Methyl Methacrylate Copolymer–SAN Miscibility

The thermodynamic miscibility of poly(methyl methacrylate) with poly(styrene-co-acrylonitrile) has been documented.[1-6] Investigations broadening this concept studied the miscibility of poly(styrene-co-acrylonitrile) and poly(α-methylstyrene-co-acrylonitrile) with the higher homologs of polymethacrylates and found miscibility to be dependent on the size of the pendant alkyl group of the polymethacrylate.[7,8]

This paper reports the miscibility of poly(methyl methacrylate co-N-phenylmaleimide) with poly(styrene-co-acrylonitrile) and the use of the MMA/N-PMI copolymer as a heat distortion temperature modifier for SAN and ABS resins. N-Phenylmaleimide was selected as the comonomer for MMA because (1) the cyclic nature of the α, β-unsaturated imide would restrict rotation of the copolymer backbone and enhance the glass transition temperature of the copolymer and (2) the reactivity ratios for polymerization of N-PMI with MMA are favorable versus other cyclic monomers, such as maleic anhydride or maleimide.[9,10]

The MMA/N-PMI copolymer used for this study was prepared in the following manner. A citrate bottle was charged with 52.5 g of methyl methacrylate monomer, 17.5 g of N-phenylmaleimide monomer, 140 g of distilled water, 1.2 g of tricalcium phosphate, 0.01 g of sodium bisulfite, 0.09 g of t-butyl peroctoate (Lucidol Division, Pennwalt Corporation), and 0.065 g of 1,1'-azobis(cyclohexanecarbonitrile) (VAZO 88 Initiator, E. I. Dupont Company). The bottle was tumbled in a heated oil bath at each of three temperatures (85, 95, and 130°C) for 1 h. Pale yellow beads were recovered (99.5% yield). The MMA/N-PMI copolymer analyzed for 1.9% nitrogen content (23.5 wt % N-PMI) and exhibited a glass transition temperature (T_g) of 417 K as measured by differential scanning calorimetry. This particular copolymer composition was selected because it is the composition containing the highest level of N-PMI and exhibiting a single, well-defined T_g. The molecular weight (M_n) of the MMA/N-PMI copolymer was measured at 197,200 with a polydispersity of 2.5.

The control sample of poly(methyl methacrylate) used in this study was prepared by the procedure cited. The PMMA exhibited a T_g of 379 K as measured by differential scanning calorimetry, a molecular weight of 181,300, and a M_w/M_n of 2.4.

Glass transition temperature measurements were made by differential scanning calorimetry (20°C/min) and dynamic mechanical analysis (10°C/min).

Molecular weights were measured versus polystyrene standards by gel permeation chromatography.

Polymer blends were prepared by melt mixing in a Brabender plastograph at 200°C for 5 min at a rotor speed of 63 rpm.

Cloud point measurements were made according to the procedure described by Paul et al.[4]

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

Poly(styrene-co-acrylonitrile) with an acrylonitrile content of 24.6% by weight from elemental analysis was obtained from Monsanto Chemical Company (Lustran SAN 31 resin).

The polybutadiene-g-poly(styrene-co-acrylonitrile) with an acrylonitrile content of 21.2% by weight from elemental analysis and a polybutadiene content of 14.1% by weight from infrared analysis[11] was the ABS resin used in this study.

The blends of MMA/N-PMI copolymer with SAN copolymer prepared in the melt phase are transparent with a pale amber color. Measurement of the glass transition temperature of the copolymer blends by both thermal and mechanical techniques shows the two copolymers to be completely miscible over the full range of polymer blend compositions (Table I and Figure 1). The relationship between copolymer blend T_g and composition is linear and described by $T_g = w_1 T_{g1} + w_2 T_{g2}$.

Infrared spectroscopic analysis of the blend from MMA/N-PMI copolymer and SAN copolymer showed no obvious shifts in either the carbonyl stretching frequency (1731 cm^{-1},

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TABLE I
MMA/N-PMI–SAN Miscibility

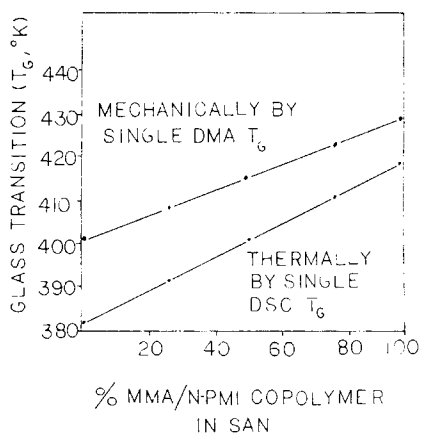| SAN	100	75	50	25	—
MMA/N-PMI	—	25	50	75	100
T_g (K, DSC)	382	391.5	400.5	408	417
T_g (K, DMA)	401	408	414	421	428

Fig. 1. MMA/N-PMI: San Miscibility
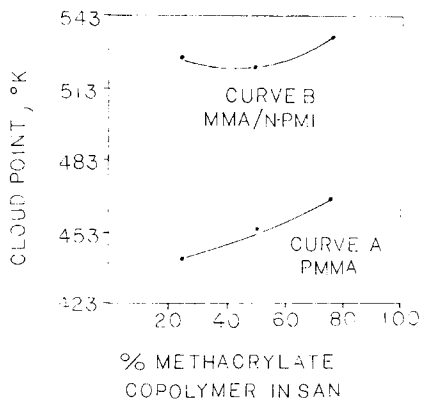

Fig. 2. Cloud Point Curve for San-MMA/N-PMI Blends

TABLE II
Heat Distortion Modification of ABS with MMA/N-PMI Copolymer

ABS	100	85	81
Modifier[a]	—	5	9
MMA/N-PMI	—	10	20
Total % polybutadiene	14.1	13.8	14.1
T_g (K, DSC)	383	386	391.5
Deflection temperature under load			
(264 psi, ⅛" unannealed, °C)	83.5	87.5	92.5
Notched Izod (J/m)	128	128	121

[a] Modifier composition: 70% polybutadiene, 30% styrene-acrylonitrile copolymer (75 : 25 wt %).

ester; 1701 cm^{-1} *imide) or the nitrile stretching frequency (2237 cm^{-1})* compared to the individual polymer film spectra. Careful examination of the main carbonyl stretching frequency indicates the existence of additional carbonyl absorption in the blend for both the ester functionality ($\Delta = -5$ cm^{-1})[5] and the imide functionality ($\Delta = -8$ cm^{-1}) as evidenced by the appearance of both new and broadened shoulder absorbances.

Poly(methyl methacrylate)–styrene/acrylonitrile copolymer blends exhibit lower critical solution temperatures (LCST) (Figure 2, curve A).[2,4] The methacrylate copolymer-SAN blends exhibit LCST behavior but at significantly higher temperatures (Figure 2, curve B). The higher LCST behavior for the methacrylate copolymer-SAN blends could be attributed to enhanced miscibility (over that of PMMA-SAN), that is, a more negative heat of mixing or a change in the free volume difference between the MMA/N-PMI–SAN blends and the PMMA-SAN blends.[12]

The practical utility of the MMA/N-PMI copolymer blends with SAN is in the heat distortion temperature modification of ABS. Since ABS is an styrene-acrylonitrile copolymer matrix rubber modified with a polybutadiene elastomer, the miscibility with the methyl methacrylate–N-phenylmaleimide copolymer would be of the same magnitude. Typically, modification of the heat distortion temperature of ABS is accomplished by incorporating α-methylstyrene. However, the significantly higher T_g of MMA/N-PMI copolymer than the styrene-acrylonitrile copolymer matrix of ABS allows for improved HDT via incorporation of the maleimide copolymer at low levels (Table II). Addition of 20 parts per hundred of MMA/N-PMI to a standard ABS along with a small amount of modifier to maintin the overall rubber content results in a 9 K increase in T_g and deflection temperature under load (DTUL) with minimal loss in impact properties.

Methyl methacrylate–N-phenylmaleimide copolymers are miscible with styrene/acrylonitrile copolymers and to a greater degree than the base polymer, poly(methyl methacrylate). Because of the high glass transition temperature and cited miscibility, the N-PMI copolymers serve as HDT modifiers for ABS resins.

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