Miscible and Immiscible Blends of ABS with PMMA. II. Mechanical and Surface Properties

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SYNOPSIS

Mechanical and surface properties of injection-molded specimens for miscible and immiscible blends of ABS with PMMA were investigated. Regardless of miscibility, hardness, modulus, and strength of the blends generally showed a smooth variation with composition, with the possible exception of impact strength. In miscible blends, impact strength decreased smoothly with PMMA; however, in immiscible blends, a drastic drop to less than the half that of ABS was obtained at 10 wt % PMMA. Compounding at higher temperature gave decreased modulus and strength and increased impact strength. Surface gloss decreased with PMMA addition in the miscible system and increased in the immiscible system up to 50 wt % PMMA. From contact-angle and FTIR measurements, it is suggested that the surface properties are governed by miscibility and the viscosity ratio of the components. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(styrene-co-acrylonitrile) (SAN)-graft-polybutadiene (hereafter called g-ABS) blended with SAN(ABS) is a most successful rubber-toughened thermoplastic and is widely used (over 1 billion kg worldwide per annum) where toughness and surface gloss are desired.[1,2]

Due mainly to the rubber(g-ABS) inclusion, ABS, however, has certain limitations.[2] In addition, ABS is facing strong competition with regard to the cost/performance ratio from other thermoplastics such as modified polyphenylene ether, polycarbonate (PC) blends, and even high-impact polystyrenes.[3]

Blending has become a major technique to overcome ABS limitations, and blends with poly(vinyl chloride) (PVC)[2] and PC[4–6] have long been commercially available. In these blends, PVC imparts flame retardation and hot melt strength and PC raises toughness, heat resistance, and UV stability in addition to other mechanical properties. The property improvement is primarily due to the mis-

cibility of the SAN phase with PVC and PC, with the g-ABS phase apparently remaining discrete.

Blends of ABS with poly(methyl methacrylate) (PMMA) seem to have certain merits.[1] Following our earlier work,[7] the miscibility of the blends essentially follows that of SAN/PMMA blends, both morphologically and rheologically (SAN/PMMA shows a lower critical solution temperature [LCST]) with SAN containing 9–29 wt % acrylonitrile (AN).[8] With ABS containing 21 wt % AN in SAN, blends with PMMA were miscible, and for the ones with 35 wt % AN, clean SAN–PMMA phase-separated blends were obtained.

This paper considers the mechanical and surface properties of ABS/PMMA blends. The blends were prepared from two types of ABS that have different AN content and PMMA with different molecular weight (MW).

EXPERIMENTAL

Materials and Compounding

ABS and PMMA resins used in the experiments are shown in Table I, together with the basic materials' parameters. Procedures for drying and compounding

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Table I   Molecular Characteristics of the Base Resins

Grade	M_w of the Matrix SAN	Composition (Bu : ST : AN)	AN Content of the Matrix SAN	Manufacturer
ABS1	85,000	18 : 65 : 17	21	Hannam
ABS2	80,000	18 : 54 : 28	35	Hyosung BASF

Grade	M_n	M_w	M_z	M_w/M_n	Manufacturer
PMMA1	31,000	66,000	106,000	2.15	Lucky
PMMA2	35,000	66,000	109,000	1.85	Lucky
PMMA3	29,400	61,000	97,000	1.69	Lucky

Bu: butadiene; ST: styrene; AN: acrylonitrile; M_n: number-average molecular weight; M_w: weight-average molecular weight; M_z: z-average molecular weight.

of the resins were described in Part I of this series.[7] After hand-mixing the resins to the desired compositions, melt blending was done using a twin-screw extruder with a temperature profile, 222–228°C, and at 30 rpm. Different temperature profiles were also applied when the effect of the compounding condition was to be examined. Specimens for mechanical testing, contact-angle, and surface gloss measurements were prepared by injection molding (Bettenfield Unilog 400).

Rheology

Complex viscosity was measured using an Rheometrics dynamic spectrometer, RDS-II) at 220°C, 15% strain level.

Mechanical Properties

Tensile strength (ASTM D-638), flexural strength (ASTM D-790), and modulus (ASTM D-790) were determined using an Instron Model 6022, with a crosshead speed of 5 mm/min (tensile) and 2.8 mm/min (flexural). Hardness (Rockwell, ASTM D-785) and impact strength (ASTM D-256) were determined using a Wilson 500 and an Izod impact tester. The above tests were made at room temperature, and at least five runs were made to report the average.

Surface Properties

Surface gloss was measured using a Glossmeter (Nippon Denshoku) with an incident angle 45°. Specimens for gloss measurement were injection-molded (DSV 30), with a specially designed mold.

The surface composition of the injection-molded specimen was measured by FTIR (Fourier transform

infrared spectrophotometer, Perkin-Elmer FTIR-1750).

The contact angle of the injection-molded surface with styrene was measured using a contact-angle meter (Erma, Goniometer G-1). Measurements were done immediately upon dropping styrene on the specimen at room temperature.

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties of the blends are given in two groups, i.e., blends of ABS1 and ABS2 each with three types of PMMA. The AN content of SAN in ABS1 and ABS2 were, respectively, 21 and 35 wt % (Table I). From the morphology and rheology measurements, ABS1 blends showed a homogeneous SAN–PMMA phase, and ABS2 blends gave a clean SAN–PMMA phase separation. The ABS1 blends will be referred to as miscible, and the other one, as an immiscible blend.

Table II(a) shows the mechanical properties of ABS1 blends. It is seen that the hardness, flexural modulus and strength, and tensile strength of these blends generally show smooth variation with composition, regardless of the type of PMMA. The impact strength (Fig. 1) shows a negative deviation from the linear additivity; however, the deviation is smooth and small. In ABS1 blends, blends with PMMA3 (the lowest MW grade) show the most irregular property–composition relationships, together with the greatest negative deviation of impact strength.

Table II(b) shows the corresponding mechanical properties of ABS2 blends. Again, the changes of hardness, flexural modulus and strength, and tensile strength are generally smooth. A significant differ-

Table II Mechanical Properties of ABS Blends

Composition ABS1/PMMA (Wt %)	Type of PMMA	Hardness (Rockwell)	Flexural Modulus (kg/cm²)	Flexural Strength (kg/cm²)	Tensile Strength (kg/cm²)	Impact Strength (kg cm/cm)
			(a) Blends with ABS1			
100/0		9.9	23,800	618	433	17.7
90/10	PMMA1	20.7	25,320	665	477	15.3
	PMMA2	18.1	25,250	663	451	15.2
	PMMA3	17.7	25,255	658	465	15.21
70/30	PMMA1	40.9	27,540	747	521	11.3
	PMMA2	39.0	27,650	741	517	10.4
	PMMA3	34.3	27,260	719	492	8.98
50/50	PMMA1	58.5	29,850	843	558	6.7
	PMMA2	55.5	30,080	833	561	6.4
	PMMA3	45.9	28,625	777	516	5.3
35/75	PMMA1	74.4	32,545	961	648	3.2
	PMMA2	74.3	32,700	952	632	3.16
	PMMA3	64.8	31,425	888	576	2.92
0/100	PMMA1	89.4	35,090	1090	710	1.36
	PMMA2	89.2	33,960	1060	700	1.35
	PMMA3	77.2	33,000	960	650	1.28
			(b) Blends with ABS2			
100/0		32.3	28,555	723	486	13.13
90/10	PMMA1	43.2	30,130	814	546	5.93
	PMMA2	42.2	30,575	820	559	5.04
	PMMA3	41.1	29,680	804	551	5.9
70/30	PMMA1	55.3	31,010	868	583	4.11
	PMMA2	55.1	31,255	876	589	3.75
	PMMA3	48.7	31,515	873	576	3.15
50/50	PMMA1	66.7	32,185	934	615	3.0
	PMMA2	65.1	32,355	937	627	2.8
	PMMA3	57.6	32,725	915	600	2.0
35/75	PMMA1	78.9	33,950	1009	656	1.94
	PMMA2	76.7	34,137	1008	658	2.0
	PMMA3	68.7	33,450	950	639	1.21
0/100	PMMA1	89.4	35,090	1090	710	1.36
	PMMA2	89.2	33,960	1060	700	1.35
	PMMA3	77.2	33,000	960	650	1.28

ence in mechanical property is not noted between miscible and immiscible blends, perhaps with the possible exception of notched impact strength. In miscible blends, impact strength varies smoothly with composition; however, in immiscible blends, a sharp drop is seen even at 10 wt % PMMA (Fig. 2).

It seems that the property variation with composition is related to the SAN–PMMA miscibility and the migration of rubber particles into the PMMA phase in immiscible blends. In miscible blends, PMMA is well mixed with the SAN matrix and the rubber particles are evenly spread in the SAN–PMMA matrix. The smooth variation of mechanical properties with PMMA in ABS1 blends may primarily come from the miscibility.[9]

In ABS2 blends, the minor component forms islands, and the major one, the matrix, and at the intermediate compositions, cocontinuous morphol-
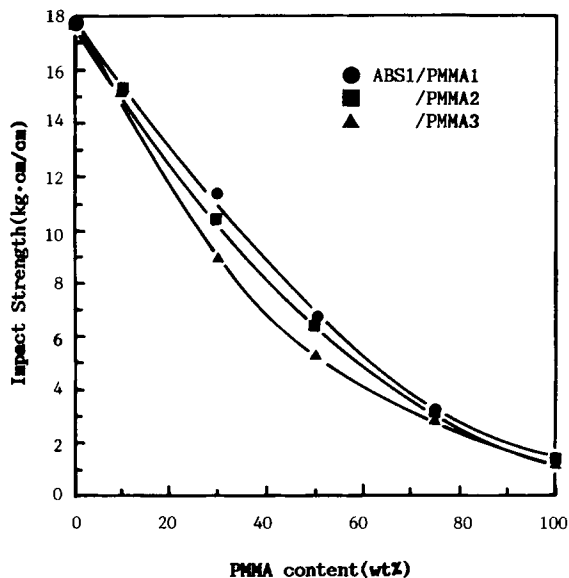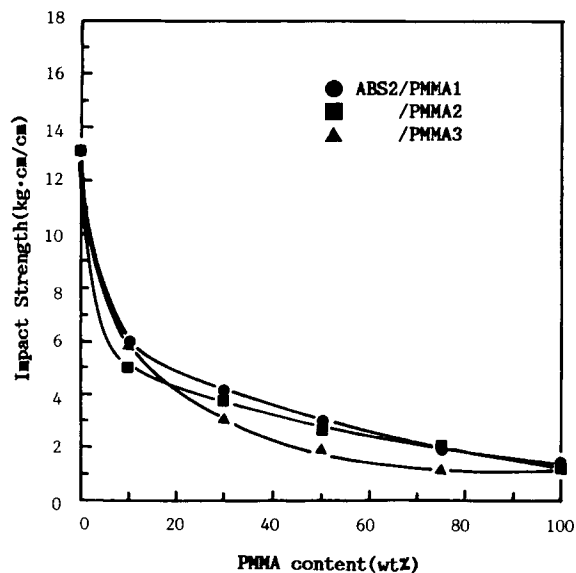
Figure 1 Notched impact strength of ABS1 blends.

Figure 2 Notched impact strength of ABS2 blends.

ogy is dominant.[7] It was also seen from TEM micrographs that rubber particles, especially larger ones, migrate toward the PMMA phase. The migration, in ABS-rich blends, might drive two conflicting effects with regard to mechanical properties: It will let the SAN exhibit its good mechanical strength due to the lowered rubber level in SAN (the mechanical property of blends generally follow that of the continuous phase), giving smooth vari-

ation of modulus and strength with composition.[10] However, this should induce a drastic drop in impact strength. The impact strength of ABS as well as other rubber-toughened plastics is obtained mainly from relatively large rubber particles so that the particles hinder crack propagation. In addition, the concentration should be large enough in order that the stress field around one particle is coupled with the neighboring ones.[11] With the migration of larger
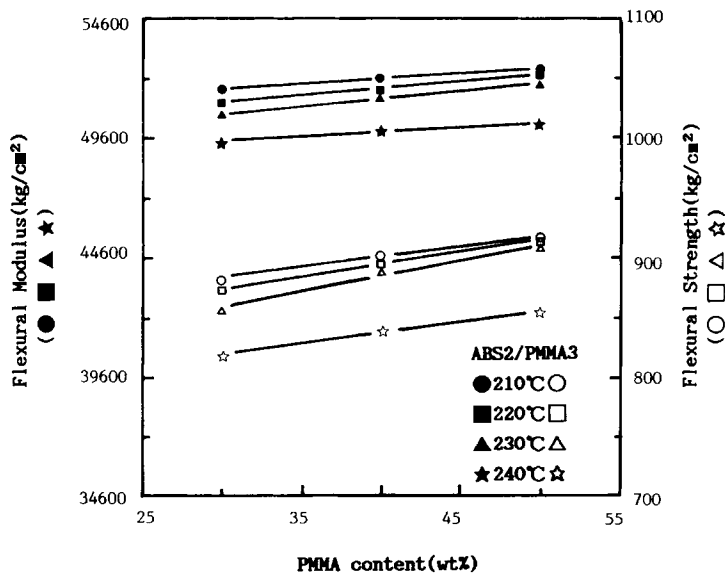

Figure 3 Effect of compounding temperature on flexural modulus and strength vs. composition relationship.
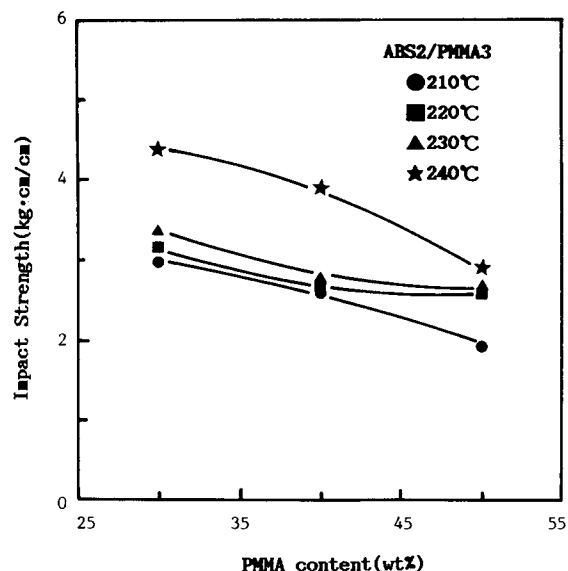
Figure 4 Effect of compounding temperature on notched impact strength vs. composition relationship.

particles to the PMMA phase, the SAN phase may not absorb sufficient fracture energy. Again, the PMMA phase may not provide toughening due to its lower concentration of rubber, resulting in a significant drop in impact strength.

Compounding Temperature vs. Mechanical Properties

For ABS2 blends, the effect of compounding temperature on the mechanical properties was examined

(Figs. 3 and 4). As the compounding temperature increases, the flexural modulus and strength (Fig. 3) decrease and impact strength (Fig. 4) increases, less at lower and more at higher temperature. In Part I, it was seen that the PMMA phase became stratified and that more rubber particles migrate toward the PMMA phase with the increase in processing temperature. Therefore, the mechanical response of the compounding temperature should come from the morphology change[12] and rubber particle migration. The smooth change of properties with composition (30, 40, and 50 wt % PMMA) should again come from the smooth morphology change with composition.

Gloss

The surface gloss of the injection-molded specimens is shown in Figure 5. In ABS1 blends, surface gloss generally decreases as the PMMA content increases. On the contrary, in ABS2 blends, surface gloss increases up to 50 wt % PMMA addition (with maximum increase over 50% based on ABS). In blends, the gloss property should be related to the refractive index difference between the components.[13] In this sense, the higher AN content of matrix SAN in ABS2 may contribute in part to the refractive index matching with PMMA. However, it seems that the effect is more likely due to the phase separation or, more precisely, to the skin-layer composition of the injection-molded specimen.

Figure 6 shows the effect of compounding temperature on surface gloss for immiscible blends
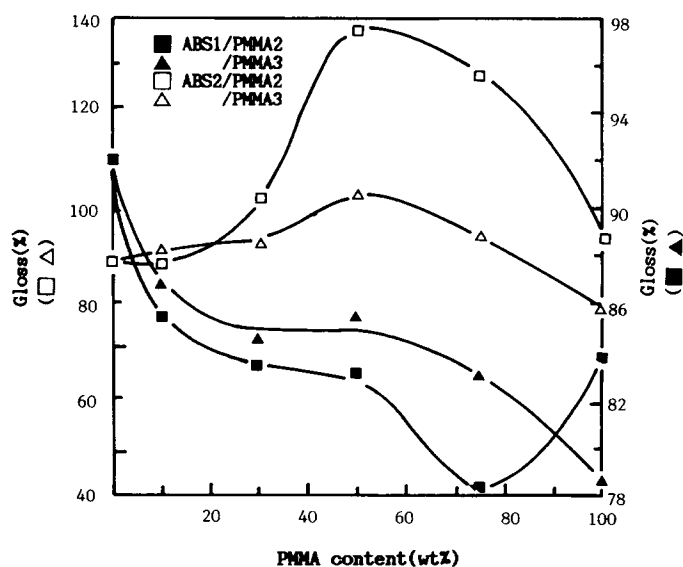

Figure 5 Gloss vs. composition for miscible (ABS1) and immiscible (ABS2) blends.

[ABS2/PMMA3 (70/30)]. The increase of surface gloss with temperature noted is due primarily to the improved flow in the mold.

Contact Angle and FTIR Measurements

Figure 7 shows the contact angle of the blends, measured by dropping the styrene monomer on the injection-molded specimen surface. In ABS1 blends, contact angle decreases monotonically with PMMA content. On the contrary, in the ABS2 blend, the contact angle increases up to 30 wt % PMMA, beyond which the value is kept constant at the PMMA level. Since the contact angle depends on the surface composition, it should give information on morphology. In miscible blends, SAN is well mixed with PMMA to form a uniform continuum, and the composition should be uniform throughout the cross section and the monotonic variation of contact angle with composition is expected. On the other hand, in immiscible blends, the composition can be varied across the cross section depending on the viscosity and elasticity ratio of the components.[14] Following Han[12] and Utracki et al.,[15,16] the lower viscosity and higher elasticity component migrates toward the skin, and, hence, a skin–core morphology can be obtained in immiscible blends. In this regard, the viscosity function of PMMAs and matrix SAN of ABS2 were measured (Fig. 8), and this will be discussed later.

In an attempt to confirm the contact-angle measurement and to further explain the greatest gloss increment with PMMA2, FTIR measurements were
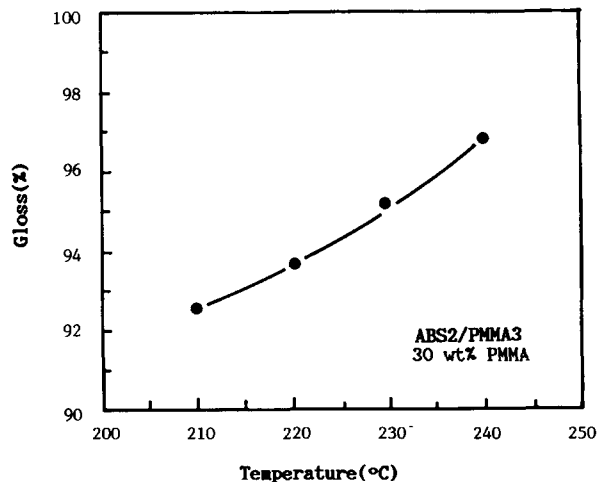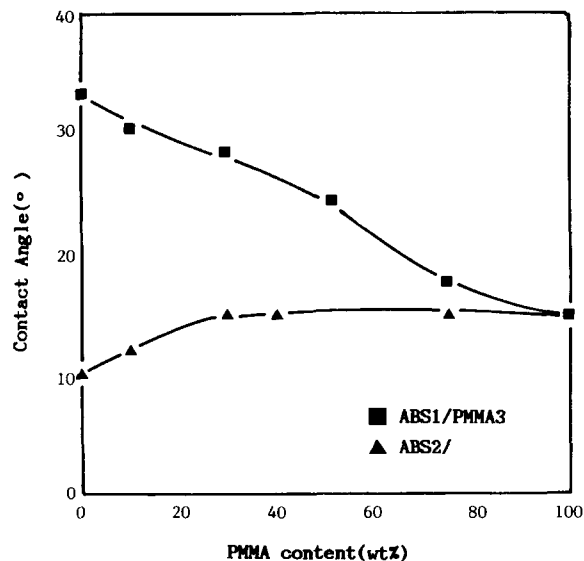
Figure 7 Contact angle vs. composition for miscible (ABS1) and immiscible (ABS2) blends.

made with samples obtained from the surface and inside an injection-molded specimen and the absorption ratios (A_{PMMA}/A_{ABS}) are tabulated in Table III. In doing this, absorption peaks at 1720 cm^{-1} (ketone group) and 700 cm^{-1} (phenyl group) were assigned to PMMA and ABS, respectively. The absorption ratio of inside and outside is similar in ABS1/PMMA1 blends, indicating miscibility.
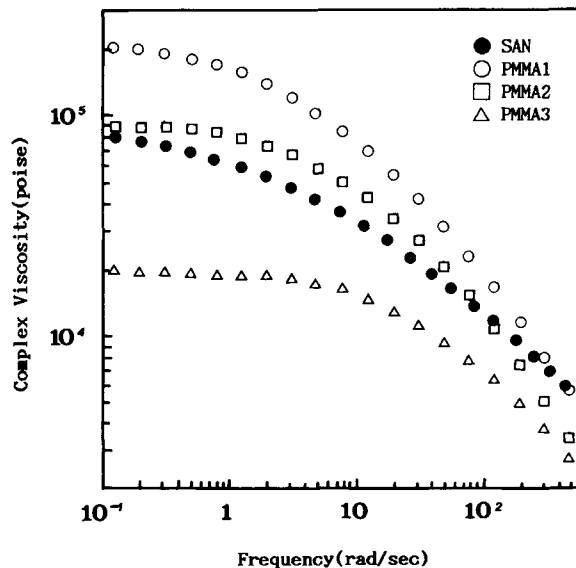
Figure 6 Gloss vs. compounding temperature.

Figure 8 Complex viscosity of the base resins at 220°C.

Table III Absorption Ratio (A_{PMMA}/A_{ABS}) of ABS/PMMA Blends

ABS/PMMA	A_{PMMA}/A_{ABS}	
	Inside	Surface
ABS1/PMMA1	1.137	1.125
ABS2/PMMA1	1.174	1.194
/PMMA2	1.087	1.325
/PMMA3	1.039	1.208

However, a significant difference is noted for ABS2/PMMA2 and ABS2/PMMA3 blends (immiscible). Unexpectedly, the absorption-ratio difference of ABS2/PMMA1 is insignificant. It seems that these results come from the different viscosity ratios of the components. When the viscosity is compared at high frequency, say at about 10^2 rad/s (resembling the compounding condition), viscosity of PMMA2 is similar to, and PMMA3 is lower than, that of matrix SAN of ABS2, whereas that of PMMA1 is significantly higher (Fig. 8). Therefore, PMMA2 and PMMA3 would have migrated toward the wall during injection, but not PMMA1. The great increase of gloss with PMMA2 blends would come from the combined effect of viscosity and retardation of particle migration. With PMMA1, PMMA does not form a skin.[12] With PMMA3 (lowest viscosity), PMMA would form a skin,[15,16] but with excessive rubber particle inclusion. Only with PMMA2 would PMMA form a skin layer together with a retarded migration of rubber particles.

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