	55	100
Tensile strength (MPa)	52	49.7	48.6	42.6	41.3	47.5
Deflection temperature under load (°C)	92	123	155	120	151	192
Notched izod (J/M)	32	21	21	218	156	11
Falling weight impact strength (N-m)	< 1	< 1	< 1	20.7	17.4	< 1

graft copolymer is identical to copolymer CNS-B and the EPDM content of the modifier is 52 weight percent.

The poly(styrene-*alt*-*N*-phenylmaleimide) copolymer exhibits a sufficient level of mixing with cyanostyrene copolymers to produce thermodynamically miscible polymer pairs which exhibit useful properties.

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BARRY D. DEAN

ARCO Chemical Company
Division of Atlantic Richfield
Newtown Square, Pennsylvania 19073

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