

Compatibility and Thermal Properties of Poly(acrylonitrile–butadiene–styrene) Copolymer Blends with Poly(methyl methacrylate) and Poly(styrene-*co*-acrylonitrile)

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ABSTRACT: The mechanical and heat-resistant properties of acrylonitrile–butadiene–styrene (ABS) binary and ternary blends were investigated. The relationship of compatibility and properties was discussed. The results show that poly(methyl methacrylate) (PMMA) and styrene–maleic anhydride (SMA) can improve the thermal properties of conventional ABS. The Izod impact property of ABS/PMMA blends increases significantly with the addition of PMMA, whereas that of ABS/SMA blends decreases significantly with the addition of SMA. Blends mixed with high-viscosity PMMA are characterized by higher heat-distortion temperature (HDT), and their heat resistance is similar to that of blends mixed with SMA. For high-viscosity PMMA, from 10 to 20%, it is clear that blends appear at the brittle–ductile transition, which is related to the compatibility of the two phases. TEM micrographs show low-content and high-viscosity PMMA in large, abnormally shaped forms in the matrix. Compatibility between PMMA and ABS is dependent on both the amount and the viscosity of PMMA. When the amount of high-viscosity PMMA varied from 10 to 20 wt %, the morphology of the ABS binary blends varied from poor to satisfactory compatibility. As the viscosity of PMMA decreases, the critical amount of PMMA needed for the compatibility of the two phases also decreases. SMA, as a compatibilizer, improved the interfacial adhesiveness of ABS and PMMA, which results in PMMA having good dispersion in the matrix. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2652–2660, 2002

Key words: acrylonitrile–butadiene–styrene copolymer; poly(methyl methacrylate); styrene–maleic anhydride; brittle–ductile transition; heat-distortion temperature

INTRODUCTION

Acrylonitrile–butadiene–styrene (ABS) resin is one of most successful rubber-toughened thermoplastics. However, its application is restricted because of its low thermal stability and lack of flame retardancy. These shortcomings can be overcome, to some extent, by the following methods. (1) Chemically modified ABS: α -methyl–styrene was

employed for synthesis of thermally resistant copolymer α -methyl–styrene–acrylonitrile; butadiene latex was grafted onto it to obtain a modified ABS resin. (2) Physical blending method: with high heat resistant resin blends with conventional ABS resin, the thermal properties of ABS blends will be enhanced, and new properties may be obtained. (3) Appending inorganic materials: low-cost ABS blends can be obtained, although fluidity and impact properties of ABS will be sacrificed.¹ Generally, blending with other polymers such as bisphenol-A polycarbonate (PC) is widely used to improve the properties of ABS.

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Table I Physical Characteristics of ABS 9815

Property	Unit	ASTM Standard No.	9815
Tensile strength	MPa	D638	44.5
Flexural modulus	MPa	D790	2300
Flexural strength	MPa	D790	75
Izod impact strength	J/m	D256	175
Rockwell hardness	R	D785	104
Heat-distortion temperature	°C	D648	85
Melt-flow rate	g/10 min	D1238	20.0

Many investigations about ABS blends were reported.²⁻⁹ Poly(methyl methacrylate) (PMMA) is compatible with poly(styrene-co-acrylonitrile) (SAN), is characterized by higher heat-distortion temperature (HDT), and is cheaper than other high-performance polymers. We investigated the morphology of the two phases and improved thermal properties of ABS by PMMA and other polymers. It was reported that PMMA was located at the polycarbonate/SAN interface.

The compatibilizing effect of PMMA in blends was critical to the impact strength of ABS blends and depends on the SAN content of ABS.^{7,8} SMA resins are of low molecular weight, having low viscosity and high functionality. They are usually employed as leveling agents in floor polishes, as embrittling/anti-resoil agents in rug shampoos, and as pigment dispersants in paints, inks, and plastics. In this case, SMA was used to enhance the compatibility of ABS/PMMA blends. The morphology that determines the physical properties of immiscible polymer blends can be controlled by rheological and thermodynamic factors. A fine and uniform distribution of the minor component in the major component is generally observed when the melt viscosities of the components are similar. The phase inversion generally occurs at

the composition where the higher melt viscosity component is richer, given that the component with lower melt viscosity is more prone to be the continuous phase at balance composition. Homopolymers, as well as a block or graft copolymer, can be used as compatibilizers that act as interfacial agents, thus reducing the interfacial tension and promoting the adhesion at the interface.⁹⁻¹¹

To obtain the good thermal properties and low price of ABS, in this present study, the properties, compatibility, and morphology of ABS blends were investigated.

EXPERIMENTAL

Commercial-grade 9815 ABS resin, with the physicochemical properties listed in Table I, was used. The ABS was produced by Jinlin Chemical Industrial Co. The particles of polybutadiene rubber ranged in size from 2.8 to 3.5 μm . The percentage of SAN in ABS resin was about 40 wt %.

The physical properties of PMMA of different viscosities (purchased from Chi Mei Corp., Taiwan) are listed in Table II.

SMA resins were produced by Atofina (Channelview, TX); SMA-1000 resins were selected, as unmodified styrene (St)/maleic anhydride (MAH) polymer with St/MAH anhydride ratio of 1:1. The SMA resin was characterized by relatively high melting temperatures, high thermal stability, and narrow molecular weight distribution. The physical properties of the SMA product are listed in Table III.

Resins, dried for 4 h at 80°C in vacuum, were mixed at proper compositions, followed by melt blending using a corotating twin-screw extruder (ϕ 30, $L/D = 32$) at a zone temperature profile of 210–240°C and 120 rpm. Extrudates were quenched in water and pelletized. Extruded blends were molded into Izod bars ($\frac{1}{8}$ in. thick) and tensile bars using an

Table II Physical Properties of PMMA (Acryrex)

Property	ASTM Standard No.	High Viscosity CM-205	Moderate Viscosity CM-207
Specific gravity	D792	1.19	1.19
Melt-flow index (g/10 min)	D1238	1.8	8.0
Water absorption (%)	D570	0.3	0.3
Heat-distortion temperature (°C)	D648	100	92
Izod impact strength (J/m)	D256	196	196

Table III Physical Properties of SMA-1000

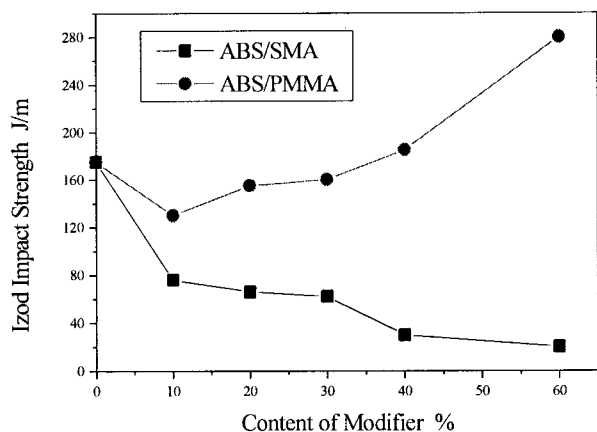
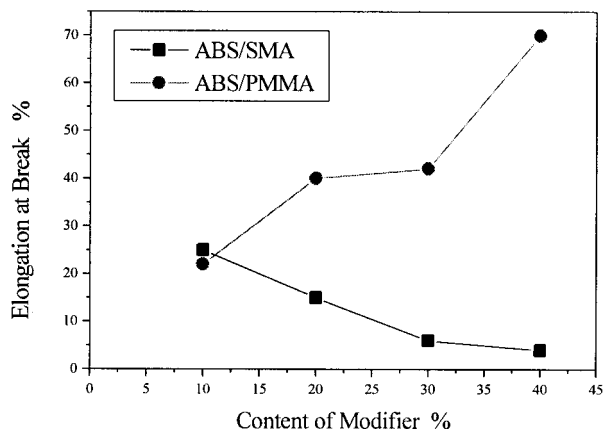
Property	Unit	Value
Melting range	°C	150–170
Acid no.		154
Gardner color (max)		465–495
Typical viscosity of 20% solids solution	cP at 30°C	28
Typical viscosity of 20% solids solution	cP at 30°C	50

injection-molding machine with the mold temperature set at 220°C. Izod specimens were machined with a notch cutter. Notched Izod impact strength, heat-distortion temperature, and tensile strength of the injection-molded specimen were determined according to the standard procedures described in ASTM D256, D1525, and D638, respectively. Notched Izod impact strengths of dry molded samples were measured at room temperature. Tensile tests were carried out according to ASTM D638 at a crosshead speed of 10 mm/min on an Instron model 4201. Morphology of the blends was investigated by SEM (Model S-250MK3; Cambridge Biotech, Rockville, MD) and TEM (Model H-800, Hitachi, Japan).

RESULTS AND DISCUSSION

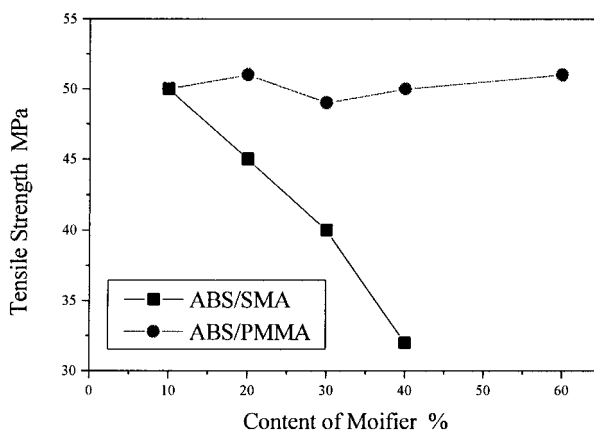
Mechanical and Thermal Properties

The ABS/PMMA and ABS/SMA binary blends were investigated. PMMA with moderate viscosity and SMA-1000 with 50% MAH were used to improve the thermal property HDT. Both poly-

**Figure 1** Izod impact strength of ABS binary blends varied as a function of SMA and PMMA.**Figure 2** Effect of modifiers on elongation of ABS binary blends.

mers have higher thermal properties than that of conventional ABS. The amount of PMMA and SMA was increased from 10 to 60 wt %. The Izod impact strength of ABS binary blends is illustrated in Figure 1.

The Izod impact property of ABS modified by either SMA or PMMA is very different. For ABS/PMMA blends, the value increased dramatically with the addition of PMMA. After a 40% amount of PMMA is mixed, the Izod impact strength is higher than that of conventional ABS. For ABS/SMA blends, the value decreased significantly with the addition of SMA, and after an amount of only 10% SMA was added, the ABS blends became very brittle. It was reasoned that, because of the high amount of MAH, the molecular chain of SMA became rigid. Although the molecular chain of PMMA is slightly rigid, it has a lower viscosity

**Figure 3** Effect of modifiers on tensile strength of ABS binary blends.

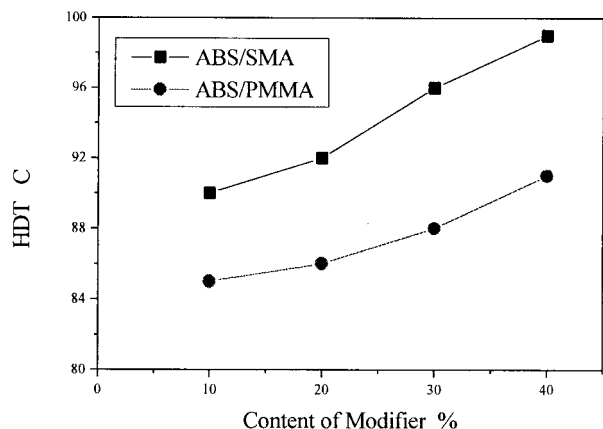


Figure 4 Heat-distortion temperature of blends as a function of amount of modifiers.

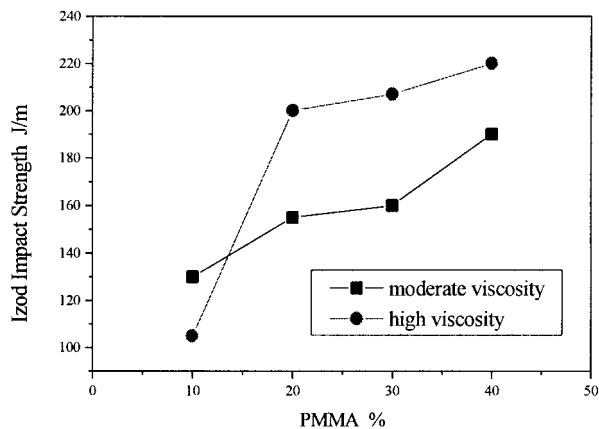


Figure 6 Effect of viscosity of PMMA on Izod impact strength of ABS binary blends.

than that of polybutadiene in ABS, and thus emerged in continuous phase with SAN. The PMMA matrix is easily induced to form numerous crazes by rubber particles, and to absorb impact energy. Elongations of both blends follow the same shift rule. Figure 2 shows the elongation of ABS binary blends as a function of PMMA and SMA.

The tensile strength values of ABS binary blends with PMMA and SMA show significant differences. Figure 3 illustrates the tensile property with various modifiers. In general, the lower the impact strength of the polymer, the higher the tensile strength. When ABS was modified by SMA-1000, the tensile strength declined significantly. If PMMA is mixed with ABS, the tensile strength of the blends remains at balance; it does not vary with PMMA and its curve presents just

slight waves. With regard to Izod impact strength and tensile strength of both blends, ABS/PMMA blends have better performance.

Although SMA modification results in lower impact and tensile properties, the heat resistance of ABS increases with an increase of SMA. A high MAH content in SMA is responsible for high thermal resistance. Figure 4 shows the heat-distortion temperature results of two blends. For ABS/PMMA blends, the HDT gradually increases with the increase of PMMA. With respect to the mechanical properties of the binary blends, the enhanced performance of ABS can be obtained by blending with PMMA.

Effect of Viscosity of PMMA

The moderate-viscosity PMMA has good mechanical properties, although the thermal resistance of

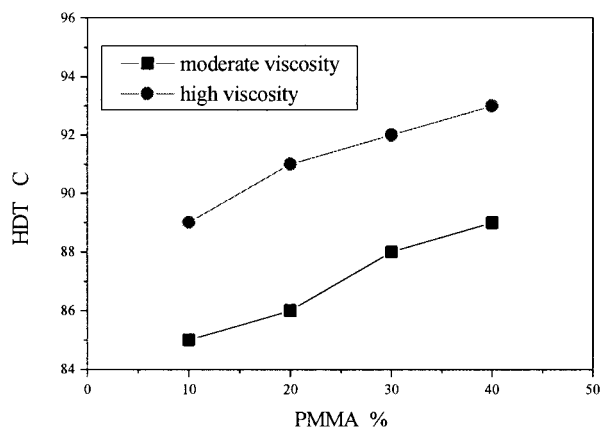


Figure 5 Effect of viscosity of PMMA on HDT of ABS binary blends.

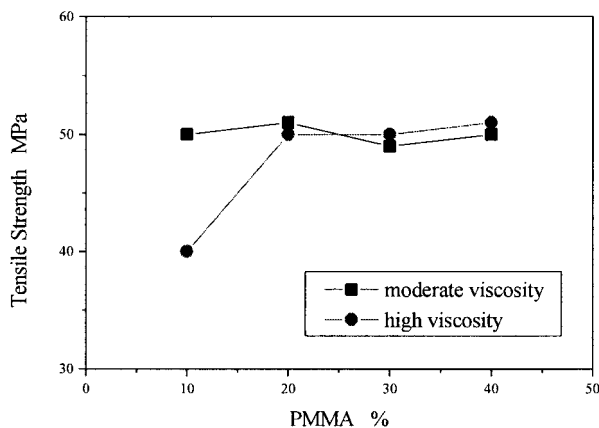
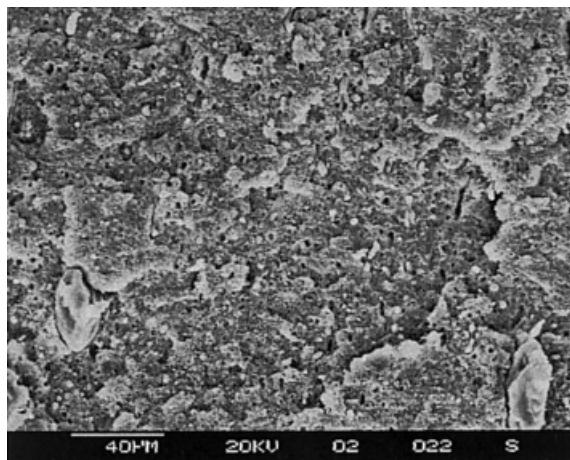
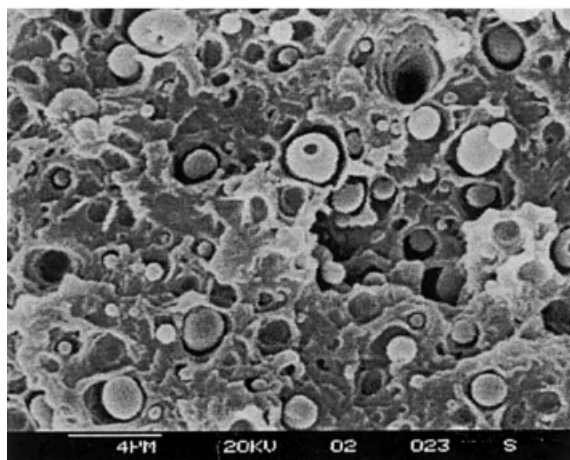


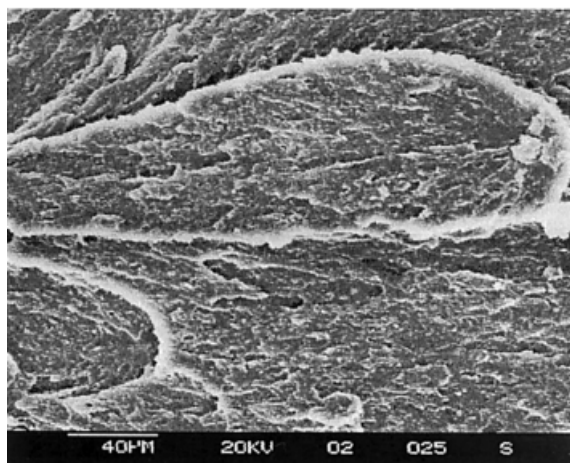
Figure 7 Effect of viscosity of PMMA on tensile strength of ABS binary blends.



(a) ABS/high viscous PMMA, 90/10 ×400



(b) ABS/high viscous PMMA, 90/10 ×4000



(c) ABS/high viscous PMMA, 80/20 ×400

Figure 8 SEM micrographs of ABS/high-viscosity PMMA blends with a $\frac{1}{8}$ -in. notch and fractured at room temperature: (a) 90/10, $\times 400$; (b) 90/10, $\times 4000$; (c) 80/20, $\times 400$.

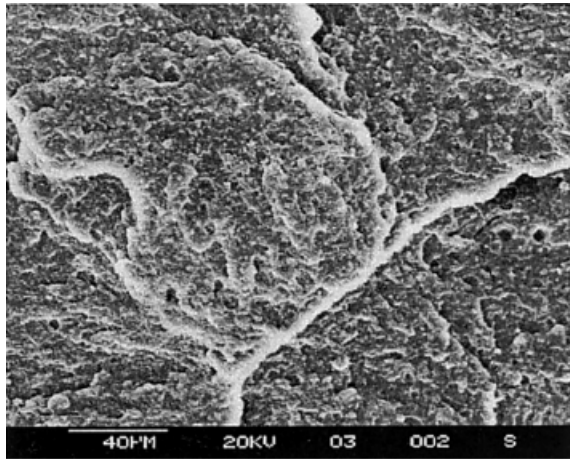
its blends does not increase significantly. High-viscosity PMMA was employed to overcome this deficiency. Figure 5 illustrates the effect of the viscosity of PMMA on HDT of blends. Blends mixed with high-viscosity PMMA are characterized by higher HDT values, similar to those of blends mixed with SMA. The high molecular weight of PMMA means that its molecular chains are difficult to move. The rigidity of molecular chains also increases with increasing molecular weight.

Figure 6 shows that, as expected, the Izod impact strength of blends increases with increasing amounts of PMMA. For high-viscosity PMMA (from 10 to 20%), but not for moderate-viscosity PMMA, it is clear that blends appear at the brittle–ductile transition, which is related to the compatibility of the two phases, as discussed in the next section.

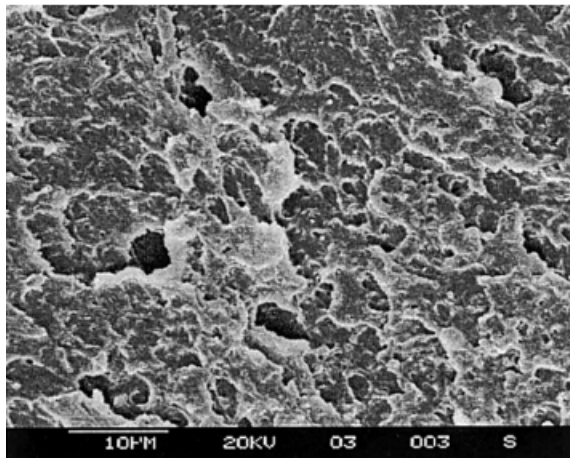
The shift rule of tensile strength is similar to that of the impact property, after 10% of high-viscosity PMMA was blended. The tensile property presents a transitional value (Fig. 7); there is no significant increase in this property after 20% of high-viscosity PMMA was blended, resulting from the change of morphology of blends. When a low percentage of PMMA was mixed with ABS, the two phases were marked by poor compatibility.

Morphology and Compatibility

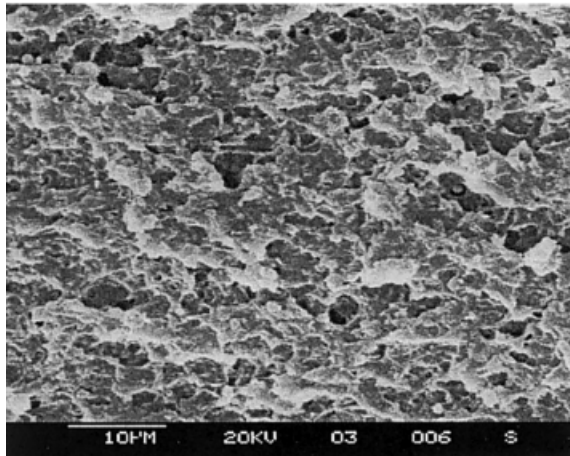
The properties of blends are dependent on both the chemical structure and the morphology of the polymer. When 10% PMMA was blended with ABS, these properties showed some unexpected features, which were the result of a different micromorphology. The SEM micrographs of the fracture surface of ABS blends with both high-viscosity PMMA and moderate-viscosity PMMA are shown in Figures 8 and 9, respectively. It is clear that there are many holes and round particles on the fracture surface when 10% high-viscosity PMMA was blended with ABS [Fig. 8(a) and (b)]. The round particles should be PMMA, with sizes ranging from 0.8 to 4 μm . Thus it can be deduced that ABS and PMMA lack enough interface adhesiveness and are characterized by phase separation and low compatibility. PMMA is difficult to uniformly disperse into the ABS matrix, and it aggregates to form either large particles or small particles. Phase separation is shown directly and clearly from TEM micrographs [Fig. 10(a)]. PMMA in



(a) ABS/moderate viscous PMMA,90/10, ×400

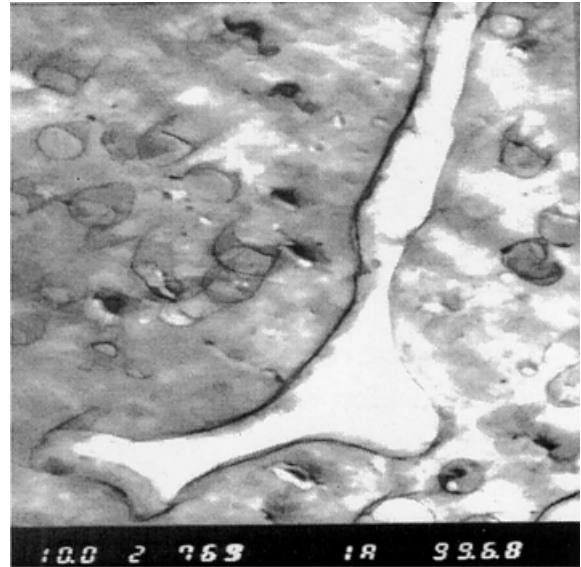


(b) ABS/moderate viscous PMMA,90/10, ×1600

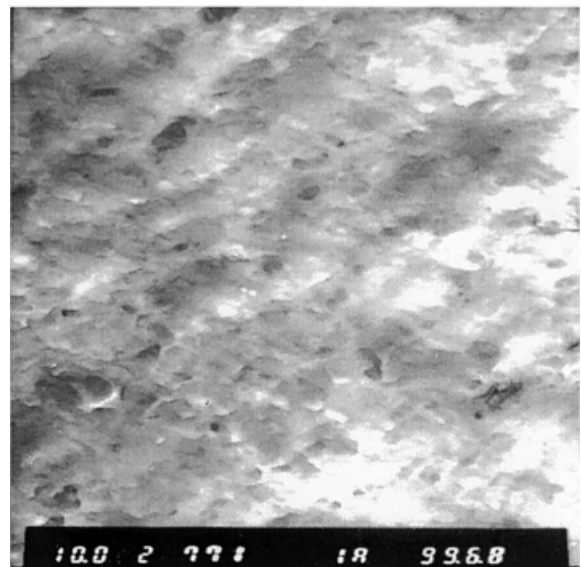


(c) ABS/moderate viscous PMMA,80/20, ×1600

Figure 9 SEM micrographs of ABS/moderate-viscosity PMMA blends with a $\frac{1}{8}$ -in. notch and fractured at room temperature: (a) 90/10, ×400; (b) 90/10, ×1600; (c) 80/20, ×1600.



a. ABS/high viscous PMMA,90/10, ×10000



b. ABS/high viscous PMMA,80/20, ×10000

Figure 10 TEM micrographs of ABS/high-viscosity PMMA blends dyed with RhO_4 : (a) 90/10, ×10,000; (b) 80/20, ×10,000.

large abnormally shaped forms populates the matrix, which can explain why ABS/PMMA blends (90/10) are characterized by low impact properties, low tensile strength, and comparatively high fluidity. The lubricity crack between PMMA and the matrix induces stress focus and easily results in material breakage. With the addition of 20% high-viscosity PMMA, although

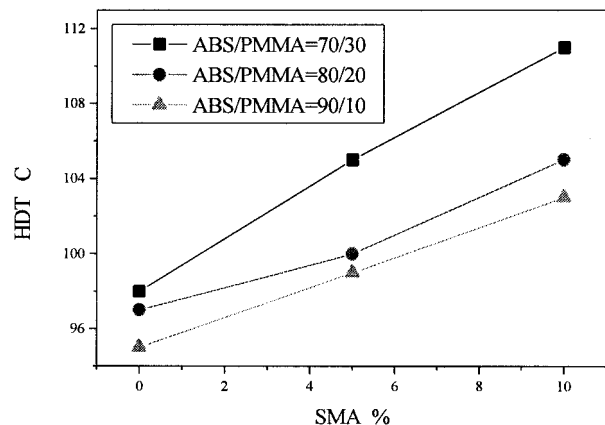


Figure 11 Effect of SMA on thermal resistance of ABS/high-viscosity PMMA/SMA ternary blends.

the SEM micrographs do not show the holes and particles on the fracture surface of blends, they do show some kind of lamina status, in which the edge of the lamina is whitened [Fig. 8(c)]. This phenomena looks like that of a fracture of tough nylon. The TEM phase morphology of blends, illustrated in Figure 10(b), shows that the abnormal shape of PMMA in the matrix has disappeared, thus certifying that the compatibility between PMMA and ABS is improved. Relevant properties of blends are also improved.

Figure 9 illustrates the fracture morphology of ABS/moderate-viscosity PMMA binary blends. There are no holes and round particles on the surface of blends, regardless of whether 10 or 20% PMMA is blended. It means that PMMA particles dissolved, as it were, in the matrix, with characteristically good compatibility.

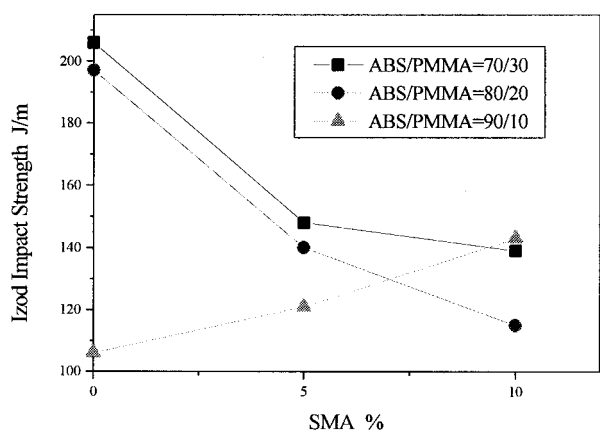
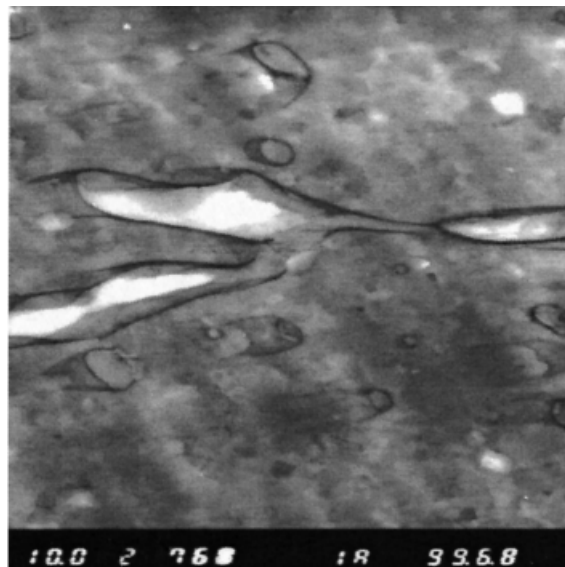
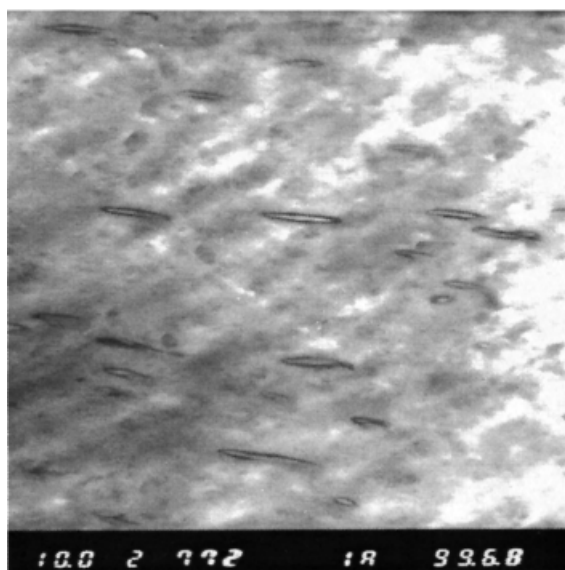


Figure 12 Effect of SMA on Izod impact strength of ABS/high-viscosity PMMA/SMA ternary blends.



a. ABS/high viscous PMMA/SMA,90/10/0



b. ABS/high viscous PMMA/SMA,90/10/5

Figure 13 TEM micrographs of ABS/high-viscosity PMMA/SMA ternary blends dyed with RhO_4 : (a) 90/10/0; (b) 90/10/5.

It can be concluded that compatibility between PMMA and ABS is dependent on both the amount and the viscosity of PMMA. When the amount of high-viscosity PMMA varied from 10 to 20 wt %, the morphology of ABS binary blends varied from poor to satisfactory compatibility. As the viscosity of PMMA decreases, the critical amount of PMMA needed for the compatibility of the two phases also decreases.

ABS/PMMA/SMA Ternary Blends

From the preceding discussion, it has been established that ABS/high-viscosity PMMA blends are marked by higher performance than that of ABS/moderate-viscosity PMMA blends. A small amount of SMA was induced to further improve the thermal properties, and at the same time it also enhanced the compatibility of ABS/PMMA blends. Figure 11 illustrates that the HDT of ABS ternary blends increases with increased amounts of SMA, irrespective of the varying proportions of ABS and PMMA. HDT increased from 98 to 105°C at 5% SMA when PMMA varied from 10 to 30%.

Shift rules of Izod impact strength of ABS ternary blends as a function of SMA are shown to be different as the content of high-viscosity PMMA varied from 10 to 30% (Fig. 12). When the proportion of ABS to PMMA is 90/10, the impact property increases with SMA. It has been well established in the preceding discussion that ABS has poor compatibility with a low content of PMMA. SMA, as compatibilizer, improved the interfacial adhesiveness of two components. PMMA has good dispersion in the matrix when SMA is blended in, as attested by TEM micrographs of ternary blends (Fig. 13). It is very clear that the status of PMMA dispersed in the ABS matrix changed from large abnormally shaped forms to small-size particles and then dissolved, as it were, in the matrix as a function of SMA.

When the proportion of ABS to PMMA is more than 80/20, the impact properties of ternary blends declined with increased amounts of SMA because brittle SMA results in a poor impact property. The elongation of ABS ternary blends is

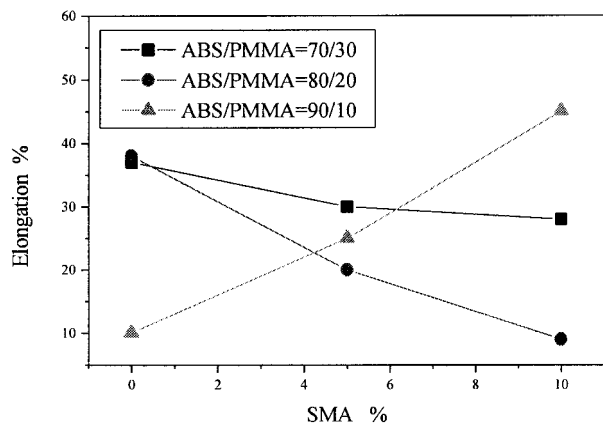


Figure 14 Effect of SMA on elongation of ABS/high-viscosity PMMA/SMA ternary blends.

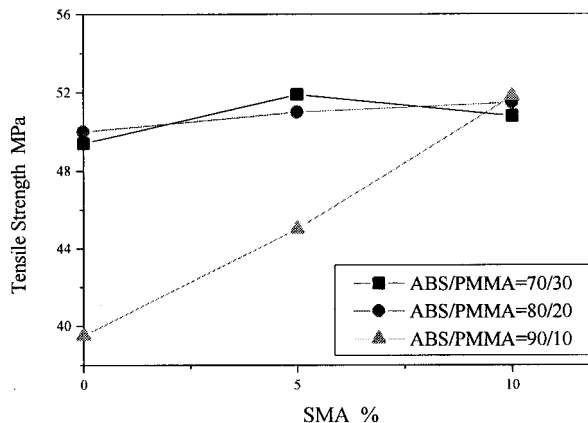


Figure 15 Effect of SMA on tensile strength of ABS/high-viscosity PMMA/SMA ternary blends.

governed by the same shift rule as a function of SMA (Fig. 14).

The tensile strength of ABS ternary blends remains the same with increased amounts of SMA, as the proportion of PMMA to ABS is more than 20% (Fig. 15). However, tensile strength increases not only with an increase of SMA as 10% PMMA is blended but also from compatibility of the two phases.

CONCLUSIONS

SMA can improve the thermal properties of conventional ABS, although other mechanical properties of ABS decreased significantly with addition of SMA. The Izod impact property of ABS/PMMA blends increases dramatically with the addition of PMMA. Blends mixed with high-viscosity PMMA are marked by higher HDT. ABS/high-viscosity PMMA blends appear at the brittle-ductile transition after 10% PMMA was mixed. Compatibility between PMMA and ABS is dependent on both the amount and the viscosity of PMMA. When the amount of high-viscosity PMMA varied from 10 to 20 wt %, the morphology of ABS binary blends varied from poor to satisfactory compatibility. As the viscosity of PMMA decreases, the critical amount of PMMA needed for the compatibility of the two phases also decreases. SMA, as compatibilizer, improved the interfacial adhesiveness of ABS and PMMA.

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