Compatibilization of High-Impact Polystyrene/High-Density Polyethylene Blends by Styrene/Ethylene–Butylene/Styrene Block Copolymer

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ABSTRACT: Compatibilization of polymer blends of high-impact polystyrene (HIPS) and high-density polyethylene (HDPE) blend by styrene/ethylene–butylene/styrene (SEBS) was elucidated. Polymer blends containing many ratios of HIPS and HDPE with various concentrations of SEBS were prepared. The Izod impact strength and elongation at break of the blends increased with increases in SEBS content. They increased markedly when the HDPE content was higher than 50 wt %. Tensile strength of blends increased when the SEBS concentration was not higher than 5 pphr. Whenever the SEBS loading was higher than 5 pphr, the tensile strength decreased and a greater decrease was found in blends in which the HDPE concentration was more than 50 wt %. The log additivity rule model was applied to these blends, which showed that the blends containing the HIPS-rich phase gave higher compatibility at the higher shear rates. Surprisingly, the blends containing the HDPE-rich phase yielded greater compatibility at the lower shear rates. Morphology observations of the blends indicated better compatibility of the blends with increasing SEBS concentration. The relaxation time (T_2) values from the pulsed NMR measurements revealed that both polymer blends became more compatible when the SEBS concentration was increased. When integrating all the investigations of compatibility compared with the mechanical properties, it is possible to conclude that SEBS promotes a certain level of compatibilization for several ratios of HIPS/HDPE blends. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 742–755, 2004

Key words: compatibilization; high-density polyethylene/high-impact polystyrene (HDPE/HIPS); block copolymers; interfaces; phase separation

INTRODUCTION

Polymer blends have gained increasing popularity in the field of polymer science and in industry during the past few decades. The blending of polymers provides an efficient way of developing new materials with tailored properties, which is often a faster and more cost-effective means of achieving a desired set of properties than synthesizing new polymers. However, most polymer blends are immiscible or incompatible at the molecular level because the combinatorial entropy of mixing two polymers is drastically smaller than that of low molecular weight mixtures, whereas the enthalpy of mixing is often positive or near zero.[1] The incompatibility of polymeric blends is responsible for poor mechanical properties because of a lack of physical and chemical interactions across the phase boundaries and poor interfacial adhesion. Therefore, compatibilization is demanded to obtain a blend with desired properties. A common way to improve the compatibility and interfacial adhesion of polymer blends is to add a compatibilizer or interfacial agent.[2] The compatibilizer may be a homopolymer or suitable block or graft copolymer. It is well known that a block copolymer is an efficient compatibilizer for immiscible polymer blends. Here each block of a diblock or triblock copolymer is usually either miscible, or has strong affinity, with one of the two homopolymer phases.[3]

Compatibilization of polystyrene and polyethylene blends has been the subject of considerable research and development in recent decades. When polystyrene is blended with polyethylene, to combine the toughness and solvent resistance of polyethylene with the high modulus and thermoformability of polystyrene, however, the blending is complicated by the incompatibility of these two polymers.[4]

For this study, a styrene/ethylene–butylene/styrene (SEBS) triblock copolymer was used as a compatibilizer of high-impact polystyrene (HIPS) and

high-density polyethylene (HDPE) blends at many blend ratios and various compatibilizer concentrations. The compatibilization effect is then elucidated through several instrumentation techniques.

EXPERIMENTAL

Materials

The materials used in this study were of commercial grade. The high-impact polystyrene (HIPS) Porene HI650 (MFI$_{5, 473 K}$ = 8.0 g/10 min) had 7.0–8.0% polybutadiene content (particle size between 3 and 4 μm) and was supplied by the Thai Petrochemical Industry Public Co. (Rayong, Thailand). The commercial injection grade high-density polyethylene (HPDE) Polene R1760 (MFI$_{2.16, 463 K}$ = 9.0 g/10 min) was supplied by Thai Petrochemical Industry Public Company. The compatibilizer used in this study was a styrene/ethylene–butylene/styrene triblock copolymer (SEBS), Kraton G1652 (MFI$_{5, 473 K}$ = 1.0 g/10 min; M_w values of the EB and the PS blocks were 35,000 and 7500, respectively) from Shell Chemicals (Houston, TX). The compatibilizer contained 70 wt % ethylene–butylene random copolymer and 30 wt % of styrene.

Blend preparation

All blends were prepared in a counter-rotating intermeshing twin-screw Brabender extruder model 42/7 (D = 42 mm, L/D = 7) attached to a Brabender Plasti-Corder, PL2000, with a rotational speed of 40 rpm. All materials were dry mixed in a mechanical mixer for 10 min. The mixed materials were then introduced into a hopper of the twin-screw extruder, with the controlled temperature of 473 K at all heating zones and the die zone. Long-strand extrudates were chopped into granules using the pelletizer and subsequently dried at 343 K for 6 h. Weight ratios of HIPS and HDPE were 90/10, 70/30, 50/50, 30/70, and 10/90. The compatibilizer concentrations used were 5, 10, 15, and 20 pphr for each HIPS/HDPE weight ratio.

Rheological properties

An RH7 Rosand single-bore capillary rheometer was used to characterize shear flow properties in terms of shear stress and shear viscosity. The tests were carried out at a wide range of shear rates (20 to 9000 s^{-1}) at a test temperature of 473 K. Dimensions of the capillary die used were 1 mm in diameter, 16 mm in length, and 180° entry angle with an aspect ratio (L/D) of 16 : 1. The material was first preheated in a barrel for 5 min under a pressure of about 3–5 MPa to obtain a compact mass. The excess material was then automatically purged until no bubbles were observed. The test was then carried out at a set of shear rates programmed by a microprocessor. During the test, the pressure drop across the capillary channel, and melt temperature were captured by a data-acquisition system. The apparent values of wall shear stress (τ, Pa), wall shear rate ($\dot{\gamma}_{app}$, s^{-1}), and shear viscosity (η_s, Pa s), respectively, were calculated using the derivation of the Poiseuille law for capillary flow[5–8]:

$$\tau = \frac{R\Delta P}{2L} \qquad (1)$$

$$\dot{\gamma}_{app} = \frac{4Q}{\pi R^3} \qquad (2)$$

$$\eta_s = \frac{\tau}{\dot{\gamma}_{app}} \qquad (3)$$

where ΔP is a pressure drop across the channel (Pa), Q is the volumetric flow rate (m^3 s^{-1}), R is the capillary radius (m), and L is the length of the capillary (m). The values of R and L used in this work were 1 and 16 mm, respectively.

Furthermore, the log additivity rule model was used to validate thermodynamic compatibility of the polymer blend for deviations of the blend viscosity from the ideal behavior[5–8] according to the following equation:

$$\log(\eta_{blend}) = \sum_i x_i \log(\eta_i) \qquad (4)$$

where η_{blend} and η_i are the shear viscosity of the blend and phase i, respectively; and x_i is the weight fraction of phase i.

Morphological observation of the fracture surface

The SEM samples for morphology studies were taken directly from the broken pieces after the impact test. HIPS and SEBS were etched off from the sample surfaces with toluene to better reveal the overall microstructure. Etching was performed at room temperature for 2 h, after which the surfaces were rinsed and dried at 343 K for 6 h. The sample was immersed in 2% OsO$_4$ aqueous solution for staining the unsaturated components at room temperature for 12 h. After removal from the staining solution, the samples were carefully washed with water to remove the unreacted osmium tetroxide, and then the dried samples were coated with gold to prevent charging before they were examined under SEM observation (JSM-5800LV JEOL scanning electron microscope, Tokyo, Japan).

Thermal properties

The melting and glass-transition temperatures of the blend were studied using a DSC200 differential scan-

ning calorimeter (Netzsch, Germany) under a nitrogen atmosphere with heating and cooling rates of 10 K min^{-1}. The temperature cycle consisted of an initial heating from 303 to 473 K, followed by cooling to 303 K and a second heating to 473 K. Data were collected during the second heating.

Relaxation time by pulsed NMR

The phase separation or compatibility of the polymer blends can be observed by the ^{1}H-pulsed NMR technique. The ^{1}H-pulsed NMR equipment used was a Bruker PC-20 (resonance frequency of protons at 20 MHz; Bruker Instruments, Billerica, MA). Measurements were carried out under the control of a microcomputer. The PC-20 operates by beaming one or more radio-frequency (RF) pulses into a sample, examining the resulting NMR signals from protons in the sample, and extracting certain data from that signal to calculate the quantity of interest. The spin–spin relaxation time (T_2) measurement is made by both the solid-echo ($90°_x \tau 90°_y$) and the spin–echo [Carr–Purcell–Meiboom–Gill (CPMG)] method [$90°_x \tau (180°_y 2 \tau)_n$]. The T_2 was measured in this experiment at room temperature, and the related signal intensities were analyzed.

Mechanical properties

The measurement of tensile properties of the dumbbell-shape samples was carried out with an LR10K Lloyd universal testing machine (Hampshire, UK), using the ASTM D638 procedure. Notched Izod impact strength was measured using the ASTM D256 procedure and Pendulum impact testing machine 258D (State College, PA). At least five specimens were tested for each analysis at room temperature, and the average value was calculated and reported.

RESULTS AND DISCUSSION

Rheological properties of HIPS/HDPE blends

The compatibilization effect can be observed through the viscosity of the pure polymers, the blended polymers, and the triblock copolymer. We found that the viscosity of all the blends without the triblock compatibilizer decreased with increases in shear rate [Fig. 1(a)–(g)], indicating the pseudoplastic (shear-thinning) behavior of the blends. The pseudoplasticity is caused by the random orientation and high degree of entanglement of the molecules. Under a high shear rate, the molecules became disentangled and oriented, resulting in a reduction of viscosity. In polymer blends, the viscosity depends on the interfacial thickness and interfacial adhesion in addition to the characteristics of the components in the polymer.

The effects of SEBS block copolymer loading (5, 10, 15, and 20 pphr) and shear rate on the melt viscosity of HIPS/HDPE blends of each ratio (90/10, 70/30, 50/50, 30/70, and 10/90) are shown in Figure 1(b)–(f), respectively. In the compatibilized blends, all the blend compositions gave pseudoplastic flow under various shear rates. In polymer blends, an interlayer slip along with orientation and disentanglement occurs when increasing the shear rate or shear stress. The blend undergoes further elongational flow. If the interfacial bonding is strong, deformation of the dispersed phase is effectively transferred to the continuous phase. The shear viscosity of the compatibilized blends is higher than that of the noncompatibilized blends. The lower shear viscosity of the noncompatibilized blends could be caused by the weak interfacial adhesion. When the interfacial bonding is weak, the interlayer slip occurs easily to reduce the blend viscosity. The greater decrease in viscosity at the higher shear rate in the noncompatibilized blends occurs because the dispersed phase of the incompatible blend (either HIPS or HDPE) loses its structure in the solid phase to become a liquidlike phase.

The compatibilizer concentration effect may be observed from Figure 1(a)–(f) at the high temperature of mixing at 473 K. The shear viscosity of compatibilized HIPS/HDPE blends increases when increasing the amount of SEBS in the blends. This is probably because of a coupling effect of the triblock copolymer when loading the SEBS into the blends. A high temperature of mixing promotes better interfacial adhesion between the HIPS and HDPE phases as the polystyrene and poly(ethylene-*b*-butylene) blocks in SEBS preferentially penetrate into the HIPS and HDPE phases, respectively. In addition, the SEBS block copolymer has a higher viscosity than that of either HIPS or HDPE at 473 K at all shear rates, as shown in Figure 1(a). The higher viscosity of the polystyrene block and poly(ethylene-*b*-butylene) block contributes to the higher viscosity of the blends.

The indication of a strong or weak interaction between phases of the blends can be determined by a positive or negative deviation of the measured viscosity, calculated by the log additivity rule model for validation of the interfacial interaction.

The HIPS/HDPE blend ratios from 90/10 to 30/70 in relation to the log additivity rule model are shown in Table I. Figure 2(a) (90/10 of HIPS/HDPE) shows slight negative deviation behavior (NDB) at low shear rates, and a positive deviation behavior (PDB) at high shear rates (7500 s^{-1}). This indicates incompatibility at low shear rates, and more compatibility at the higher shear rates. In contrast, the 10/90 HIPS/HDPE blend ratio [Fig. 2(b)] gives a PDB at low shear rates, with a very small amount of NDB at very high shear rates (7500 s^{-1}). This 10/90-blend ratio provides high compatibility at low shear rates and relatively good com-
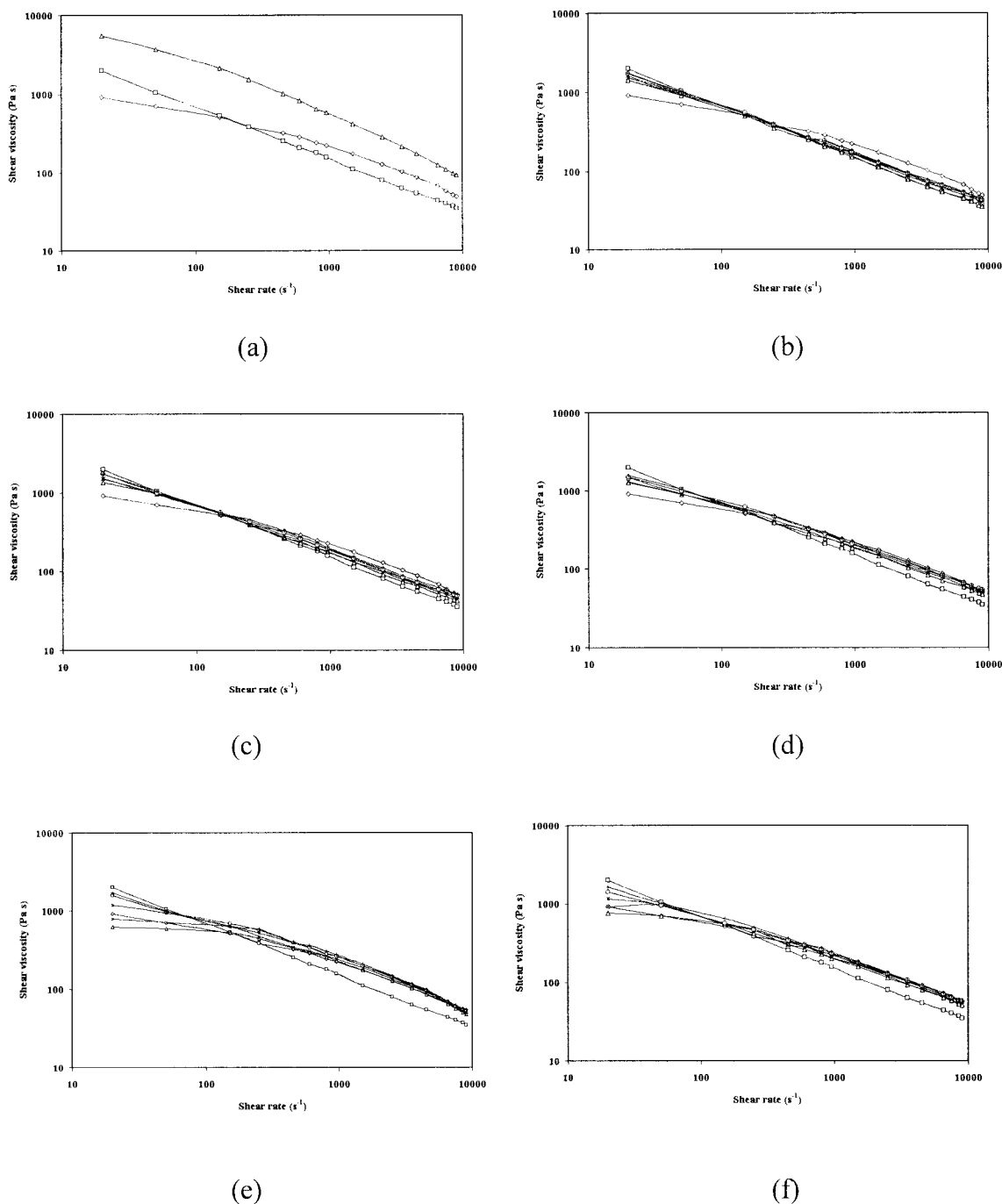
Figure 1 Flow curve of pure component (a) and HIPS/HDPE blends with various SEBS concentrations. HIPS : HDPE: (b) 90 : 10; (c) 70 : 30; (d) 50 : 50; (e) 30 : 70; (f) 10 : 90 (◇, pure HDPE; □, pure HIPS; △, 0 pphr SEBS; ×, 5 pphr SEBS; *, 10 pphr SEBS; ○, 15 pphr SEBS; +, 20 pphr SEBS).

patibility at high shear rates. In addition, the compatibility of other blend ratios of HIPS/HDPE (70/30, 50/50, and 30/70) also improves gradually through the addition of SEBS polymer. At blend ratios greater than 50/50 (HIPS/HDPE), the blend is compatible at all shear rates. This may give some indication that the overall morphological dispersion of the small component of HIPS functions as a disperse phase in the

HDPE matrix phase for HIPS/HDPE (10/90) blend. We anticipate that the 10/90 ratio of HIPS/HDPE has a morphology different from that of other blends. In Figure 1(a), the shear viscosity of HDPE at low shear rate is lower than that of HIPS because of the rigidity of the latter. At the high shear rate, the shear viscosity of HIPS becomes lower than that of HDPE because of the breakdown of the rigid structure of the former. In

TABLE I
Shear Viscosity of HIPS/HDPE Blends Compatibilized with SEBS from Experimental Data
Versus Log Additivity Rule Model

HIPS/HDPE	Shear rate (s^{-1})	SEBS (pphr)									
		0		5		10		15		20	
		Log η blend	Log η add	Log η blend	Log η add	Log η blend	Log η add	Log η blend	Log η add	Log η blend	Log η add
90/10	150	2.7	2.73	2.71	2.76	2.74	2.79	2.75	2.81	2.73	2.83
	600	2.31	2.34	2.34	2.37	2.37	2.39	2.39	2.41	2.39	2.44
	1500	2.05	2.07	2.09	2.1	2.11	2.12	2.12	2.14	2.13	2.16
	4500	1.74	1.76	1.79	1.78	1.80	1.81	1.83	1.82	1.84	1.84
	7500	1.62	1.63	1.67	1.65	1.69	1.67	1.70	1.68	1.71	1.70
70/30	150	2.73	2.73	2.73	2.76	2.74	2.78	2.74	2.81	2.75	2.83
	600	2.36	2.37	2.38	2.39	2.40	2.42	2.41	2.44	2.43	2.46
	1500	2.12	2.11	2.12	2.13	2.15	2.16	2.17	2.18	2.18	2.20
	4500	1.81	1.80	1.83	1.82	1.84	1.84	1.85	1.86	1.88	1.88
	7500	1.67	1.66	1.71	1.68	1.73	1.69	1.75	1.71	1.76	1.72
50/50	150	2.73	2.72	2.75	2.75	2.77	2.78	2.80	2.80	2.77	2.82
	600	2.40	2.39	2.41	2.42	2.45	2.44	2.46	2.46	2.47	2.48
	1500	2.17	2.15	2.17	2.17	2.20	2.19	2.22	2.21	2.22	2.23
	4500	1.85	1.84	1.89	1.86	1.91	1.88	1.92	1.89	1.92	1.91
	7500	1.72	1.69	1.75	1.71	1.77	1.72	1.78	1.74	1.78	1.75
30/70	150	2.74	2.72	2.74	2.75	2.75	2.77	2.76	2.80	2.82	2.82
	600	2.42	2.42	2.45	2.44	2.47	2.46	2.48	2.48	2.49	2.50
	1500	2.20	2.19	2.22	2.21	2.23	2.23	2.26	2.24	2.27	2.26
	4500	1.91	1.88	1.92	1.90	1.94	1.91	1.96	1.93	1.97	1.94
	7500	1.77	1.72	1.78	1.74	1.80	1.75	1.82	1.76	1.83	1.78
10/90	150	2.72	2.71	2.80	2.74	2.82	2.77	2.84	2.79	2.81	2.82
	600	2.48	2.44	2.49	2.47	2.54	2.49	2.53	2.51	2.56	2.52
	1500	2.25	2.23	2.28	2.24	2.30	2.26	2.30	2.28	2.32	2.29
	4500	1.94	1.92	1.96	1.93	1.98	1.95	1.99	1.96	2.00	1.97
	7500	1.75	1.75	1.77	1.77	1.78	1.78	1.78	1.79	1.80	1.80

the compatibilized blends, the compatibility is generally considered in terms of the viscosity ratio of the blends. If the minor component has a lower viscosity than that of the major component, the minor component will then be finely and uniformly dispersed in the major component. Conversely, the minor component will be coarsely dispersed if its viscosity is higher than that of the major component.[9] In the case of the HIPS matrix phase and HDPE dispersed phase, the higher shear rate is required to impose the HDPE dispersed phase to give the lower viscosity. The HDPE can thus become finely and uniformly dispersed into the HIPS matrix. Through this behavior, HDPE can be compatible with HIPS matrix. Likewise, the HDPE matrix
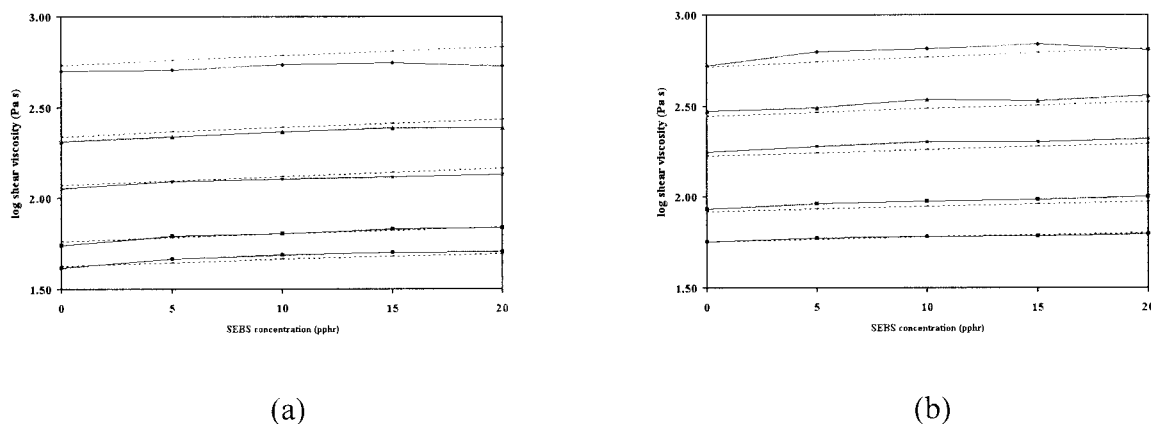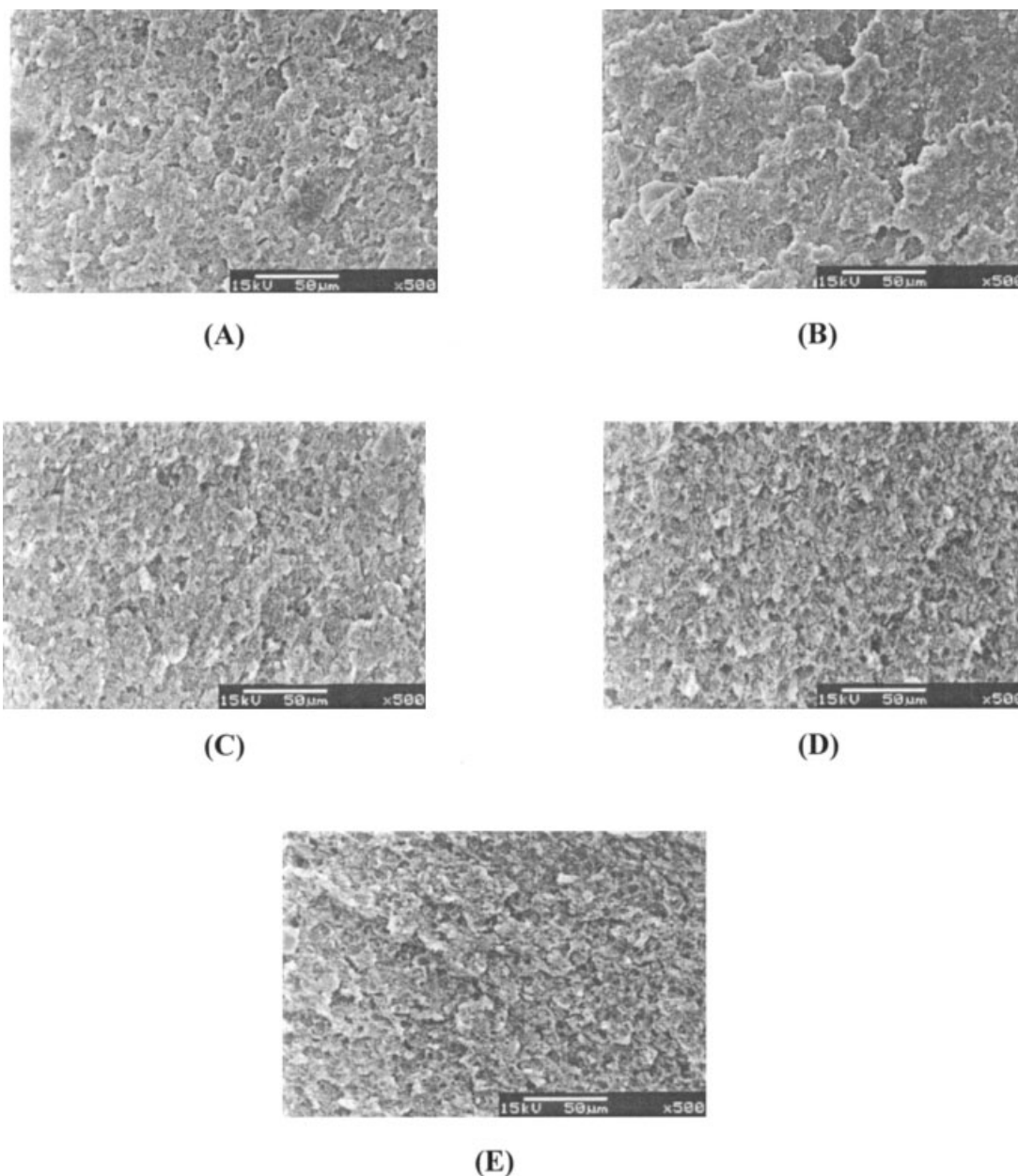
Figure 2 Variation of viscosity with SEBS concentration in HIPS/HDPE blends at various shear rates: (a) HIPS : HDPE = 90 : 10; (b) HIPS : HDPE = 10 : 90 (—, experimental values; - - -, additives values; ♦, 150 s^{-1}; ▲, 600 s^{-1}; *, 1500 s^{-1}; ■, 4500 s^{-1}; ●, 7500 s^{-1}).
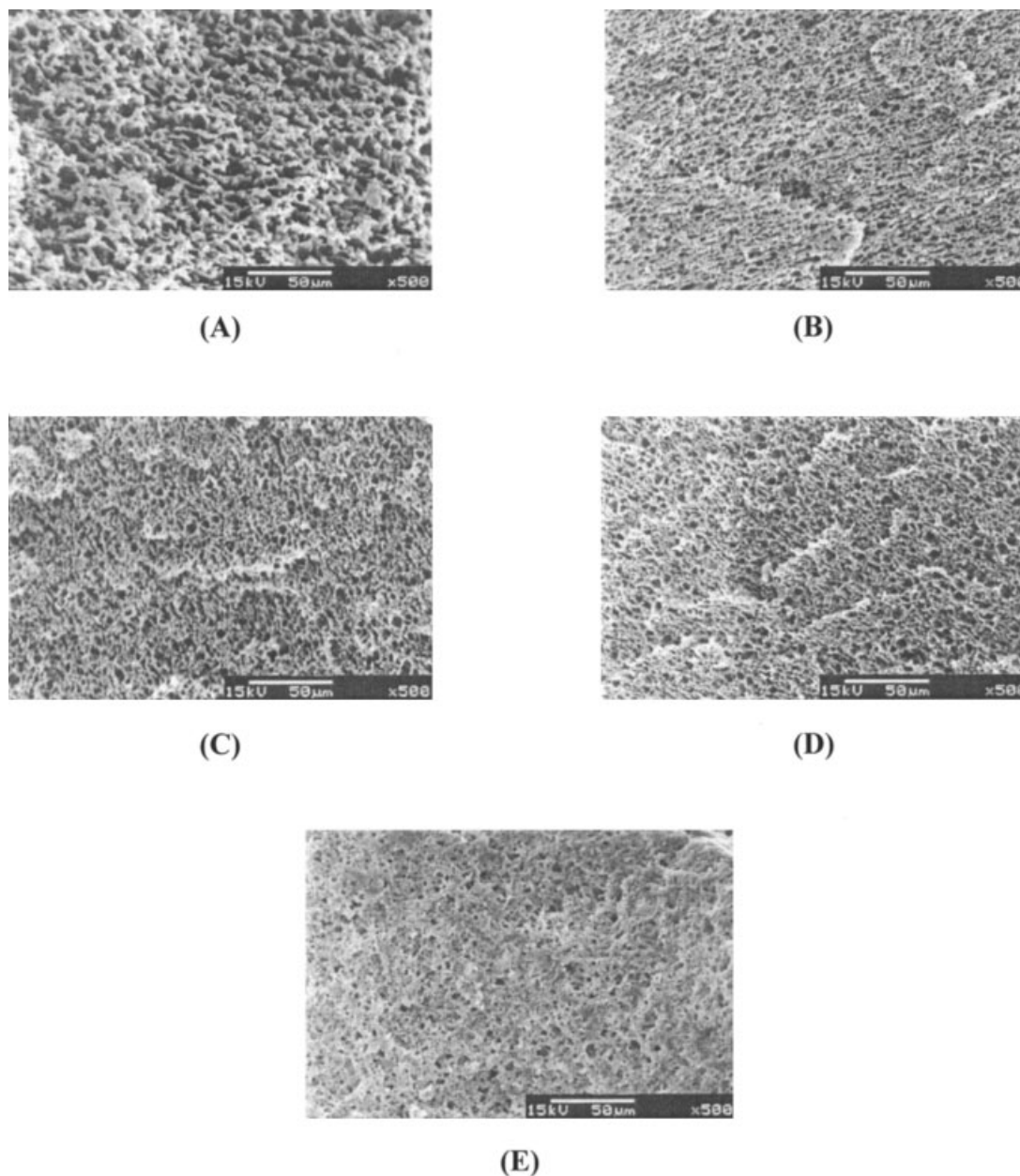
Figure 3 Scanning electron micrographs showing unetched impact fracture surfaces of HIPS/HDPE (90/10) blends compatibilized with SEBS: (A) without SEBS; (B) 5 pphr; (C) 10 pphr; (D) 15 pphr; (E) 20 pphr.

phase and HIPS dispersed phase can be compatible by the same technique. When incorporating the SEBS triblock compatibilizer, a high shear rate is required because it has a much higher viscosity than that of either HIPS or HDPE. It is possible to state that the melt flow index (MFI) of the SEBS is higher than that of HIPS and HDPE because of its content of both ethylene–butylene copolymer and PS.

Morphological observation of HIPS/HDPE blends

The morphology of noncompatibilized and compatibilized blends of HIPS and HDPE (90/10, 70/30, 50/50, 30/70, and 10/90) with SEBS block copolymer as compatibilizer is shown in Figures 3–7, respectively. Because of the inherent incompatibility of HDPE with PS, their blends produce a two-phase material. Generally speaking, it is easier to blend a soft polymer as a dispersed phase into a hard polymer as a matrix phase, and vice versa. The blend weight or volume ratio also plays a predominant role in determining which of the two component forms the dispersed phase and which the matrix phase. The blend volume indicates that, in the HIPS-rich blend, HDPE forms the dispersed phase in the HIPS matrix, and the reverse is true in the HDPE-rich blends. The morphology of the
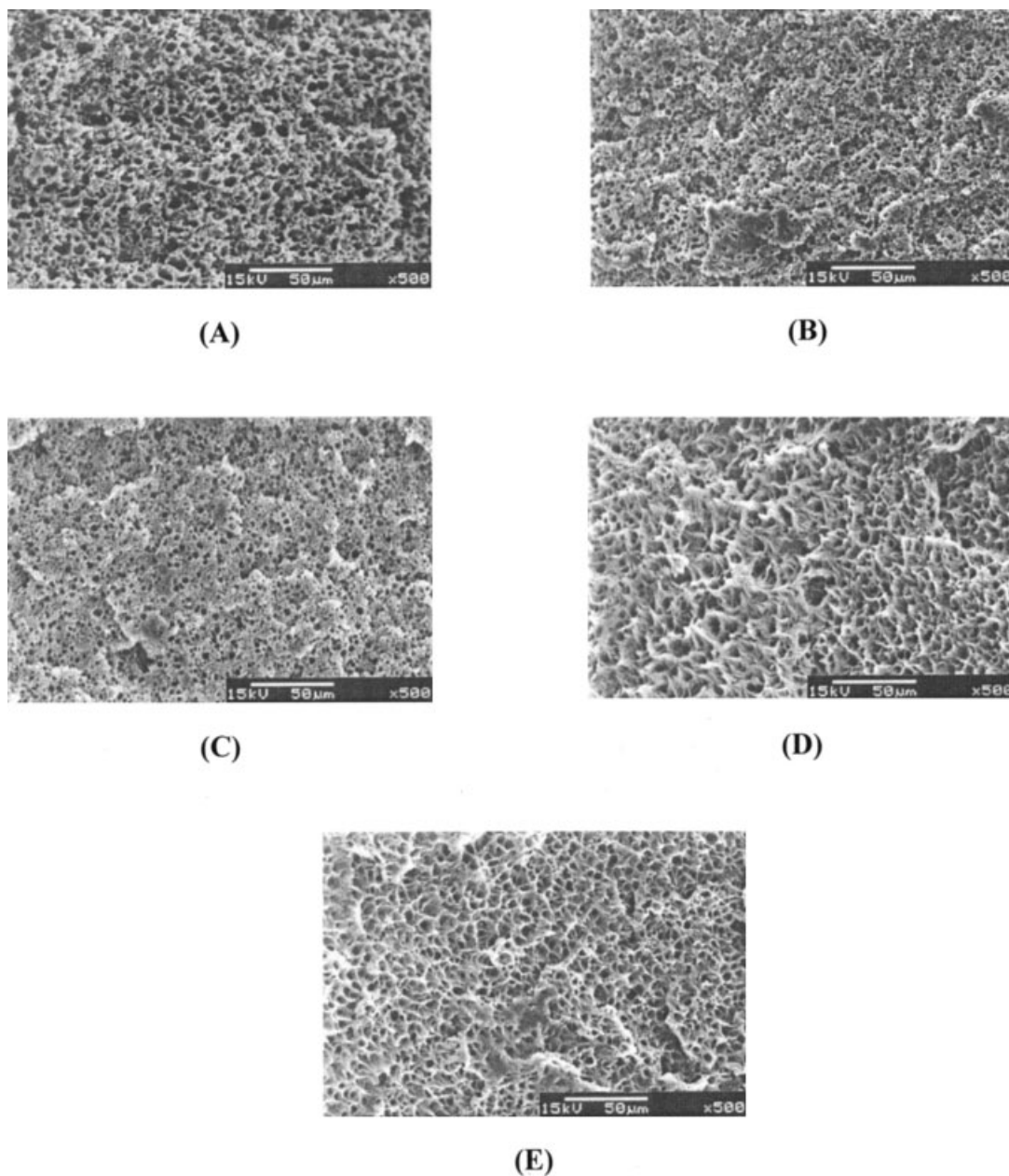
Figure 4 Scanning electron micrographs showing etched impact fracture surfaces of HIPS/HDPE (70/30) blends compatibilized with SEBS: (A) without SEBS; (B) 5 pphr; (C) 10 pphr; (D) 15 pphr; (E) 20 pphr.

noncompatibilized blends [Figs. 3(A)–7(A)] exhibits coarse and heterogeneous dispersion. In Figure 7(A), the major matrix HDPE obstructed the presence of PS domains or extracted holes by toluene.

Regarding the morphology of the 90/10 HIPS/HDPE blend [Fig. 6(A)], the binary blends exhibit coarsely dispersed HDPE domains in the HIPS matrix. Upon the addition of 5, 10, 15, or 20 pphr of SEBS as a compatibilizer, the blend compositions gradually show a finer and more homogeneous dispersion of HDPE particles in the HIPS matrix as shown in Figure 3(B)–(E).

The effect of compatibilizer concentration on blend morphology was further examined in a 70/30 ratio

HIPS/HDPE blend with 0, 5, 10, 15, and 20 pphr of SEBS. Figure 4(A) shows that larger and more coarsely dispersed cavities developed and poor interfacial adhesion between phases could occur, as observed in the toluene-extracted HIPS of the 70/30 HIPS/HDPE blend. A small decrease in the particle size was observed with the incorporation of 5 pphr of the compatibilizer. Dispersions of the HIPS/HDPE blends were much finer when the compatibilizer concentration was increased. Finer dispersion of one phase into another phase was observed because the compatibilizer reduces the interfacial tension in the melt, causing an emulsifying effect in both polymers. Additionally, adhesion between the dispersed and matrix
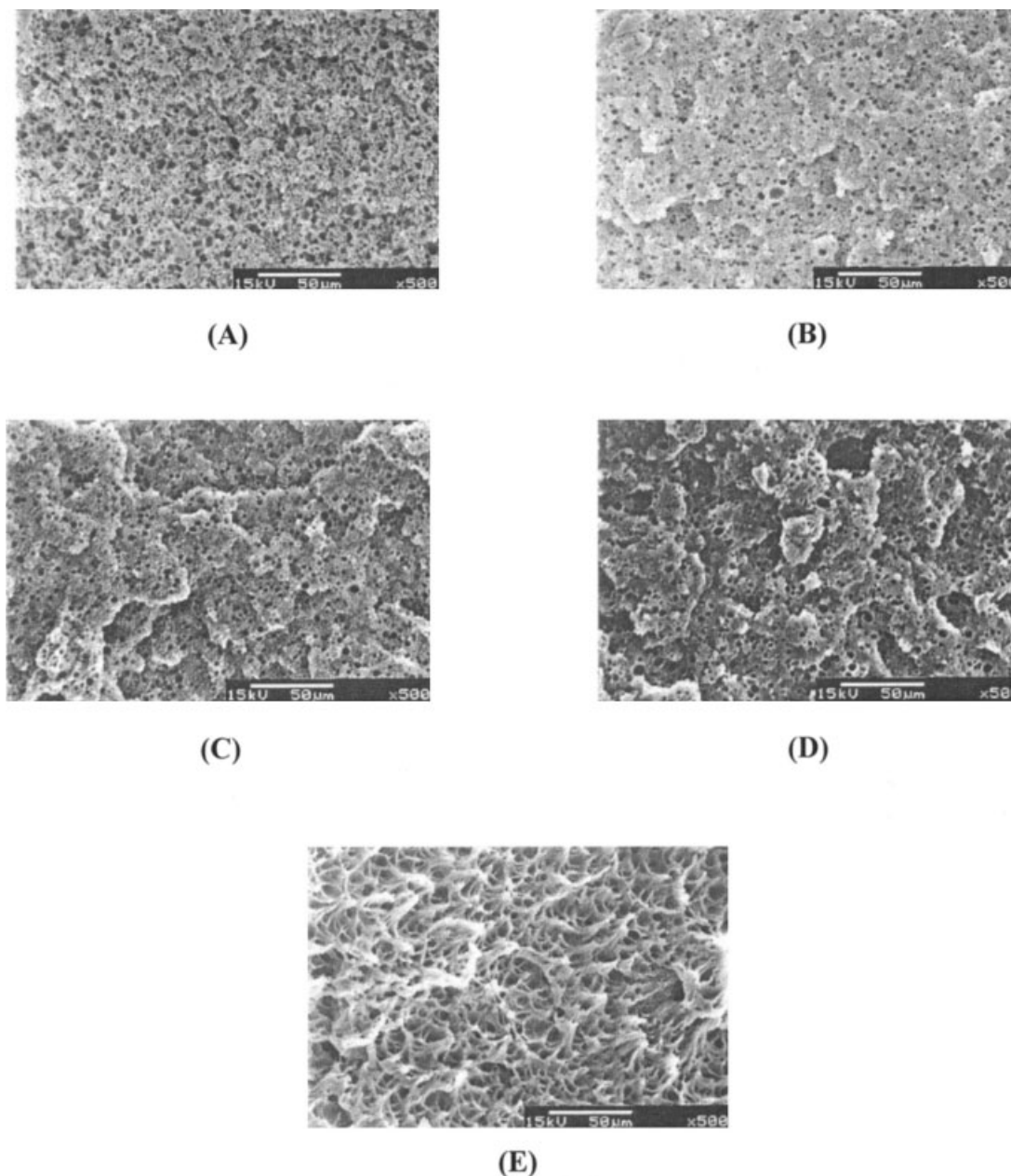
Figure 5 Scanning electron micrographs showing etched impact fracture surfaces of HIPS/HDPE (50/50) blends compatibilized with SEBS: (A) without SEBS; (B) 5 pphr; (C) 10 pphr; (D) 15 pphr; (E) 20 pphr.

phases was markedly better in the 50/50 HIPS/HDPE blends (Fig. 5) with increasing SEBS concentrations. A smaller interfacial area of HIPS particles (Fig. 5) compared with the blend with 30 wt % of HIPS (Fig. 6) is indicated by the small domains of HIPS (minute holes). Finally, it exhibits cocontinuous phase morphology (Fig. 7). The size of the dispersed HIPS particles is drastically reduced upon the addition of more SEBS triblock copolymer. The reduction is clearly observed in the 10/90 HIPS/HDPE blends with the SEBS block copolymer compatibilizer. In all micrographs, when the SEBS content was at 20 pphr, a smaller domain size and more domains were clearly seen. It

can be anticipated that at a higher SEBS concentration, a third domain could exist with greater inclusion of the PS phase and EB phase into the matrix polymer (HIPS or HDPE). We can thus posit the effectiveness of the interfacial activity of SEBS as follows. In compatibilized systems, the main effect of a compatibilizer on particle size of the dispersed domain is to reduce the size of coalescing droplets. These droplets were removed by toluene extraction (for all PS domains: PS in HIPS and in the compatibilizer). Interfacial tension between the dispersed domain and the continuous phase decreases as the concentration of compatibilizer added increases, as is evidenced by Figures 4(E)–7(E).

Figure 6 Scanning electron micrographs showing etched impact fracture surfaces of HIPS/HDPE (30/70) blends compatibilized with SEBS: (A) without SEBS; (B) 5 pphr; (C) 10 pphr; (D) 15 pphr; (E) 20 pphr.

More extractable PS domains are observed that result in widely spreading droplet sizes. Our observation is in agreement with that of Macaúbas and Demarqette,[8] who previously indicated that a decrease in coalescence of the dispersed phase was observed.

Thermal analysis of HIPS/HDPE blends

Table II indicates that calculated T_g values of mixtures of HIPS/HDPE/SEBS by Fox's equation [eq. (5)] were far different from the experimental values:

$$(1/T_g) = (W_A/T_{gA}) + (W_B/T_{gB}) + (W_C/T_{gC}) \quad (5)$$

where T_g is the glass-transition temperature of the blend; T_{gA}, T_{gB}, and T_{gC} are the glass-transition temperatures of polymers A, B, and C, respectively; and W_A, W_B, and W_C are the corresponding weight fractions of polymers A, B, and C in the blend.

The glass-transition temperatures in the experiment were dominated by HIPS; that is, T_g values of the experiment were close to that of HIPS rather than that of HDPE, given that HIPS also contains polybutadiene. Very interestingly, for three blend ratios, the noncompatibilized blends had glass-transition temperatures similar to those of compatibilized blends at all compatibilizer ratios. The compatibilized blends of
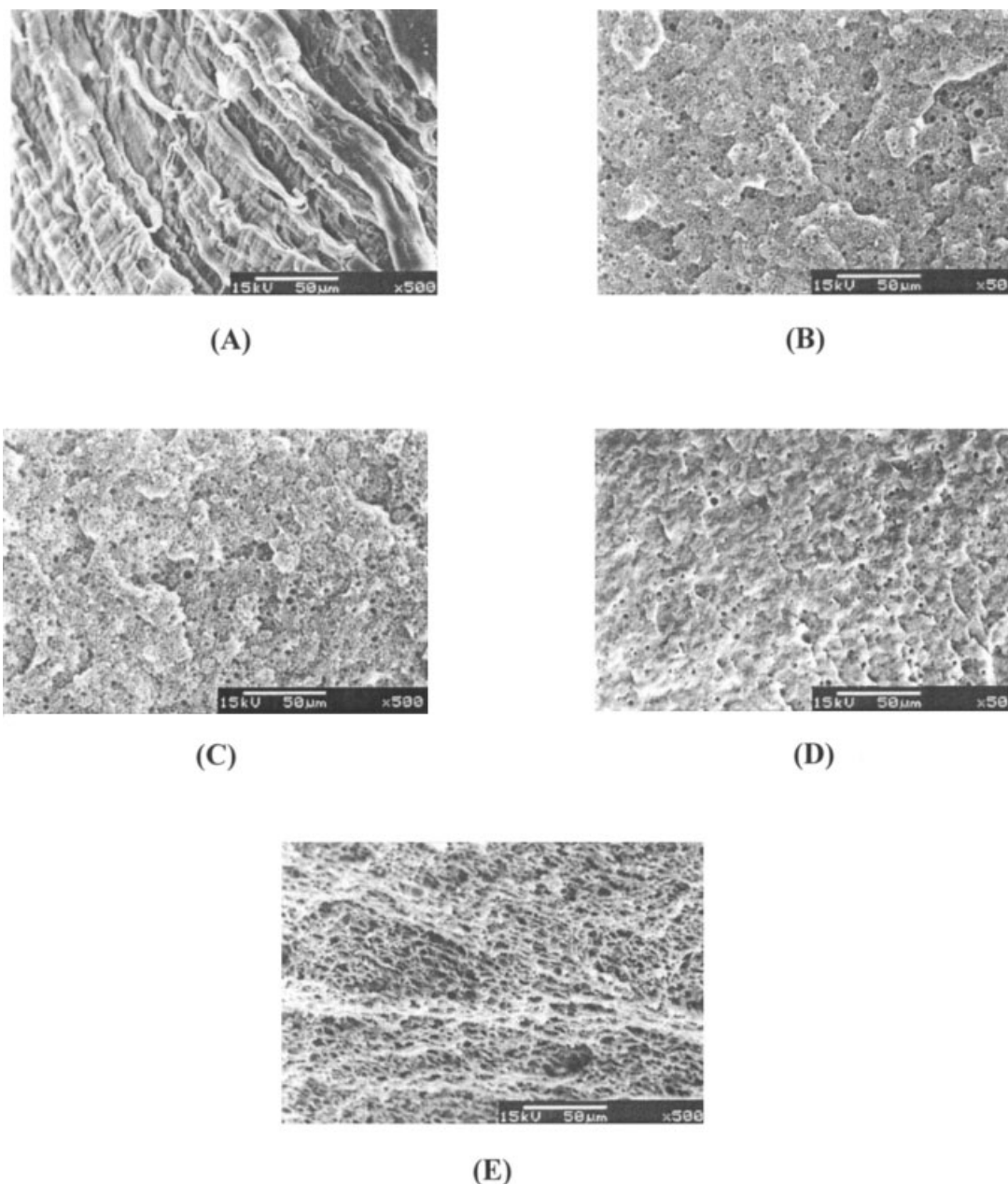
Figure 7 Scanning electron micrographs showing etched impact fracture surfaces of HIPS/HDPE (10/90) blends compatibilized with SEBS: (A) without SEBS; (B) 5 pphr; (C) 10 pphr; (D) 15 pphr; (E) 20 pphr.

HIPS/HDPE blends did not show any appreciable shift in T_g values compared with those of noncompatibilized blends. This indicates that addition of the SEBS increases T_g values of the blends because of the two blocks of PS in the compatibilizer; it slightly alters the level of miscibility. In other words, incorporation of the compatibilizer promotes some extent of molecular level miscibility. When two polymers are far from being miscible, they are unlikely to form a one-phase system (e.g., at HIPS/HDPE ratios of 30/70 and 10/90). In a completely immiscible system, the main role of the copolymer is to act as an interfacial agent.[10]

Based on the T_g values, there is still no evidence that the SEBS compatibilizer makes the two polymer phases more miscible. Inclusion of SEBS promotes greater complexity to the glass-transition temperature of the blend system because the SEBS compatibilizer contains styrene block (30%) and ethylene–butylene random copolymer (70%), and may interfere with the measurement. The inclusion of SEBS compatibilizer in HIPS/HDPE did not add significant miscibility to the blends, as indicated by glass-transition temperatures. We may then conclude that SEBS is just an interfacial agent.

TABLE II
T_g of HIPS/HDPE Blends with Various SEBS Concentrations

HIPS/HDPE	SEBS (pphr)	T_g (K)	
		Measurement	Calculation[a]
100/0	0	361.2	—
0/100	0	148[b]	—
90/10	0	366.1	315.7
	5	367.0	309.3
	10	368.1	303.6
	15	368.5	298.7
	20	368.5	294.3
70/30	0	370.7	252.2
	5	369.4	250.2
	10	372.5	248.9
	15	370.4	247.4
	20	370.4	246.1
50/50	0	373.5	210.0
	5	372.1	210.4
	10	368.8	210.8
	15	371.0	211.2
	20	373.7	211.5
30/70	0	NA[c]	179.8
	5	NA	181.4
	10	NA	182.9
	15	NA	184.2
	20	NA	185.4
10/90	0	NA	157.3
	5	NA	159.4
	10	NA	161.4
	15	NA	163.3
	20	NA	165.1

[a] Based on Fox's equation.
[b] Literature value.
[c] NA, No available data.

Phase separation investigation by pulsed NMR

The spin–spin relaxation time (T_2) is mostly used to obtain information on a system where small domains of low molecular mobility are dispersed, given that spin diffusion often loses the information in the mea-

surements of the spin–lattice relaxation time (T_1) and the spin–lattice relaxation time in the rotating frame ($T_1\rho$).[11–13] In addition, T_2 directly reflects the mobility of molecules and we can gain information on the temporal change of mobility from the real-time measurement of T_2. Furthermore, we can obtain information on the degree of heterogeneity from the difference in mobility and the temporal change of both fractions and T_2 values. Normally, a shorter T_2 indicates a glassy or crystalline stage, whereas a long T_2 is caused by a rubbery portion with less-constrained molecular motion. The signals of pulsed NMR for the heterogeneous system of HIPS/HDPE blends, which is compatibilized by SEBS, can be obtained from the mobility and fractional amount of each phase by decomposing the NMR signals.

Figures 8 and 9 show the results of the pulsed ^{1}H-NMR measurements at room temperature and resonance at 20 MHz, including the temporal change of T_2 and the fractional amount (f) for HIPS (A) and HDPE (B). Two T_2 values were found for each blend ratio. The shorter T_2 is usually related to a glassy or crystalline phase and the longer T_2 is usually related to a rubbery phase. In our case, the crystalline polystyrene phase in HIPS, the crystalline phase in HDPE, and the hard segments of two styrene blocks in SEBS correspond to the short T_2 component. In other words, the rubbery phase in HIPS, the amorphous phase in HDPE, and the soft segments of SEBS correspond to the longer T_2 component.[11–13] The suppression of mobility of crystalline polymers like the HDPE component in the blends is attributed to the perfection of the crystalline structure. Crystals with fewer internal defects have lower mobility, and they also suppress the mobility at the interface, which results in the short T_2 that can be seen in Figure 8(A) and (B), where the value of T_2B for the HDPE component is almost constant when acting as both the major phase (HIPS/
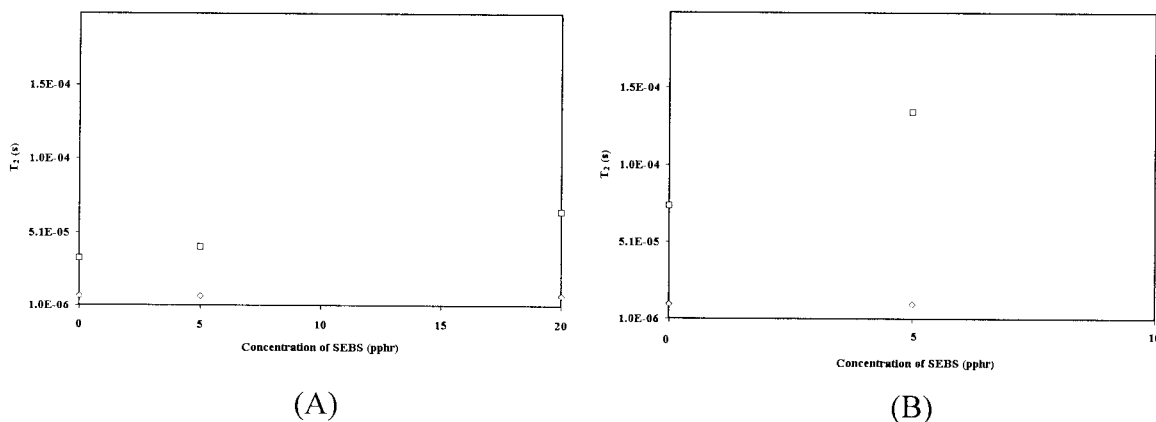

(A)

(B)

Figure 8 Dependency of T_2 of HIPS and HDPE phase in the blends: (A) HIPS/HDPE = 10/90; (B) HIPS/HDPE = 90/10 (◇, T_2A; □, T_2B).
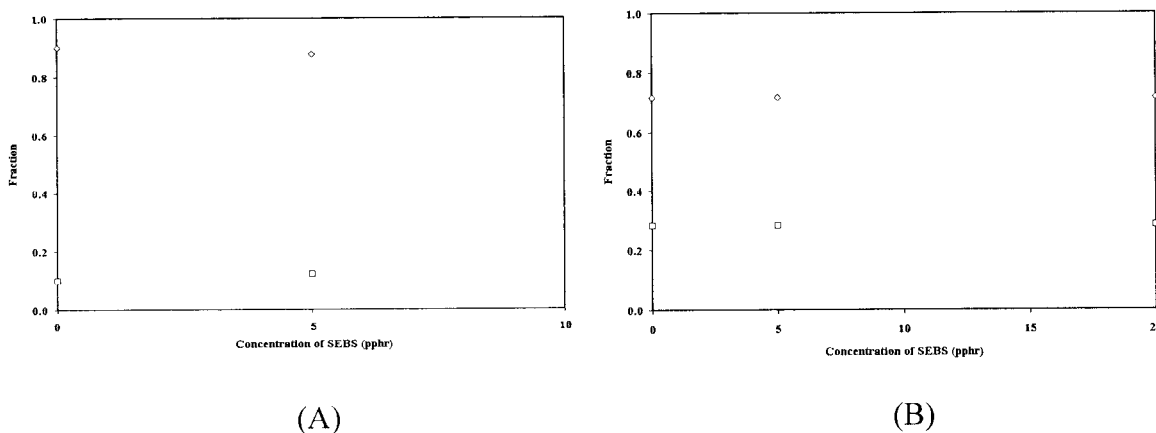
(A)   (B)

Figure 9 Dependency of fractional amount of HIPS and HDPE phase in the blends: (A) HIPS/HDPE = 10/90; (B) HIPS/HDPE = 90/10 ($\diamond$, T_2A_f; $\square$, T_2B_f).

HDPE = 10/90) and the minor phase (HIPS/HDPE = 90/10).

On the other hand, HIPS is acting as the amorphous component in the blends, consisting of the relatively mobile amorphous domains outside the spherulites and relatively immobile interlamellar amorphous chains constrained by the lamellae.[13] From Figure 8(A) and (B), we found that the T_2A value of the amorphous component slightly increases with the SEBS concentration in the amorphous minor phase and sharply increases when the amorphous component is the major phase. There are some changes in molecular structure between HIPS and HDPE, which have better interfacial adhesion when incorporating the segments of SEBS, leading to increases in T_2A for each blend ratio when increasing the interfacial agent SEBS. For the HDPE-rich phase system (HIPS/HDPE = 10/90), both T_2A_f and T_2B_f were stable, regardless of the amount of SEBS added, as shown in Figure 9(A). The increase in T_2B_f and decrease of T_2A_f occur in the HIPS-rich phase (HIPS/HDPE = 90/10), as shown in Figure 9(B), where an increasing SEBS concentration is added to give growth of the crystals by incorporating the amorphous chains of SEBS with more interfacial adhesion between the two phases.

Mechanical properties of HIPS/HDPE blends

Generally, it has been long established that immiscible polymer blends have inferior mechanical properties because of the existence of weak interfacial adhesion and poor dispersion of the components. In this study, the mechanical properties after the compatibilization effect of HIPS/HDPE blends by the SEBS block copolymer were investigated in terms of the impact strength, tensile strength, and flexural strength.

Impact strength of HIPS/HDPE blends

The Izod impact strength of HIPS/HDPE blends either noncompatibilized or compatibilized with the

SEBS triblock copolymer is shown in Figure 10. It can be seen that the Izod impact strength of the noncompatibilized blends is poor. This result indicates the poor interfacial adhesion between the two phases. When compatibilized by the SEBS block copolymer, the impact strength was improved and increased with increasing SEBS content for each blend ratio. The poorly dispersed phase was improved to become much finer and more uniformly dispersed. The impact strength of the blends of HIPS/HDPE blends with SEBS triblock copolymer shows a similar trend. Tjong and Xu[14] reported that the impact strength of compatibilized blends increased slowly with HDPE content in the blends of less than 50 wt %. When the HDPE became the matrix phase (HDPE content > 50 wt %), the impact strength sharply increased with increasing HDPE content. The sharp increase in impact strength after 50 wt % HDPE indicates the rubbery behavior of the blend, which does not break or fracture. These phenomena can be explained similarly as described previously. The HDPE-rich phase (>50 wt %) is more compatible with SEBS than the HIPS-rich phase. In
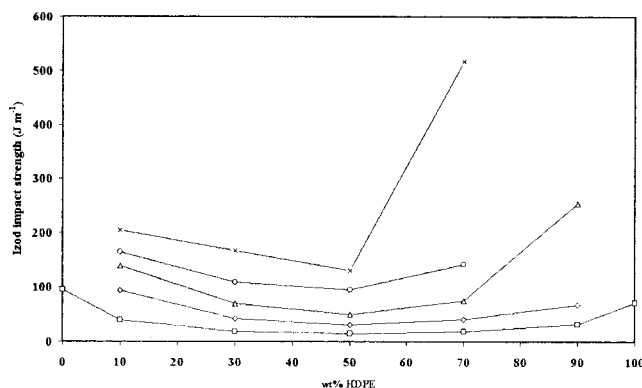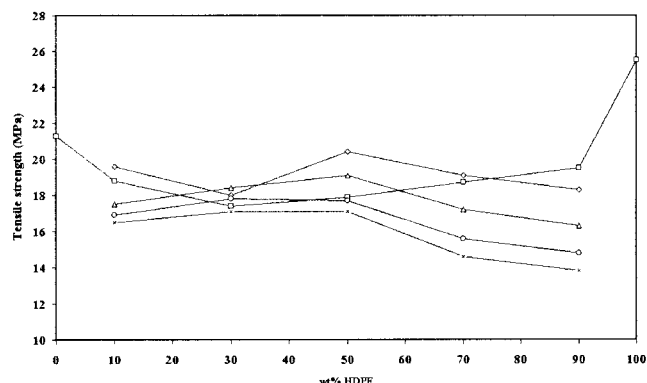

Figure 10 Izod impact strength of HIPS/HDPE blends with various SEBS concentrations ($\square$, SEBS 0 pphr; $\diamond$, SEBS 5 pphr; $\triangle$, SEBS 10 pphr; $\bigcirc$, SEBS 15 pphr; $\times$, SEBS 20 pphr).

other words, the HIPS domain in the former can uniformly disperse in the HDPE matrix. In addition, the rubbery portion (7–8% polybutadiene) of HIPS and the block of ethylene–butylene (70%) in the SEBS play a major role for the blend ratios of 50 : 50 or higher HDPE content. However, SEBS can be regarded as an impact modifier for HDPE blends.

Tensile strength of HIPS/HDPE blends

It is worthwhile mentioning that the neat single polymers (HIPS alone or HDPE alone) have higher tensile strength than that of the blend because of the presence of the rubbery portion in the former and the crystalline portion in the latter. The single polymer of either HIPS or HDPE provides its unique property for a particular application. Tensile strength as shown in Figure 11 indicates clearly that the noncompatibilized and compatibilized blends yield lower tensile values at all blend ratios and SEBS concentrations when compared with that of pure HDPE. In the absence of SEBS, PS gives a lower tensile strength than that of HDPE because PS is a hard and rigid polymer, whereas HDPE is a flexible polymer with some degree of crystallinity. Increasing the HDPE content in the noncompatibilized blends increases the tensile strength of the blends. Considering the blends themselves, tensile strength increases and reaches a maximum for the blends (HIPS/HDPE) of 50/50 at 5 pphr SEBS inclusion. However, the increased tensile strength is not very significant when compared with the noncompatibilized blends. It is possible to claim that the SEBS triblock polymer can, nonetheless, somewhat enhance the interfacial adhesion of phase boundaries between the two polymers. In the 10/90 HIPS/HDPE blend, the addition of SEBS leads to inferior properties at all SEBS concentrations. The HDPE matrix contains quite a large crystalline portion, which is difficult for the
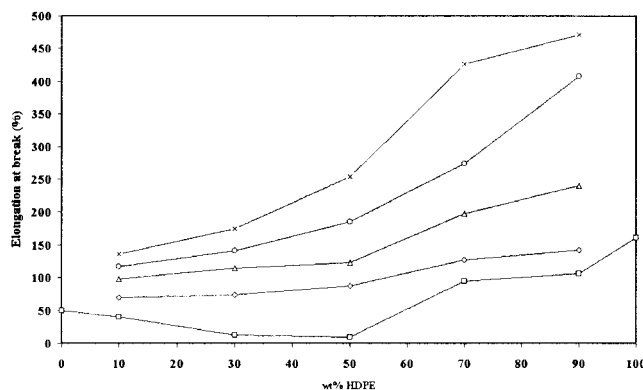
Figure 12 Elongation at break of HIPS/HDPE blends with various SEBS concentrations (□, SEBS 0 pphr; ◇, SEBS 5 pphr; △, SEBS 10 pphr; ○, SEBS 15 pphr; ×, SEBS 20 pphr).

hard polymer to disperse even in the presence of the SEBS compatibilizer.

The elongation at break, another tensile property, yields striking results. Comparing the neat HIPS or HDPE, HDPE gives more than 300% higher elongation at break. The blends (HIPS/HDPE) of 90/10, 70/30, and 50/50 ratios yield lower values when decreasing the concentration of HIPS because of the decrease of polybutadiene content in HIPS. The elongation at break for these blend ratios illustrates the poor dispersibility of the HIPS domain in the HDPE matrix polymer. When the blend ratios of HIPS/HDPE are 30/70 and 10/90, the elongation at break of the blends is controlled by the concentration of the HDPE matrix polymer. Basically, HDPE is a low modulus and ductile or rubberlike material with some degree of crystallinity. However, these blends still indicate the influence of the high modulus and hard segment HIPS, given that the elongation at break is still lower than that of neat HDPE.

For the compatibilized blends, elongation at break increases with increasing SEBS concentration. Very interesting results are obtained at high SEBS concentrations incorporated in 30/70 and 10/90 blend ratios of HIPS/HDPE. The blends of 30/70 and 10/90 HIPS/HDPE with 15 to 20 pphr SEBS behave like a rubbery material because the elongation at break is as high as 400–500%, similar to that of rubber. Our results for the elongation at break of these blends are similar to the work of Tjong and Xu[14] and Chen et al.[15] Tjong and Xu reported earlier that the atatic-PS/HDPE blends compatibilized with SEBS triblock copolymer showed the major influence of the HDPE matrix. Chen et al.[15] obtained the same results when syndiotactic-PS/HDPE blends were compatibilized by various types of block copolymers.

CONCLUSIONS

HIPS and HDPE are basically incompatible blends. The SEBS triblock copolymer, which contains 70 wt %

Figure 11 Tensile strength of HIPS/HDPE blends with various SEBS concentrations (□, SEBS 0 pphr; ◇, SEBS 5 pphr; △, SEBS 10 pphr; ○, SEBS 15 pphr; ×, SEBS 20 pphr).

of a random copolymer of ethylene–butylene and 30 wt % of styrene, can be used to solve the problem of incompatibility of HIPS/HDPE blends. The roles of the SEBS triblock copolymer regarding compatibility were found, in this work, to be as an interfacial agent and impact modifier to provide better interfacial adhesion between HIPS and HDPE.

The SEBS compatibilizer's effects on mechanical properties relevant to industrial applications of HIPS/HDPE blends were determined. The impact strength and elongation at break of the blends were improved by increasing the SEBS content, and sharply increased when HDPE became the major phase or when the HDPE content in the blends was more than 50 wt %. The tensile strength also improved when the compatibilizer loading was below 5 pphr: if the compatibilizer loading was higher than 5 pphr, the tensile strength decreased and a greater decrease was found in the HDPE-rich phase. The addition of SEBS compatibilizer could not significantly improve the flexural strength.

Positive deviation behavior, compared with the log additivity rule measured at 473 K, was observed at high shear rates for the HIPS-rich phase and at low shear rates for the HDPE-rich phase. At the higher SEBS concentrations, every blend was more compatible than the neat blends. The pseudoplastic behavior (shear thinning) was observed for every blend ratio. The morphology of the blends was improved by inclusion of the SEBS block copolymer. We observed finer dispersion of the polystyrene portion on the fractured surface, etched and removed with toluene to holes in the micrographs. Increasing the HDPE contents gave finer and fewer holes of PS because of the finer dispersion of HIPS in the HDPE matrix. The SEBS could reduce the dispersed phase particles, which produced more uniform dispersions and finer particles to form the cocontinuous phase of the blends. The extent of phase compatibility depends on the blend conditions (i.e., blend composition, viscosity ratio of blends, and compatibilizer loading). Glass-transition temperature measurements cannot be precisely evaluated because of the extent of compatibility. The relaxation time by pulsed NMR measurements confirmed some extent of compatibility in HIPS/HDPE blends compatibilized by SEBS. Two T_2 values were found at each blend ratio. The T_2 value of the HDPE component was almost constant in both blends as the major phase (HIPS/HDPE = 10/90) and as the minor phase (HIPS/HDPE = 10/90). The T_2 of the amorphous component slightly increased with the SEBS concentration. The better interfacial adhesion achievable by incorporating the SEBS led to increases of T_2 in each blend. We could then conclude that increasing the SEBS concentration provides better interfacial adhesion between the two phases.

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