

Effect of Matrix SAN in ABS/PMMA Blends

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SYNOPSIS

The effect of the molecular weight and acrylonitrile (AN) content of the styrene-acrylonitrile copolymer (SAN) on the morphology, mechanical properties, and rheological properties of acrylonitrile-butadiene-styrene terpolymer/poly(methyl methacrylate) (ABS)/PMMA (60/40 by weight) blends were studied. When the AN content of matrix SAN (32%) was close to that of graft SAN (30%), rubber particles existed separately. However, with matrix SAN having 35% AN, rubber particles showed tendency to agglomerate each other. With increasing molecular weight of matrix SAN, impact strength, ultimate elongation, and abrasion resistance of the blend generally increased. Yield strength increased with molecular weight at a constant AN content of matrix SAN, and it decreased with the decrease of AN content in spite of the increasing molecular weight of SAN. Melt properties, rather than the morphological and mechanical properties, were more sensitive to the AN content, rather than the molecular weight of matrix SAN. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Being a most successful rubber-toughened thermoplastic, the acrylonitrile-butadiene-styrene terpolymer (ABS) is manufactured mainly by graft polymerization of acrylonitrile and styrene onto polybutadiene (PB) (SAN-*g*-PB, or *g*-ABS), followed by blending it with free styrene-acrylonitrile copolymer (SAN) to form a multiphase polymer blend where rubber particles, viz., *g*-ABS forms a dispersed domain in the SAN matrix.^{1,2}

In the ABS resin, properties, notably the toughness, depend on a number of factors including the type, size, concentration of the rubber, and the adhesion between the rubber and matrix.³⁻⁵ The effect of the grafting ratio⁶ and AN content⁷ of graft SAN on ABS properties was also extensively studied.

ABS has certain limitations such as the lack of flame retardance, poor resistance to UV and ketone, in addition to relatively low use temperature. These limitations have been overcome to some extent by blending with other polymers including poly(vinyl chloride)⁸ and polycarbonates.⁹⁻¹²

In our earlier studies of ABS/poly(methyl methacrylate) (PMMA) blends,^{13,14} where three types of

ABS having different AN content of matrix SAN (24, 27, and 35%) were used, it was found that ABS containing 24 and 27% AN formed miscible blends and the one containing 35% AN formed immiscible blends with PMMA. The miscibility of ABS/PMMA blends seems to follow that of SAN/PMMA blends that show lower critical solution temperature at $7 \leq \text{AN} \leq 2\%$. In immiscible blends, synergism in terms of mechanical properties was obtained in ABS-rich compositions.

The present work considers the ABS/PMMA blend at a specific composition of 60/40 by weight. Three types of base SAN having different molecular weights and/or different AN content were used. Combinations of these SANs led to the 13 different types of SAN, which are different in molecular weight and/or AN content. The difference in interaction with the rubber (AN content of graft SAN is 30%) and with the PMMA, in addition to the molecular weight effect, is considered with regard to morphological, mechanical, and rheological points of view.

EXPERIMENTAL

Materials

The basic material parameters of the resins are tabulated in Table I. The molecular weight of SAN1 is

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Table I Molecular Characteristics of the Base Resins

	M_n	M_w	PDI	% AN
SAN 1	50,000	85,600	1.74	35
SAN 2	34,000	54,500	1.60	35
SAN 3	45,100	91,000	2.08	32
PMMA	35,000	66,000	1.85	—

The *g*-ABS (rubber) has a grafting ratio (graft SAN/rubber) of 0.36 and the AN content of graft SAN is 30%.

higher than that of SAN2, but the AN content is the same (35%). The molecular weight of SAN3 is almost the same as that of SAN1, but the AN content of SAN3 is 32%. Combination of SAN1 and SAN2 (called the SAN1 series) and SAN3 and SAN2 (called the SAN3 series) led to two series of matrix SAN. The SAN1 series differs in molecular weight, and the SAN3 series differs both in molecular weight and AN content. Rubber, SAN, and PMMA resins received were dried *in vacuo*, at 80°C for 24 h.

Compounding

Dried resins were thoroughly premixed using a Henschel mixer at the desired compositions, followed by melt-mixing using a Berstorff twin-screw extruder (type of gear ZE 25). Most blends were prepared at 235°C and 300 rpm. Extrudates were quenched in water and pelletized, followed by injection molding. Injection was done with a temperature profile similar to the extrusion.

Morphology

The morphology of the blends were measured using a transmission electron microscopy (TEM) (Jeol, JSM-1200 EX II). Tensile specimens were cut to 100 nm in thickness using a microtome (Reichert-Jung SuperNova), and the samples were stained with OsO₄ for over 3 days.

Rheology

Melt properties were determined from an RDS (Rheometrics Dynamic Spectrometer) using a parallel plate geometry with gap of 1.2 mm. Disks measuring 2.5 (diameter) × 0.25 cm (thickness) were compression-molded. Rate sweeps were done isothermally at 220°C. From the strain sweep, linear viscoelastic behavior was observed up to 15% strain, the level tested throughout the rate sweep.

Mechanical Properties

Tensile strength and elongation at break (ASTM D-638) were determined using an Instron (Tinius Olsen Series 1000) with a crosshead speed of 5 mm/min. Impact strength (ASTM D-256) and abrasion resistance (ISO 4649) were determined using an Izod impact tester and a Din abrasion tester. The above tests were made at room temperature, and at least 10 runs were made to report the average.

RESULTS AND DISCUSSION

Morphology

TEM micrographs of ABS/PMMA (60/40 by weight) blends prepared from solely SAN1 and SAN3 are shown in Figure 1. Regardless of the type of SAN, the dominating morphology is the co-continuous one and a clean SAN (dark phase)–PMMA (white phase) phase separation is seen, again confirming the fact that the miscibility of the blends is governed by the AN content of matrix SAN, which is 35% (SAN1 and SAN2) and 32% (SAN3), respectively.

Rubber migration into PMMA and the rubber–SAN interface do not make a significant difference between the two. This is probably due to the small difference in AN content between graft and matrix SAN. However, it is also seen that rubber particles exist separately in SAN3 blends, whereas particles are generally interconnected by several members in SAN1 blends. The state of agglomeration depends on the miscibility between graft SAN and matrix SAN in ABS. It is known that the miscibility of SAN depends on the difference in AN content and molecular weight.^{15,16} For blends of SAN having a molecular weight typical of commercial products, the AN difference must be within 5% before immiscibility is observed. The interaction between grafted rubber particles and matrix SAN is expected to be optimum when the AN content of graft SAN is exactly matched with that of matrix SAN.⁴ In our experiment, Δ AN (difference in AN content) is 5% for SAN1 blends and 2–5% for SAN3 blends. Therefore, better mechanical coupling between the rubber particle and matrix SAN is expected in SAN3 blends, especially when SAN3 is solely used, where agglomeration between rubber particles is expected to be minimum. In fact, the effect of Δ AN between graft and matrix SAN is more pronounced in melt properties,^{6,7} to follow later.

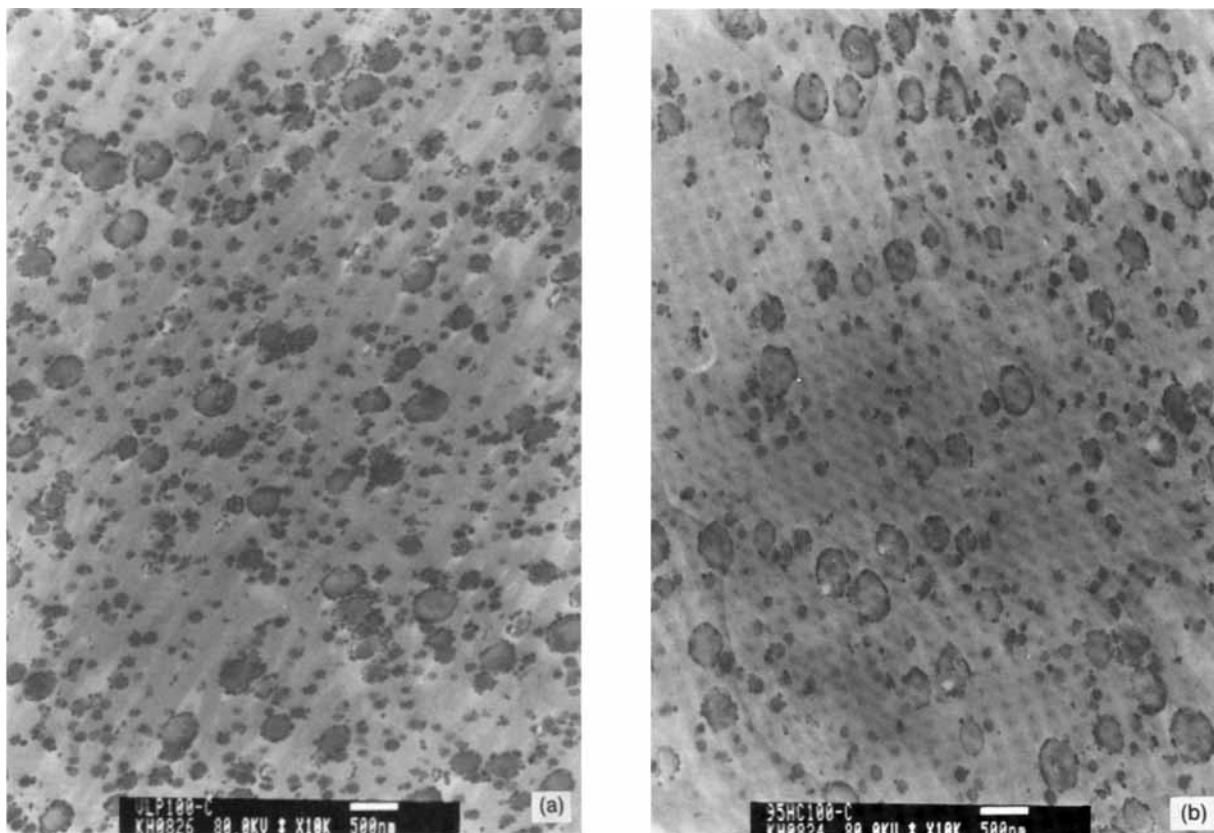


Figure 1 TEM micrographs of ABS/PMMA (60/40) blends. Matrix is solely (a) SAN1 and (b) SAN3.

Mechanical Properties

Mechanical properties of ABS/PMMA (60/40) blends having different types of matrix SAN are shown in Figures 2-5. Yield strength (Fig. 2) increases with SAN1 and decreases with SAN3 in two series of the blends, respectively.

Mechanical strength generally increases with the molecular weight of the polymer. The molecular weights of SAN1 and SAN3 are similar (SAN3's is slightly higher). In SAN1 blends, tensile yield strength increases with increasing SAN1 content due to the increased average molecular weight. In SAN3 blends, on the other hand, the decrease of tensile yield strength with increasing SAN3 content should come from the decreasing AN content of matrix SAN. Since SAN1 and SAN3 blends form ABS-PMMA phase separation having essentially identical SAN-PMMA interfacial morphology, the contribution from each phase should be similar in both series of blends.

Elongation at break of the blends is seen in Figure 3. In ABS, the ultimate elongation increases with rubber via the formation of multiple crazings.^{3,4} In

both series of the blends, elongation increases with SAN1 and SAN3, respectively. A common contribution in both series of the blends may be the in-

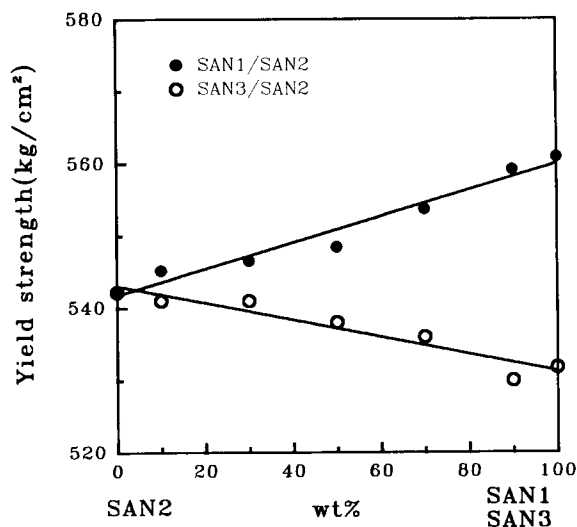


Figure 2 Tensile yield strength of ABS/PMMA (60/40) blend: (●) SAN1 series; (○) SAN3 series.

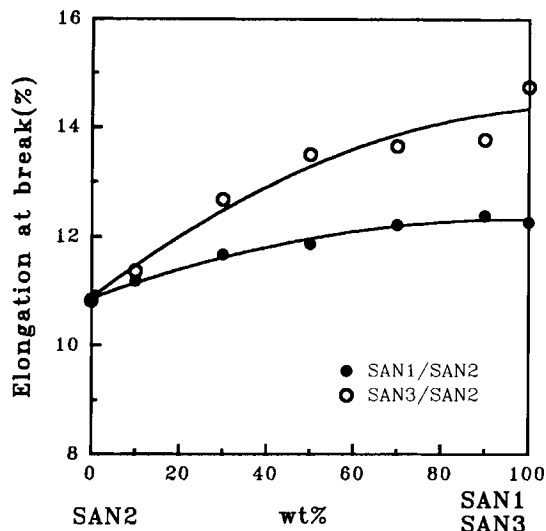


Figure 3 Elongation at break of ABS/PMMA (60/40) blend: (●) SAN1 series; (○) SAN3 series.

creasing molecular weight of SAN. A more ductile nature of SAN3 over SAN1 (T_g of SAN increases with AN content) and better miscibility of SAN3 with graft SAN as well as with PMMA should also contribute to the higher ductility of SAN3 blends.

Impact strength (Fig. 4) of the blends increases with SAN1 and SAN3, but the effect is more pronounced with SAN3. Again, a common contributing factor to the increased impact strength would be the increasing molecular weight of matrix SAN. Since the major toughening mechanism of rubber-filled SAN is the craze formation,^{3,5} better impact strength is expected with matrix SAN of lower T_g (SAN 3 blends). Impact strength of ABS can also increase

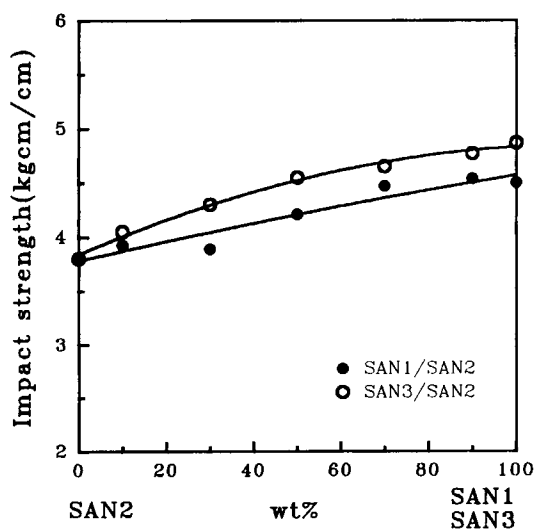


Figure 4 Impact strength of ABS/PMMA (60/40) blend: (●) SAN1 series; (○) SAN3 series.

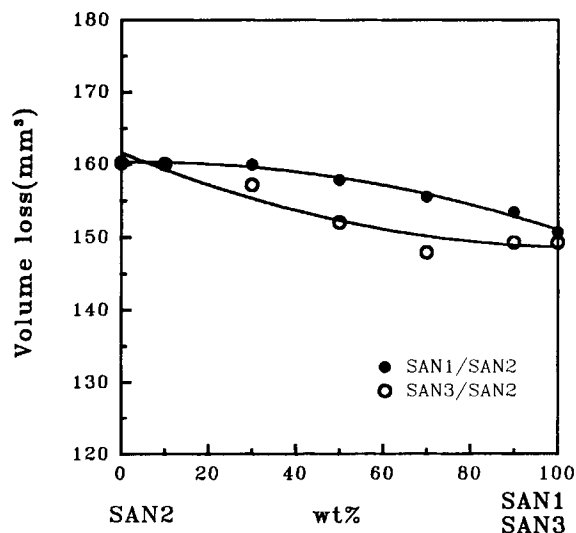


Figure 5 Abrasion volume loss of ABS/PMMA (60/40) blend: (●) SAN1 series; (○) SAN3 series.

with the AN content of SAN provided that the adhesion and dispersion remain within an acceptable limit, which are intimately connected through Δ AN between graft and matrix SAN.⁴ Since Δ AN for SAN1 blends is 5%, and for SAN3 blends, it is 2–5%, better adhesion is expected with SAN3 blends, as already mentioned. It seems that better adhesion and lower T_g of the SAN3 blend exert a stronger effect on toughening than does the AN content of matrix SAN.

Figure 5 shows the volume decrease upon abrasion. Abrasion resistance increases with the increase of SAN1 and SAN3, due probably to the increased molecular weight of matrix SAN. In addition, the abrasion resistance of SAN3 blends is better (smaller loss) than that of SAN1 blends. Since the rubber particle is most vulnerable to the abrasion in the present ternary system, stronger adhesion of rubber to the matrix SAN (SAN3) would give better abrasion resistance of SAN3 blends.

Rheological Properties

The melt rheology of ABS^{5,17} and ABS/PMMA¹⁸ blends have been reported earlier. In ABS, the effect of rubber concentration on melt viscosity¹³ and effects of grafting ratio⁶ and AN content⁵ of graft and matrix SAN have also been reported. Following Kim et al.,¹³ the lower and higher glass transition temperatures (T_g) of *g*-ABS, each corresponding to the T_g of PB and graft SAN, respectively, decreased and increased upon blending with free SAN, due presumably to the phase separation between PB and SAN of *g*-ABS.¹⁹ The degree of grafting also influ-

ences the viscositic property of ABS. At low and high grafting ratios, rubber particles cannot form a stable colloid because the particles are not completely covered with grafted chains or because the matrix chains are expelled from the grafted chains.^{6,7} In both cases, rubber particles form agglomerated or a three-dimensional network structure leading to a yield stress or a second plateau of shear moduli (G' and G'') in the long time region associated with particle-particle interactions.

Melt viscosity of ABS/PMMA blends depends on their miscibility.¹³ In miscible blends, viscosity

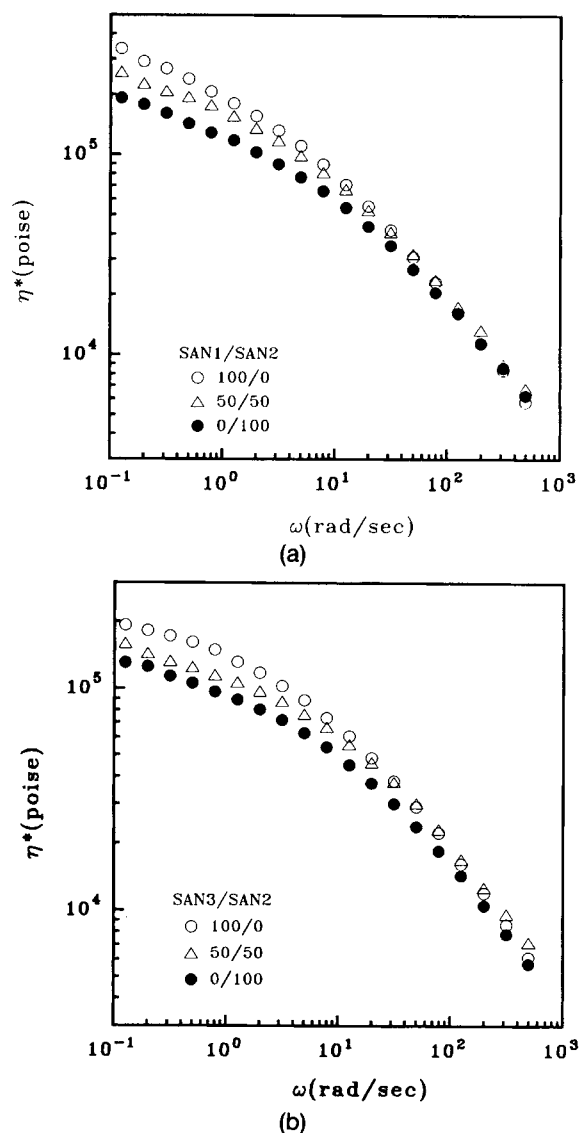


Figure 6 Complex viscosities of ABS/PMMA (60/40) blends at 220°C. (a) SAN1 series: matrix SAN is (O) SAN1, (Δ) 50/50 (SAN1/SAN2), and (\bullet) SAN2; (b) SAN3 series: (O) matrix SAN is SAN3, (Δ) 50/50 (SAN3/SAN2), and (\bullet) SAN2.

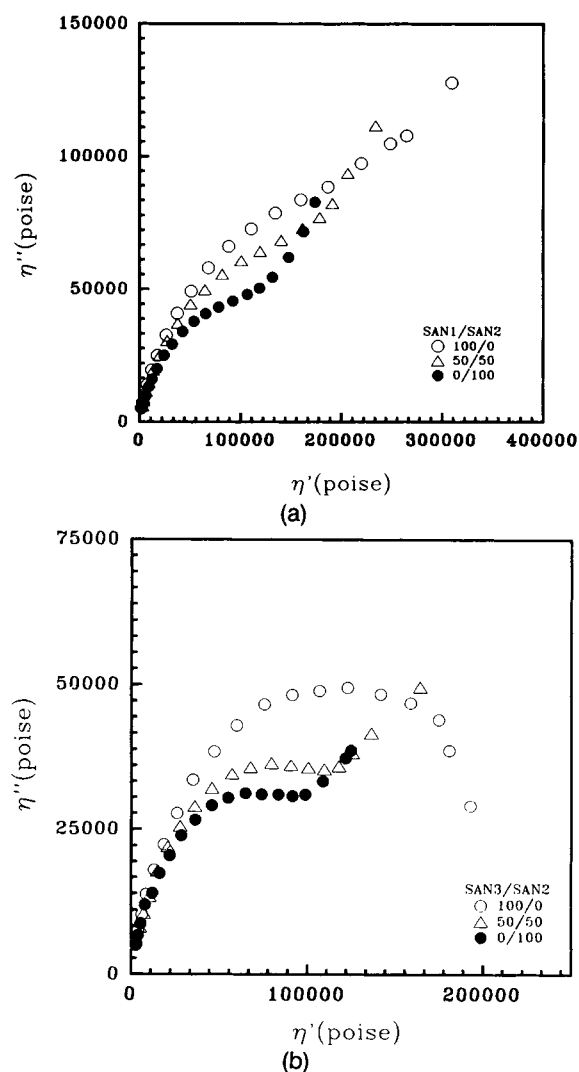


Figure 7 Cole-Cole plot of ABS/PMMA (60/40) blends at 220°C. (a) SAN1 series: (O) matrix SAN is SAN1, (Δ) 50/50 (SAN1/SAN2), and (\bullet) SAN2; (b) SAN3 series: (O) matrix SAN is SAN3, (Δ) 50/50 (SAN3/SAN2), and (\bullet) SAN2.

of ABS generally shows a sharp drop by adding PMMA due to the dilution of the rubber particle. In miscible blends, matrix SAN and PMMA form homogeneous phase and rubber particles that are evenly dispersed in the matrix. On the contrary, in immiscible ABS/PMMA blends, the dilution effect is not generally observed. Blend viscosity depends on the migration of rubber particles into PMMA²⁰ and the migration depends on the viscosity ratio of matrix SAN and PMMA.²¹ When the viscosity of PMMA is significantly lower than that of the SAN, the rubber particle may easily migrate into the PMMA phase in spite of the better chemical affinity of the rubber particle with matrix SAN.¹³

Melt viscosity of SAN1 blends [Fig. 6(a)] increases with the increases of SAN1 and shows a viscosity yield when SAN1 is solely used. On the other hand, SAN3 blends [Fig. 6(b)] do not show a viscosity yield. The viscosities of SAN3 blends are smaller than those of SAN1 at lower frequencies. A Newtonian plateau is also obtained in blends where SAN3 is solely used.

Since the molecular weight of SAN1 and SAN3 are almost the same, the higher viscosity of SAN1 blends may come from the larger Δ AN between graft and matrix SAN. Δ AN is 5% for SAN1 and 2% for SAN3 blends. Aoki and Nakayama⁷ reported that both storage and loss modulus of ABS have the smallest values when the Δ AN of graft and matrix SAN is within 1.5% and become higher with the increase of Δ AN. When the Δ AN becomes larger, miscibility of graft SAN and matrix SAN decreases. This augments the formation of rubber-phase agglomeration.

Figure 7 shows the Cole–Cole plot of the blends. In both series of the blends, immiscible drift from the semicircle is generally seen, indicative of the immiscible nature of the present ABS/PMMA blends. However, immiscible drift is not obtained when SAN3 is solely used. This implicitly indicates that this particular blend is rheologically miscible or shows single relaxation process.^{21,22}

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Received July 12, 1993

Accepted August 24, 1993