

Impact and Tensile Properties of SEBS Copolymer Compatibilized PS/HDPE Blends

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ABSTRACT: In this study, polystyrene–hydrogenated polybutadiene–polystyrene (SEBS) triblock copolymer was used as a compatibilizer for the blends of polystyrene (PS) and high-density polyethylene (HDPE). The morphology and static mechanical and impact properties of the blends were investigated by means of scanning electron microscopy, uniaxial tension, and instrumented falling-weight impact measurements. Tensile tests showed that the yield strength of the PS/HDPE/SEBS blends decreases considerably with increasing HDPE content. However, the elongation at break of the blends tended to increase significantly with increasing HDPE content. The excellent tensile ductility of the HDPE-rich blends resulted from shield yielding of the matrix. Charpy impact measurements indicated that the impact strength of the blends increases slowly with HDPE content up to 50 wt %; thereafter, it increases sharply with increasing HDPE content. The impact energy of the HDPE-rich blends exceeded that of pure HDPE, implying that the HDPE polymer can be further toughened by the incorporation of brittle PS minor phase in the presence of SEBS compatibilizer. The correlation between the impact property and morphology of the blends is discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1099–1108, 1998

Key words: impact; fibrillation; compatibilizer; polystyrene; polyethylene

INTRODUCTION

Glassy polymers form a large group of industrially important materials for structural applications, but their use is generally confined by the tendency of these materials to fracture in a macroscopically brittle manner.^{1,2} Polystyrene (PS) is a typical glassy polymer that exhibits high strength, high modulus, and excellent dimensional stability, but poor ductility. Considerable efforts have been made to improve the toughness of these polymers over the past few years.^{3–7} Conventionally, brittle thermoplastics are modified with rubber particles. The rubbery domains act as stress concentrators when subjected to external forces; hence, crazes are developed at the peripheries of rubbery do-

mains. It is this multicrazing process that promotes the toughness of the brittle thermoplastics.⁸ This impact modification has given rise to a family of polymer blends such as high-impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene copolymer. However, the addition of a low-modulus rubbery component generally leads to a sharp decrease in tensile modulus and strength of the blends. This invites investigation into the effects of modifying PS with ductile thermoplastics and the changes in mechanical behavior that they could give rise to. Polyethylene (PE) is attractive for this purpose because of its excellent ductility and superior impact performance. Several investigators have studied the morphology and tensile behavior of PS/PE blends. They reported that PS and PE are immiscible and incompatible over their whole composition ranges.^{9–11}

It is generally known that immiscible polymer blends have inferior mechanical properties due to the existence of weak interfacial adhesion and

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poor dispersion of the components. Thus compatibilizing agents are needed to enhance the interfacial adhesion between phases of the immiscible polymers. In most cases the compatibilizers act as emulsifiers, reducing the interfacial tension between immiscible polymers in the melt during blending, leading to a fine dispersion of one phase in another. The compatibilizers are normally block or graft copolymers, often containing segments chemically identical to the blend's component polymers, but can also be functionalized polymers containing reactive side groups.^{12,13} Fayt and colleagues reported that hydrogenated butadiene-PS diblock copolymer (HPB-*b*-PS) is an effective compatibilizer for PS/PE blends.¹⁴⁻¹⁹ They prepared such a diblock copolymer by polymerizing a mixture of equal amounts of styrene and butadiene in toluene.¹⁶ Scanning electron microscopy (SEM) observations revealed that HPB-*b*-PS copolymer triggers a finer and more homogeneous dispersion of PE in PS-rich blends or PS in PE-rich blends.¹⁶ Moreover, the block copolymer tends to locate at the PS/PE interface and it encapsulates dispersed particles of either PS or PE.¹⁷ Both the ultimate strength and elongation at break of blends of PS with various types of PE (low density, linear low-density, and high-density) are markedly improved by the addition of moderate amounts of HPB-*b*-PS (2-10%).¹⁰ More recently, Taha and Frerejean²⁰ have compatibilized the PS/low-density PE blends using commercial hydrogenated butadiene-polystyrene copolymer (SEB) and polystyrene-hydrogenated polybutadiene-polystyrene triblock copolymer (SEBS). They reported that the finest and more stable dispersions are obtained with diblock copolymer. Li and associates reported that both SEB and SEBS triblock copolymers are effective in reducing the PS domain size.²¹ The effects of the addition of SEBS triblock copolymer on the morphology and static tensile behavior of PS/PE blends have been investigated by several researchers.^{9,11,20-24} However, little information is available on the impact behavior of the SEBS-compatibilized PS/PE blends. This article studies the effects of SEBS addition on the tensile and impact properties of PS/high-density PE (HDPE) blends.

EXPERIMENTAL

Materials

The homopolymers used in this investigation consisted of commercial grades of PS (Styron 667;

Table I Chemical Composition of PS/HDPE/SEBS Blends

Blends	PS Content (wt %)	HDPE Content (wt %)	SEBS Content (wt %)
80/10/10	80	10	10
70/20/10	70	20	10
60/30/10	60	30	10
50/40/10	50	40	10
30/60/10	30	60	10
20/70/10	20	70	10
10/80/10	10	80	10

Dow Chemical Pacific Company, Hong Kong) and HDPE (Mobil, Saudi Arabia). The SEBS triblock copolymer (Kraton G1652) was supplied by Shell Company with respective molecular weights of PS block and central EB block being 7,500 and 37,500, and the PS weight fraction being 28.6%.

Sample Preparation

All materials were dried overnight separately in an oven. PS and HDPE homopolymers, and ternary PS/HDPE/SEBS blends with SEBS content fixed at 10 wt % were prepared in a Brabender twin-screw extruder. The chemical composition of the ternary PS/HDPE/SEBS blends is listed in Table 1. The extrudates were pelletized and then dried at 100°C for 12 h. Using these pellets, dog-bone-shaped tensile bars (ASTM D638) and plaques with dimensions of 150 × 80 × 6 mm³ were injection-molded using a Chen Hsong machine. The barrel zone temperature profiles were set at 200-210-220°C. Specimens for Charpy impact tests were machined from the injection-molded plaques according to ASTM D256.

Measurement

The tensile behavior of the blends was determined with an Instron tensile tester (model 4206) at a crosshead speed of 10 mm/min. A longitudinal extensometer was employed for strain measurements. At least five specimens of each composition were tested and an average value was used in plots.

Charpy impact tests were carried out using a CEAST falling-weight impact tester at 23°C. The impactor was equipped with an instrument tap and the signal was fed to a data acquisition board in a Spectrum system computer; thus it could record a load-displacement curve of the impact frac-

ture. The mass of the striker was 3.146 kg and the free clearance was 52 mm. The impact speed employed was 1.2 m/s. Five specimens of each composition were measured and the average values reported.

The samples used for morphological studies were immersed in liquid nitrogen and freeze-fractured. Cryogenically fractured surfaces were coated with a thin layer of gold prior to examination in a scanning electron microscope (Jeol JSM 820). In addition, the fracture surfaces of the blends after tensile and impact tests were also used for SEM studies.

RESULTS AND DISCUSSION

Tensile Behavior

Figure 1 shows the stress-strain curves of the pure PS, HDPE, and PS/HDPE/SEBS blends. Apparently, pure HDPE is a typical ductile polymer which can undergo extensive plastic deformation (exceeding 400% strain) before breaking. On the contrary, PS exhibits only elastic behavior fol-

lowed by a brittle fracture at low elongation. As illustrated in Figure 1, the addition of only 10 wt % HDPE to PS led to a dramatic improvement in tensile ductility. The tensile behavior of this blend is characterized by the presence of yield point and necking followed by homogeneous drawing. In this case, the stress-strain curve of PS/HDPE/SEBS 80/10/10 exhibited the typical behavior of toughened plastics, such as HIPS. It is noted that a high quantity of SEBS was used in this blend (10 wt %). In this case, only a part of the SEBS acted as emulsifier; the other part was dispersed in PS or PE, acting as a rubber toughening agent. Because the SEBS content in the PS/HDPE/SEBS blends is fixed at 10 wt %, it is considered that the role played by SEBS in other blends studied is similar to that of PS/HDPE/SEBS 80/10/10 blend. Further increasing the HDPE content results in a considerable decrease of yield strength but an increase in tensile ductility. The yield strength of the PS/HDPE/SEBS blends as a function of HDPE content is shown in Figure 2.

Figure 3 shows the plot of Young's modulus of the blends versus HDPE content. It can be seen

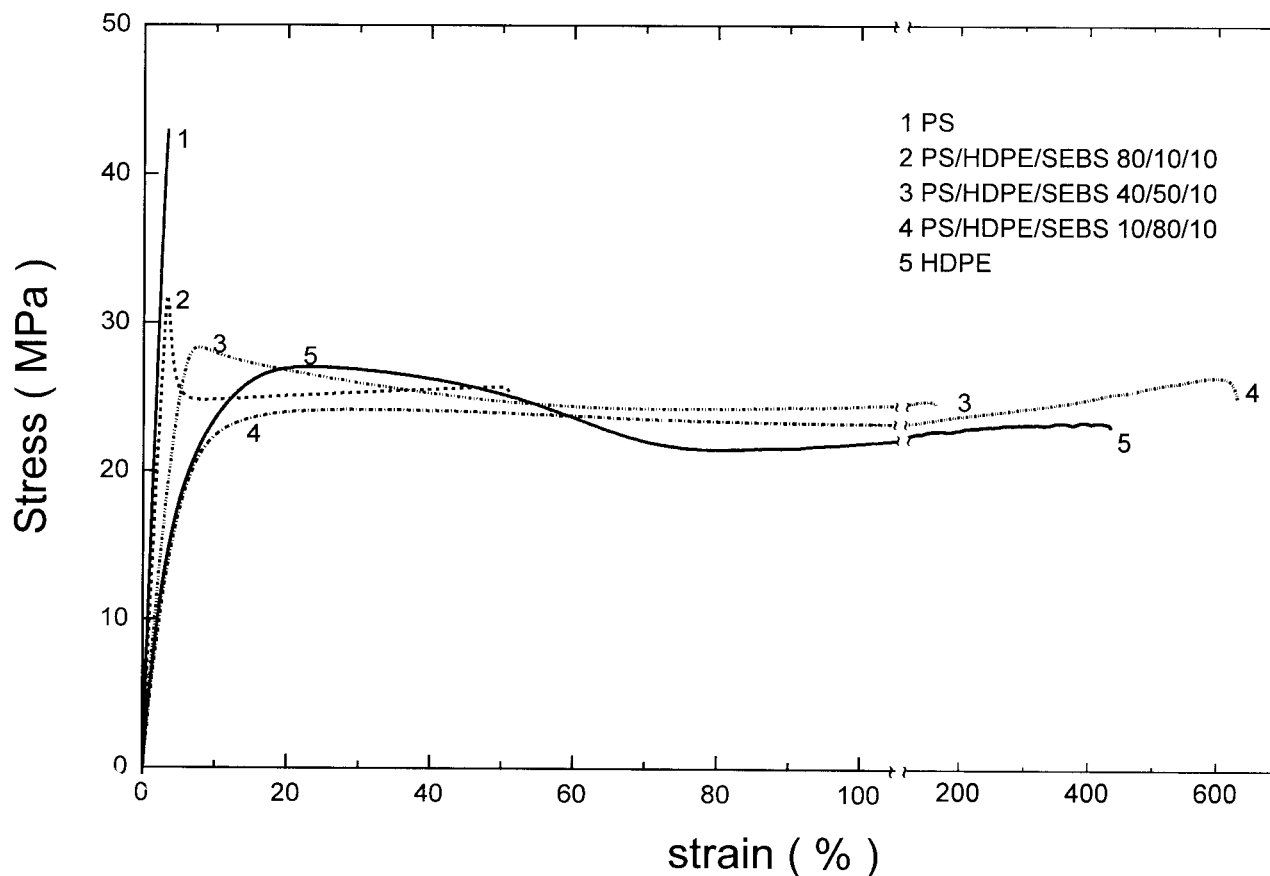


Figure 1 Stress-strain curves of PS/HDPE/SEBS blends.

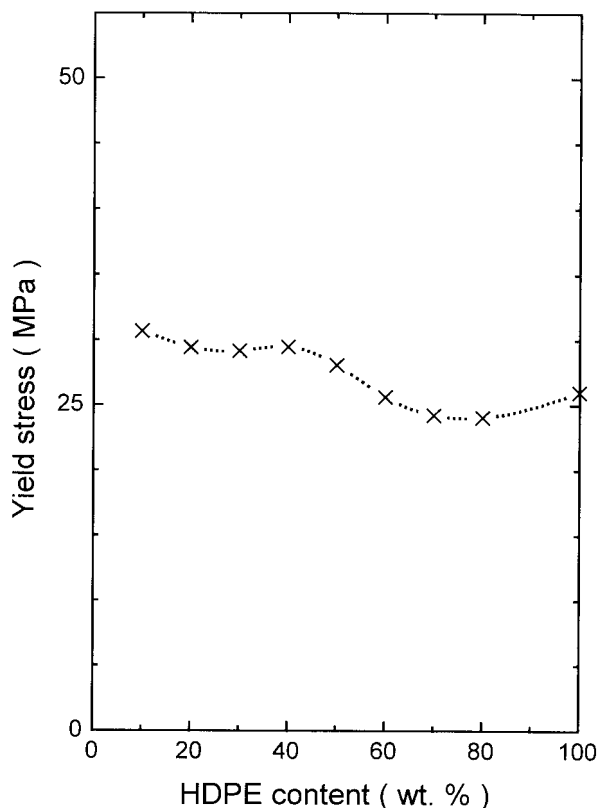


Figure 2 Variation of yield strength of the PS/HDPE/SEBS blends with HDPE content.

that the modulus of PS is significantly higher than that of HDPE (i.e., 3.2 GPa for PS and 1.2 GPa for HDPE). It is evident that the modulus of PS/HDPE/SEBS blends tends to decrease continuously with increasing HDPE content. Figure 4 shows the variations of break stress and elongation at break of the PS/HDPE/SEBS blends with HDPE content. Apparently, the break stress of the blends decreases sharply with the addition of 10 wt % HDPE, followed by a gradual decrease with increasing HDPE content. However, the elongation at break of the blends behaves differently; that is, it tends to increase significantly with increasing HDPE content [Fig. 4(b)]. It is noted that the addition of 10 wt % HDPE to PS resulted in about a 15-fold increase in the elongation at break. Furthermore, the HDPE-rich blends containing 70 and 80 wt % HDPE exhibited a higher elongation than the HDPE homopolymer. This implies that HDPE can be toughened by brittle PS polymer in the presence of SEBS compatibilizer. In this case, the HDPE-rich blend is composed of rigid PS particles in a highly ductile HDPE matrix. It is well established that ductile polymer such as polycarbonate (PC) can be

toughened by the addition of brittle glassy polymer, e.g., poly(methyl methacrylate) and styrene-acrylonitrile.²⁵⁻²⁷ In those blends, brittle glassy particles are dispersed in ductile PC matrix. The increase in ductility and toughness can be related to the adequate differences in Young's modulus and Poisson's ratio between the brittle particles and polymer matrix, thereby inducing compressive stress acting on the dispersed particles.^{25,26} Consequently, the deformation mechanism in dispersed particles may change from crazing to cold drawing, due to the compressive stress.²⁵ It is worth noting that the SEBS triblock copolymer plays an important role in improving the tensile ductility of HDPE-rich blends. The presence of SEBS leads to an increase of the adhesion between the rigid PS particles and HDPE matrix but a decrease in the dispersed phase size. In the latter case, it is known that the size of dispersed particles has a dramatic effect on deformation behavior in ductile matrix/brittle dispersed phase systems.^{28,29} The ductility of such systems generally increases with finer phase dispersions due to the lower resultant stress concen-

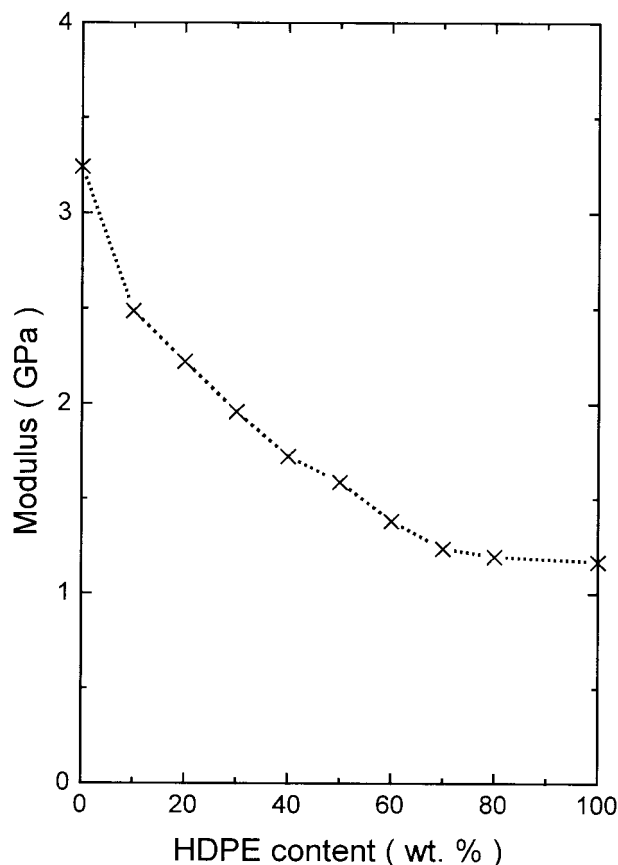


Figure 3 Variation of Young's modulus of the PS/HDPE/SEBS blends with HDPE content.

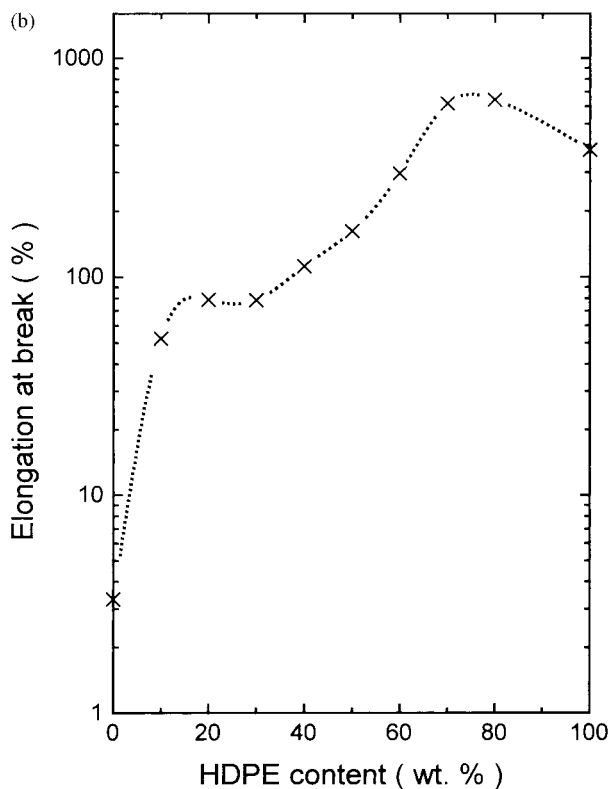
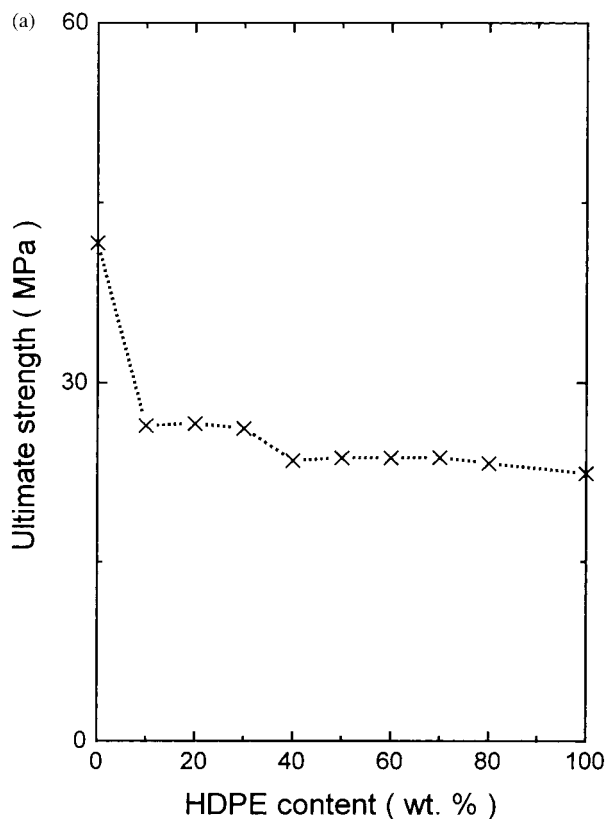


Figure 4 Variation of (a) break stress and (b) elongation at break with HDPE content in the PS/HDPE/SEBS blends.

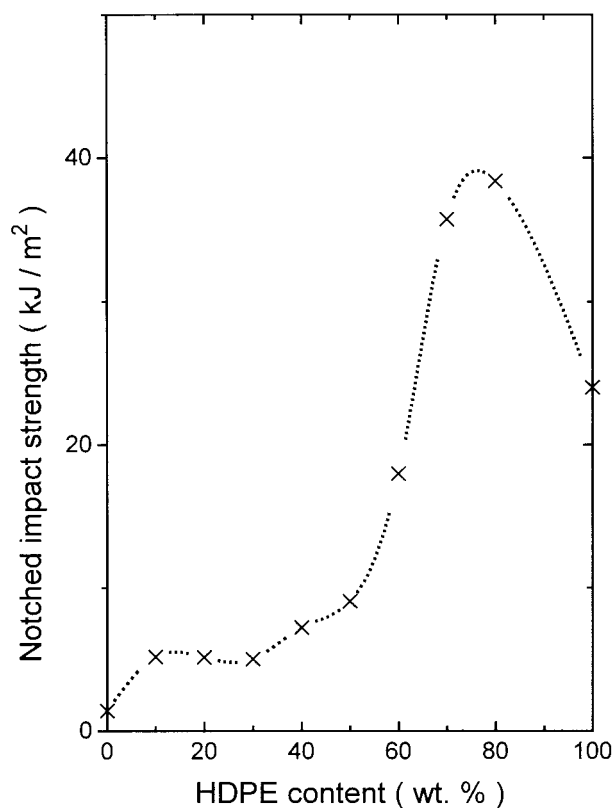


Figure 5 Variation of Charpy impact energy with HDPE content in the PS/HDPE/SEBS blends.

tration when a small particle cracks.²⁸ As the PS forms immiscible blends with PE, the PS/PE blends exhibit poor ultimate tensile properties. Fayt and colleagues¹⁰ reported that the tensile strength and ductility of PS/HDPE blends exhibit a minimum value smaller than that of either pure component. However, the addition of poly(hydrogenated butadiene-*b*-styrene) copolymer significantly enhances the elongation at break of PS/HDPE blends. This is due to the diblock copolymer acting as an efficient emulsifier, leading to strong adhesion between the PS and HDPE phases.¹⁰ Similarly, Bureau and associates also reported that the SEBS enhances the adhesion between the PS and HDPE phases in HDPE-rich blends.²⁴

Impact Behavior

Figure 5 shows the variation in notched Charpy impact energy of the PS/HDPE/SEBS blends with HDPE content. It can be seen that the impact strength of the blend increases slowly with HDPE content up to 50 wt %; thereafter, it increases sharply with increasing HDPE content. The in-

creasing trend of the impact energy with HDPE content in the HDPE-rich blends is similar to that of tensile elongation, as shown in Figure 4(b). However, the PS-rich blends show only a small increase in impact strength while these blends exhibit a significant higher tensile elongation than pure PS. The low impact strength in the PS-rich blends could be due to the high strain rate associated with the impact test and to the plane-strain condition that exists near the notch of impact specimens. In the tensile test, plane-stress condition prevails, thereby producing higher ductility values.

Morphology

Figure 6(a) shows the SEM micrograph of the cryogenically fractured surface of PS/HDPE/

SEBS 70/20/10 blend. Apparently, there exist numerous HDPE particles dispersed in the PS matrix. As the HDPE content in the blend is increased to 40%, the SEM micrograph reveals the presence of cocontinuous or interlocking structure [Fig. 6(b)]. Such a structure is commonly observed in the PS/PE blends containing higher PE contents.²² Increasing the HDPE content to 60% and above also results in the formation of interlock morphology with HDPE as the continuous phase [Fig. 6(c,d)]. For the HDPE-rich blend (PS/HDPE/SEBS 10/80/10), brittle PS particles of about $0.4 \mu\text{m}$ are interlocked in the HDPE matrix. It is well known that the morphology of injection-molded specimens, particularly the polymer composites, consists of skin, intermediate, and core structure. The skin layer of the injection-

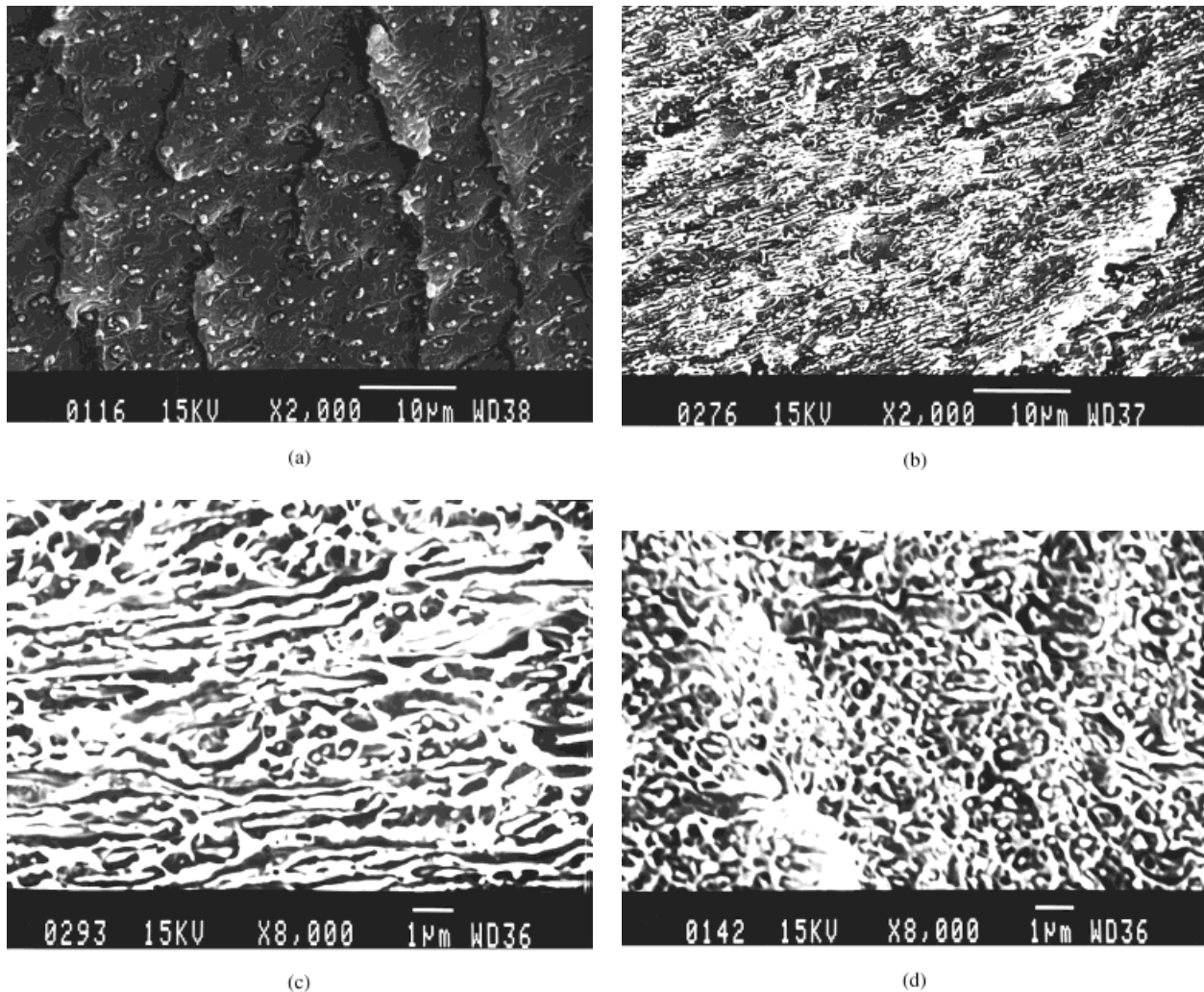


Figure 6 SEM micrographs showing the cryogenically fractured surface of (a) PS/HDPE/SEBS 70/20/20 blend; (b) PS/HDPE/SEBS 50/40/10 blend; (c) PS/HDPE/SEBS 30/60/10 blend; and (d) PS/HDPE/SEBS 10/80/10 blend.

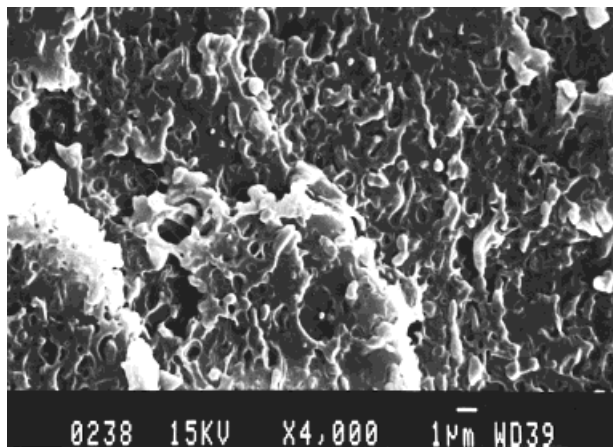
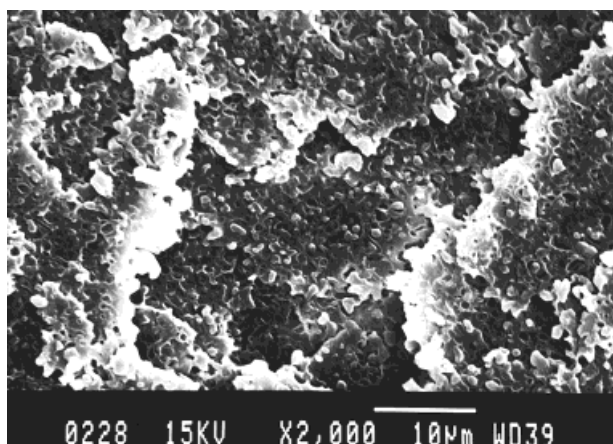


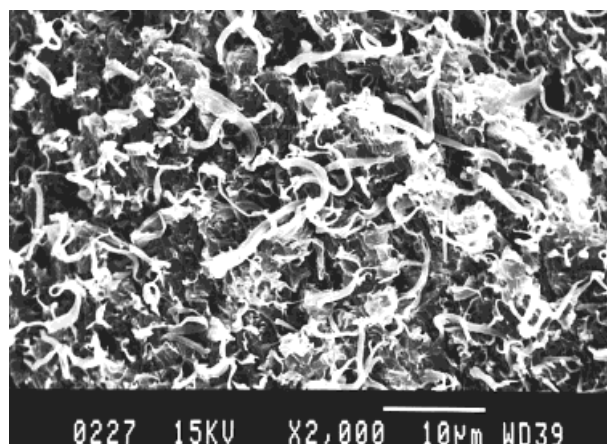
Figure 7 SEM fractograph of PS/HDPE/SEBS 80/10/10 blend after tensile test.

molded blends investigated is very thin, and no changes exist in the morphology of the blends from the intermediate to the core sections. The SEM micrographs were taken from the intermediate parts of the blends investigated.

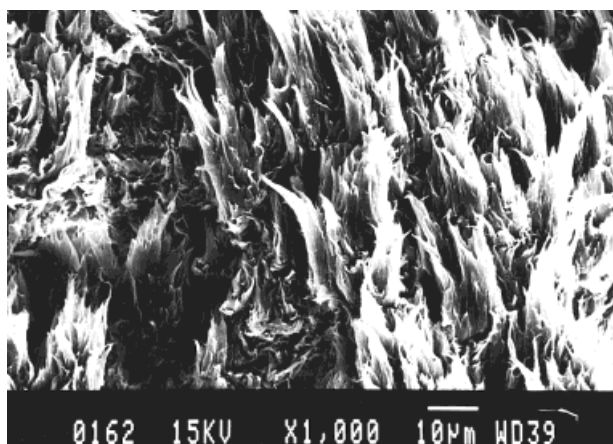
Figure 7 shows the SEM fractograph of PS/HDPE/SEBS 80/10/10 blend after tensile test. The fracture surface appears rougher after tensile tests, indicating that plastic deformation has taken place. Moreover, the HDPE particles are adhered strongly to the matrix. It is likely that the dispersed HDPE particles act as stress concentrators during the tensile process, thereby initiating crazes in the PS matrix. As the HDPE content is increased to 20 wt %, the SEM fractograph also shows a similar surface morphology [Fig. 8(a)]. However, other areas of the same specimen reveal the presence of a fibrillar struc-



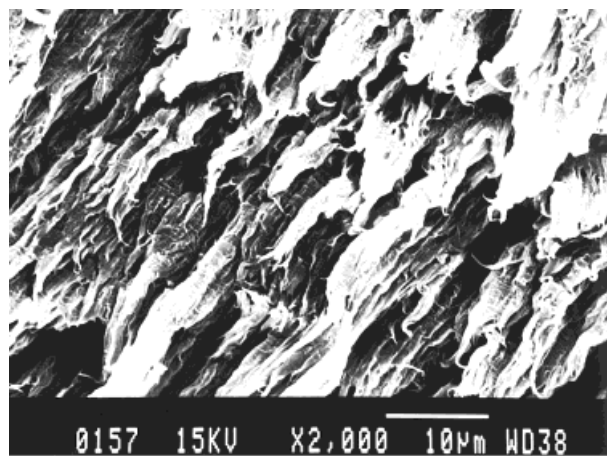
(a)



(b)



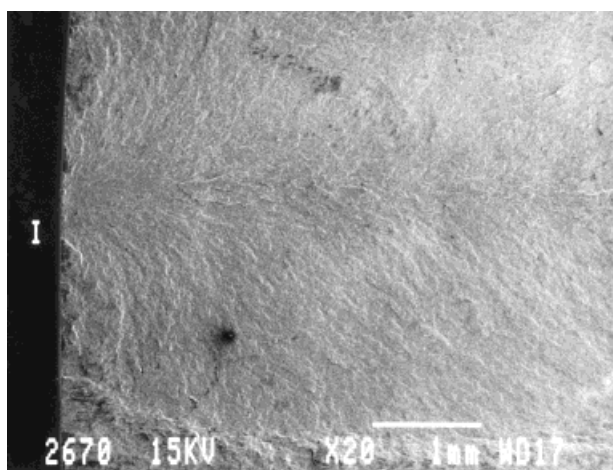
(c)



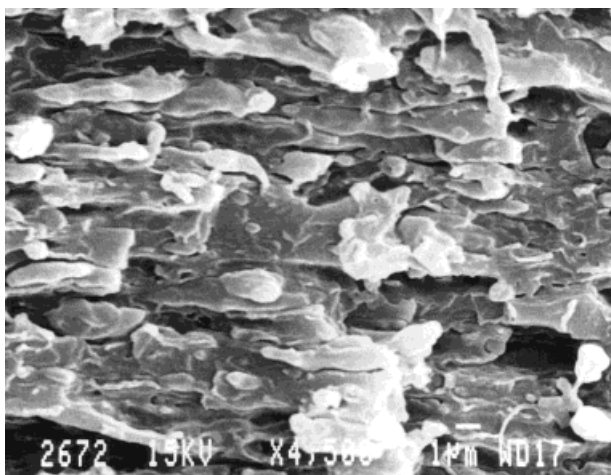
(d)

Figure 8 SEM micrographs showing the tensile fractured surfaces of (a) PS/HDPE/SEBS 70/20/10 blend; (b) another region of the same PS/HDPE/SEBS 70/20/10 blend specimen; (c) PS/HDPE/SEBS 40/50/10 blend; and (d) PS/HDPE/SEBS 20/70/10 blend.

ture [Fig. 8(b)]. This implies that both crazing and shearing occur during tensile deformation of the PS/HDPE/SEBS 70/20/10 blend. Further increasing HDPE content to 50% and above results in extensive fibrillation of the matrix phase, indicating that shear deformation has taken place during tensile tests [Fig. 8(c,d)]. As shear deformation dissipates a large amount of energy, the elongation at break of the PS/HDPE/SEBS blends begins to rise sharply when the HDPE content reaches 50%. Xu and associates have studied *in situ* tensile deformation of PS/LDPE/SEBS systems in a transmission electron microscope (TEM) equipped with a stretcher.^{22,23} They reported that crazing of the PS matrix is the main toughening mechanism for the PS-rich blends,

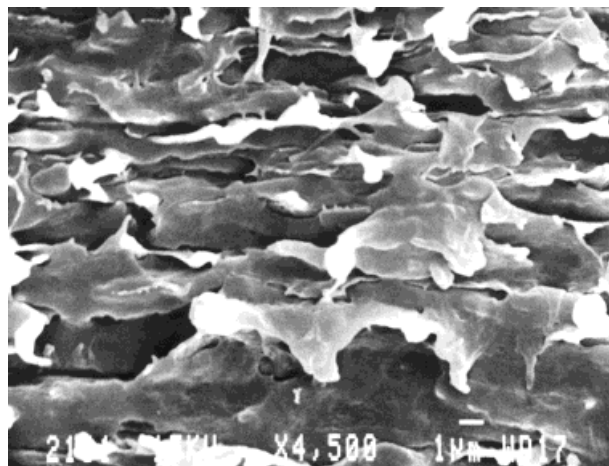


(a)

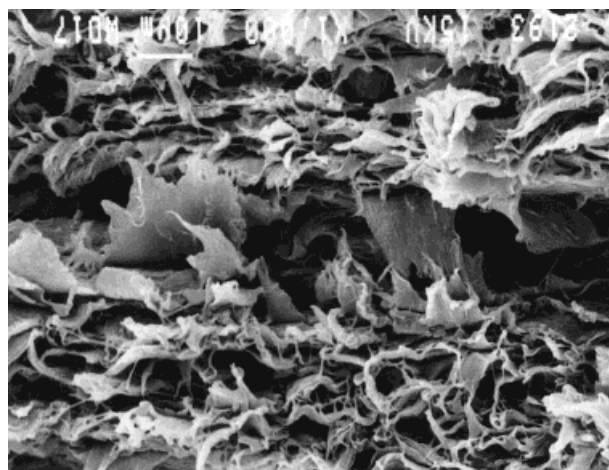


(b)

Figure 9 (a) Low-magnification fractograph of the PS/HDPE/SEBS 70/20/10 blend after impact test. I denotes the notch. (b) A higher magnification of the slow crack-growth zone next to the notch.



(a)



(b)

Figure 10 SEM micrographs showing the fracture-surface features of the slow crack-growth zone of the blends containing (a) 40 wt % HDPE and (b) 60 wt % HDPE blends after impact test.

whereas shear yielding of the matrix is the main deformation mode for the HDPE-rich blends. The SEM fractography of the PS/HDPE/SEBS blends in the present work is consistent with their TEM observations.

Figure 9(a) shows a low-magnification SEM fractograph of the PS/HDPE/SEBS 70/20/10 blend after impact test. A higher magnification of the slow crack-growth region next to the notch is shown in Figure 9(b). Apparently, this micrograph shows the absence of fibrillated structure in the slow crack-growth region. However, the tensile fractured surface of the same specimen as shown in Figure 8(b) reveals the presence of fibrils. This indicates that little plastic deformation has taken place in the slow crack-growth zone of this specimen during impact test. Therefore, the

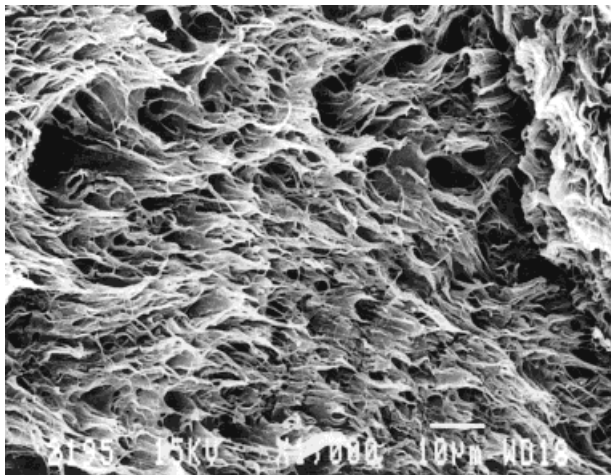


Figure 11 SEM micrograph showing the fracture surface feature of the slow crack-growth zone of the PS/HDPE/SEBS 10/80/10 blend after impact test.

impact strength of the PS/HDPE/SEBS 70/20/10 blend is relatively low. As the HDPE content is increased to 40 wt %, it is evident that drawing of the cocontinuous structure begins to occur [Fig. 10(a)]. In this respect, the impact strength appears to increase slightly. With further increase of the HDPE content to 60 wt %, drawing of the cocontinuous phase becomes more apparent [Fig. 10(b)]. Figure 11 shows the SEM fractograph of the slow crack-growth zone of the HDPE-rich blend containing 80 wt % HDPE. It can be seen that extensive fibrillation of the HDPE matrix occurs in the slow crack-growth zone. Moreover, a few small cavities (having a size of about 1–5 μm) can also be discerned in the fractograph. Such cavitation originates from debonding of the SEBS-encapsulated PS particles from the HDPE matrix during impact deformation. As the size of dispersed PS particles is $\sim 0.4 \mu\text{m}$, the larger voids observed in this fractograph can be related to the coalescence of individual voids initiated by the dispersed PS particles. Furthermore, ductile tearing of the ligaments between particles can lead to the formation of fibrils once the voids are initiated. As shear yielding of the ligaments between particles dissipates a large amount of the energy, the PS/HDPE/SEBS 10/80/10 blend exhibits excellent impact toughness. This phenomenon is analogous to the shear yielding of thermoplastic matrix induced by fine rubber particles during impact deformation.^{30–32}

CONCLUSIONS

Blends of PS/HDPE compatibilized with SEBS copolymer were injection-molded. The tensile and

impact properties of SEBS-compatibilized PS/HDPE blends were investigated. Tensile tests showed that the yield stress of the PS/HDPE/SEBS decreases substantially with increasing HDPE content but the elongation at break appeared to increase dramatically with increasing HDPE content. The improvement in tensile ductility in the PS-rich blends was caused by the crazing of the PS matrix whereas the increase in elongation in the HDPE-rich blends resulted from the shear yielding of the HDPE matrix. SEM observations revealed that SEBS addition leads to a finer dispersion of either PS or HDPE particles, and to a stronger adhesion between these two phases. Charpy impact measurements indicated that the impact strength of the blends increases slowly with HDPE content up to 50 wt %, followed by a significant increase with increasing HDPE content. The impact strength of the HDPE-rich blends exceeded that of the HDPE polymer. This implies that ductile HDPE can be further toughened by the incorporation of a minor PS phase in the presence of SEBS copolymer. Such behavior can be related to extensive fibrillation of the HDPE matrix associated with debonding of the PS particles from the matrix.

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