The Effect of Diblocks and Ripening on the Izod Impact of Bulk PS/PB Blends

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Received 11 April 1998; accepted 31 August 1998

ABSTRACT: Bulk blends were used to study the effectiveness of various PS-PB diblock copolymers in improving the impact strength of PS/PB blends. The blends were produced by compositional quenching, and further ripened to control particle size and the diblock concentration at the homopolymer interface. It was found that an optimal molecular weight of diblock copolymer exists for the maximum notched Izod. Low molecular weight diblocks provided insufficient adhesion due to lack of entanglements, and high molecular weight diblocks provided insufficient interfacial concentration due to stearic crowding. The maximum notched Izod, for 23% rubber phase volume, was achieved with 1- μ particles, a copolymer surface density of 0.17 chains/nm², some crosslinking, and a medium molecular weight, tapered diblock, $M_w = 154,000$, having a 30% PS content. The combination of high impact strength, 6.2 ft.-lbf./in., and high modulus, 2.2 GPa, significantly exceeds that of commercially available super high-impact polystyrene. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1165–1176, 1999

Key words: blends; polystyrene; polybutadiene; diblocks; impact strength

INTRODUCTION

The most common blending techniques are mechanical, solution, polymerization, and reactive. Blends in this article have been produced by compositional quenching, which is a form of solution blending.¹ Bulk blends were produced with fine dispersions of the second phase, excellent control of particle size, and independent control of the amount of compatibilizer at the interface.

It is readily understood that compatibilization influences blend properties. It increases the adhesion at phase boundaries, giving improved stress transfer. The addition of block and graft copolymers represents the most extensively researched approach to compatibilization of blends. Block copolymers containing blocks chemically identical to the component homopolymers are the most investigated, and are obvious choices as compatibilizers, because miscibility between the copolymer segment and the corresponding blend component is assured. The classical view of how such copolymers locate at interfaces is well known.²⁻⁴

Copolymer structure and molecular weight have important influences on their effectiveness as compatibilizers. Block copolymers are better compatibilizers than graft, and diblock copolymers are more effective compatibilizers than triblocks or star blocks.⁵ The amount of block required to saturate the interface has been the subject of various studies.^{6–8}

Studies done recently show that the reinforcement at the interface depends on the copolymer concentration at the interface, Σ , the molecular weight, M, of each segment of the block, and its

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Contract grant sponsor: Petroleum Reserach Fund (American Chemical Society).

Journal of Applied Polymer Science, Vol. 72, 1165-1176 (1999)

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relation to the entanglement molecular weight M_e .^{9,10} Three fracture mechanisms were proposed based on a study of the PS/PVP [polystyrene/poly(2-vinylpyridine)] system. (a) Chain pullout if $M_A < M_{eA}$ or $M_B < M_{eB}$. The fracture toughness increased linearly with Σ , and scaled as M_A^2 (if $M_A < M_{eA}$). (b) Chain scission if $M_A > M_{eA}$ and M_B M_{eB} and low (Σ The fracture toughness increases linearly with Σ . (c) Plastic deformation and crazing if $M_A > M_{eA}$ and $M_B > M_{eB}$ and high Σ . The fracture toughness scales as Σ^2 , and is greatly enhanced in this regime.

Our results are discussed on the basis of the above fracture mechanisms.

There are many ways to influence the molecular and morphological structures of rubber-toughened styrene polymers in industrial production processes. The most important characteristics of these two phase blends are molecular weight of the matrix, phase volume ratio, type of particle, particle size, interfacial bonding, and rubber crosslinking density.¹¹

The impact strength of rubber-toughened styrene polymers increases with rubber phase volume, but good adhesion between the rubber particle and the PS matrix is critical. If the bond between rubber and PS is weak, voids form at the interface, and cracks are initiated.^{12,13} The effects of particle size are not well known, except that an optimal exists.¹¹ A critical particle size, below which the impact strength falls drastically, for HIPS was found to be 0.8 μ m.¹³ Commercial highimpact polystyrene, HIPS, contains rubber particles ~ 1–2 μ m in diameter.^{14,15} Polystyrene is toughened effectively with a dual rubber particlesize population if most of the rubber particles are below 1 μ m.^{16,17} Cook et al.¹⁸ found that monodisperse particles, $2-3 \mu m$, gave optimum impact toughness for latex rubber-modified polystyrene. Durst et al. got maximum strength for solid rubber particles of $\sim 1 \ \mu m$ with 25% SBS copolymer.¹⁹ Moore²⁰ studied rubber-reinforced polystyrenes prepared by graft copolymerization using various butadiene polymers and copolymers, and concluded that a particle size of $\geq 2 \ \mu m$ with a polybutadiene molecular weight \geq 110,000 was required to obtain significant reinforcement. Liu and Baker²¹ found that the optimum rubber particle size for toughening PS was influenced by the interfacial adhesion, with the best results being obtained for 0.2-µm particles of acrylonitrilebutadiene rubber. Thus, there are many conflicting results in the literature with respect to particle size, whether the particles are occluded or solid, and the importance of interfacial adhesion.

The tensile properties and modulus of various high impact polystyrene blends has been well characterized. Yokouchi et al.²² have shown in their studies on HIPS that the elongation at break decreased from 35 to 15%, and the yield stress increased when the tensile speed was varied from 2.8×10^{-4} to 0.0282 m/s. Bucknall et al.²³ studied 14 different HIPS blends and concluded that the modulus and yield stress depended principally upon particle volume fraction, with a modulus of 2.2 GPa for 23% rubber volume fraction. Dağli et al.²⁴ found that the yield strength depended on the particle size for HIPS. For particle sizes of 1.03 and 3.97 μ m, the yield strength, elongation to break, and modulus relative to PS were 19.1 and 23.8 MPa, 19.2 and 3.6%, and 0.44 and 0.58, respectively.

It is generally believed that crosslinking in the rubber particle decreases impact strength and increases tensile strength. Cook et al.²⁵ found that notched impact decreased with increased crosslinking of poly(n-butyl acrylate) rubber particles. Grocela²⁶ found that the yield strength of PS/PB blends increased with increasing radiation exposure, but found a slightly detrimental effect on impact strength.

In this article, bulk blends of polystyrene, polybutadiene, and their respective diblock copolymers have been produced by compositional quenching (CQ). The effect of various diblocks on interfacial adhesion has been studied by measuring the resultant notched Izod impact strength. Detailed studies have been done for a medium molecular weight diblock, 730A, on the effect of particle size and copolymer concentration on impact strength.

EXPERIMENTAL

Materials

Table I gives the various starting polymers used, their molecular weights, and their manufacturers. All the materials used in this work have been commercially obtained. The polystyrene is a general purpose grade supplied by Novacor Chemical Ltd. Our measurements gave $M_n = 82,000$ and $M_w = 202,000$. The polybutadiene rubber, Diene 55NF, was obtained from Firestone. It has a 40% cis, 50% trans, and 10% vinyl content. The

Material	Manufacturer	${M}_w$	Polydispersity	
Polystyrene GP	Novacor Chemical Company	202,000	2.4	
Polystyrene			2.4	
Polybutadiene Diene® 55 NF	Firestone	320,000	2.4	
HIPS Styron [®] 484	Dow Chemical Company	Close to PS above	Close to PS above	
PS-PB Diblock Stereon®210	Firestone	35,000	1.1	
PS-PB Diblock Europrene®Sol S183	Enichem	109,000	1.1	
PS-PB Diblock Stereon®205	Firestone	79,400	1.05	
PS-PB Diblock Europrene®Sol E142	Enichem	90,000	1.1	
PS-PB Diblock Fina®502	Fina Oil and Chemical	110,000	1.1	
PS-PB Diblock Stereon®730A	Firestone	154,000	1.1	
PS-PB Diblock Buna 6533	Bayer Corporation	222,000	1.07	
PS-PB Diblock Fina®411	Fina Oil and Chemical	270,000	1.1	

Table IMaterials Used

diblocks obtained are fairly monodisperse, ~ 1.1 . Table II gives the block lengths of the diblocks. Because there is a difference between the bound PS content and the block PS content, the individual block lengths calculated do not add up to the diblock M_n obtained. Table III lists the bound PS content in each diblock copolymer. Xylene was used as a solvent, and was purchased from Ashland Chemical Company. During dissolution, 0.1 wt % of Irganox[®] 1010 antioxidant was added.

Blend Production

A 5% polymer solution was prepared in xylene, and a single phase solution was obtained. This homogenous solution was heated to a temperature of $220-240^{\circ}$ C, and quenched under a vacuum of 5 Torr to remove the solvent. The total minor phase (PB) volume was held constant at

Table II Diblock Segment Lengths

Polymer	Total M_n	PS Block M_n	PB Block M_n
F411	246,000	74,000	172,000
B6533	207,000	63,000	125,000
730A	140,000	33,000	98,000
F502	100,000	30,000	70,000
E142	77,000	35,000	23,000
205	75,600	14,000	57,000
S183	95,000	5,000	86,000
D210	31,000	7,000	23,000

23%. The amounts of polybutadiene and diblock copolymer added were varied. Spherical particles, having a size of ~ 0.3 μ , and no visible micelles were obtained. Thus, the diblock is localized at the PS-PB homopolymer interface.^{4,27-29} The blend was dried by further devolatilization and ground to a powder. The final solvent content was 600–900 PPM. The mean particle size and concentration of the diblock at the interface was varied at this stage by ripening at 200, 240, and 270°C for various times in a Carver press.

Characterization

At least 10 Izod bars obtained from the Carver press were notched and then tested with a 3-lb. hammer.³⁰ The tensile modulus was measured using an Instron 4204 tensile testing machine with a 0.5-in. extensimeter attachment. Elongations to yield and break were measured using a 5-kN load cell.³¹

An Amray model AMR 1000 scanning electron microscope (SEM) was used to examine the fracture surface of the molded blends. The broken sample was carefully removed from the impact tester so that the surface was not altered. A thin layer (~ 100 Å) of gold was sputtered on the surface to minimize charging. The sample was attached to the holder with silver paint and left in the vacuum oven for 30 min before imaging.

Solvent in the final blend was measured using a Perkin-Elmer Thermogravimetric Analyzer, TGA 7, interfaced to an automatic computer-con-

Blend	% PB in the Blend	% Diblocks in the Blend	% Bound PS in Diblock	Maximum Izod ft lbf./in.
PS	0			0.4
PS/PB	23	_	_	0.6
HIPS	23	_	_	1.5
PS/PB/D210	23	8.6	25	1.1
PS/PB/S183	23	8.8	10	1.3
PS/PB/E142	23	8.1	70	5.2
		16.2		4.4
		30.0		No Break
PS/PB/205	23	8.6	25	4.4
PS/PB/F411	23	9.1	30	4.2
PS/PB/B6533	23	10.4	39.5	5.9
PS/PB/F502	23	9.1	30	4.1
PS/PB/730A	23	4.0	30	3.6
		9.1		6.2
		12.7		4.7
		18.1		4.1
		31.5		7.2

Tabl	e III	Maximum	Izod	Strengt	\mathbf{hs}
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trolled data acquisition system by a thermal analysis controller, TAC 7/DX. The degree of crosslinking in the blends was determined by a Soxhlet extraction.³² The sample was placed in a preextracted cellulose thimble, with xylene as the solvent for 48 h. The swelling index was calculated as the ratio of wet and the dry weights after the extraction. The percent gel was determined from the dry weight after extraction.

The molded blends were cut, shaped to form a sharp pyramid, and stained in 4% aqueous osmium tetraoxide.³³ Thin sections (approx. 800 Å) were cut using a Reichert-Jung UltracutE Ultramicrotome with a diamond knife. The morphology was observed under a 100-KV electron beam using a Philips CM12 Transmission Electron Microscope.

Standards and Blend Design

The experimental blends were compared to three different standards processed under the same conditions. The first standard was general purpose polystyrene having a Young's modulus of 3.73 GPa. The second standard was an uncompatibilized blend of PS and PB, PS/PB (77/23 by volume), which had a modulus of 2.37 GPa. The third standard was a commercial HIPS sample obtained from Dow having a modulus of 2.18 GPa and containing a 23%

rubber phase by volume. The rubber particles in commercial HIPS are highly occluded with PS. The actual PB content of the HIPS standard is believed to be approximately 8%. The impact strength for PS, PS/PB, and HIPS remained constant at 0.4, 0.6, 1.5 ft.lbf./in., respectively, for ripening times up to 6 h. Figure 1 shows the impact strength as a function of ripening time. The yield strength and elongation to break for PS and HIPS are given in Table IV.

All the blends in this article contained a 23% rubber phase by volume with the polybutadiene coming from the pure rubber, the rubber portion of the diblocks, or both. The compositions stated for each blend are in vol %. A constant phase volume was maintained so that a comparison with commercial HIPS could be made, and the impact strength quantified as a function of particle size and interfacial compatibilization. Rubber phase volume, which directly correlates to impact strength, was not a subject of this study. With increasing rubber content, the impact strength goes up but the tensile strength and modulus decrease.

Submicron rubber particles, $\sim 0.3 \mu$, were uniformly dispersed in the PS matrix when the blends were compositionally quenched. This particle size was suboptimal, and was not effective for impact modification. Thus, blends were rip-



Figure 1 Impact strength as a function of ripening time at 200°C for various diblock copolymer blends with a 23% overall rubber phase volume.

ened in the mold to grow the particles and study the effect of particle size on impact strength.

RESULTS AND DISCUSSIONS

Effect of Various Diblock Copolymers

The impact strengths of various diblock copolymer blends are shown in Figure 1. The initial increase in impact strength is attributed primarily to an increasing copolymer concentration, Σ , at the PS/PB particle interface. As the particle diameter increases, the total interfacial area decreases. This leads to increasing interfacial adhesion and higher impact. The impact strength eventually goes down because the particle size becomes larger than optimal. For polymers that fail by crazing, small particles promote craze initiation and large particles promote termination. No termination would mean that one of the crazes would grow long and lead to catastrophic failure. Low initiation would mean low craze volume and lower impact strength. Thus, an optimal particle size is expected.

The best performing system was PS/PB/730A (74.5/16.4/9.1), having an impact strength of 6.2 ft.-lbf./in. The tensile modulus was 2.21 GPa, marginally higher than the HIPS standard. This combination of impact strength and modulus exceeds that of commercial super high-impact polystyrene (SHIPS), for example, Huntsman 850 has

Sample	Molding Time (min)	Speed of Test $\times 10^{-4}$ (m/s)	Yield Stress (MPa)	Strain at Break (%)
Polystyrene (PS)	30	0.846	50.03	3.75
		8.466	52.99	4.36
		84.666	56.19	4.42
High impact polystyrene (HIPS)	30	0.846	28.34	37.22
		8.466	32.71	31.05
		84.666	34.99	24.66
PS/PB/730A (74.5/16.4/9.1)	3	0.846	15.28	1.50
		8.466	19.47	1.58
		84.666	21.44	2.78
	30	8.466	21.93	4.6
	180	0.846	17.74	7.83
		8.466	18.73	11.68
		84.666	20.45	18.66
	480	8.466	19.96	6.16

Table IV Tensile Properties of Selected Blends

an Izod of 4.2 ft.-lbf./in. with a modulus of 1.96 GPa. The entanglement molecular weights are 30,000 for PS and 5900 for PB.³⁴ Because both block segment lengths for 730A are greater than M_e , adequate adhesion was expected. A large amount of crazing was apparent for these blends judging by the stress whitening of the fracture surface. Regions of dense craze material penetrated nearly 1 mm into the Izod bars.

A lower maximum strength of 5.4 ft.-lbf./in. was obtained for PS/PB/E142 (71.6/20.3/8.1), even though the PB block length remained substantially higher than M_{ePB} . This suggests that the classic viscosity-based measurement of M_{ρ} does not provide an adequate measure of entanglements in bulk. However, the value for M_{ePS} was found to be adequate. Surprisingly, PS/PB/205 (75.1/16.3/8.6) provided reasonable impact strengths even though the molecular weight of the PS block was only 14,000. A lower maximum strength (4.1 ft-lbf./in.) was obtained for PS/PB/F502 (74.5/16.4/9.1) compared to the 730A blend, even though the block lengths are similar. This is attributed to the fact that diblock F502 is not a tapered diblock. Tapered diblocks such as 730A, and E142 are believed to provide higher adhesion. Fayt et al.35 previously found that tapered diblock copolymers were more effective than diblock copolymers with a sharp transition in chain composition.

Poor impact strengths were obtained with the low molecular weight diblocks, S183 and D210, PS/PB/S183 (76.2/15.0/8.8), and PS/PB/D210 (75.1/16.3/8.6). This was expected because the PS block lengths were lower than $M_{e\rm PS}$. It is speculated that the PS blocks were pulled out of the fracture interface, leading to low-notched Izods. There was brittle fracture with no observable stress whitening. The marginal increase in impact strength from 1.1 to 1.3 ft.-lbf./in. in going from the D210 diblock to the S183 diblock is apparently due to the increase in PB block length, even though both PB blocks are well beyond the entanglement value of 5900.

Diblocks with higher block lengths than 730A gave lower impact strengths. The maximum impact strength for the PS/PB/B6533 (73.3/16.3/10.4) and PS/PB/F411 (74.5/16.4/9.1) blends was 5.9 and 4.2 ft.-lbf./in., respectively. Lower Izods compared to the 730A blend are attributed to the very high molecular weight of the diblocks. Stearic effects limit Σ to values lower than those in the 730A blends. The much lower impact

strength obtained with F411 may also be attributed to the fact that it is a nontapered diblock.

Our results on impact strength show that there is an optimal diblock molecular weight. We attribute this to a tradeoff between Σ and block length. Short block lengths gave poor impact strength. This is presumably due to chain pullout and poor stress transfer between the PS and PB boundaries. A high Σ for these short diblocks does not help in toughening. High block lengths do provide sufficient entanglement but may have a low areal chain density. Again, stress transfer across the interface is limited. The accepted guideline is that block lengths must exceed the entanglement molecular weight as determined by solution viscosity.³⁴ Our results confirm this as a rule of thumb, but suggest that the effective M_e in bulk experiments may be different than in solution. Polybutadiene block lengths substantially higher than $M_{e} = 5900$ give incremental benefits, while polystyrene block lengths less than M_e = 30,000 are still effective.

Particle Morphology and Surface Coverage

These studies were done for the blends containing 730A diblock with a composition of 74.5/16.4/9.1. The effects of ripening time and temperature are shown in Figure 2. The time needed to attain maximum Izod strength goes down dramatically with ripening temperature. Optimal ripening times of 180, 30, and 5 min were found for temperatures of 200, 240, and 270°C, respectively. However, the maximum impact strength was compromised at higher temperatures. Figure 3 is a representative micrograph of a blend ripened at 240°C for 30 min. A large amount of coalescence, leading to nonspherical particles is apparent. The resulting nonuniform stress fields may be the cause of the lower impact strength.

Crosslinking may also contribute to the decrease in maximum impact strength with increasing molding temperature. Table V gives results for swelling index and gel content. For a mold temperature of 200°C and time of 180 min, the maximum Izod of 6.2 ft.-lbf./in. was obtained. The swelling index was 36.3, and the gel fraction was 11.1%, showing a low degree of crosslinking. When the blend was ripened at 270°C for 5 min, an Izod of only 5.0 ft.-lbf./in. was obtained. The swelling index had dropped to 22.6, and the measured gel content was 17.0%, indicating that most of the rubber had been crosslinked.



FIGURE 2 Impact strength as a function of ripening time for 730A blends at various ripening temperatures.

The results of impact strength versus particle size are plotted in Figure 4. When particles are ripened, their diameter increases as $(time)^n$, where *n* is 1/3 in a binary system but is lower when a copolymer is added. In Figure 4, the filled data points (\blacklozenge) were used to determine a growth exponent of 0.12. This value is similar to the 0.14 obtained experimentally for the 8% diblock³⁶ and the 0.19 obtained from Monte Carlo simulations.³⁷ It has been used to extrapolate the parti-



Figure 3 TEM of a PS/PB/730A blend molded at 240° C for 30 min.

Table VCrosslinking and Gel Phase Contentfor Various 730A Blends

Sample with Processing Conditions	Swelling Index	Gel %
PS/PB/730A (74.5/16.4/9.1)		
200°C, 3 min	∞	0
200°C, 180 min	36.3	11.1
200°C, 300 min	26.7	11.2
200°C, 480 min	23.5	16.6
270°C, 5 min	22.6	17.0
270°C, 30 min	17.2	17.9
270°C, 120 min	13.2	18.7
Polystyrene	∞	0

cles sizes in the open data points (\diamond) . There is a sharply defined optimum at 1 μ that is much smaller than the $\sim 2 \mu$ reported for HIPS. The difference is likely due to the lower modulus of the blended rubber particles compared to the highly occluded particles typical of HIPS. The optimal particle size as observed here is not confounded by varying areal density of the diblock chains. Micelles were observed in the 75.5/16.4/9.1 blend at a mean particle size of 0.6 μ .³⁸ Thus, results for all larger sizes correspond to a saturated interface. For sizes less than about 0.6 μ , the surface



Figure 4 Effect of particle size on impact strength for PS/PB/730A.



Figure 5 TEM of a PS/PB/730A blend molded at 200°C for 240 min.

may not be saturated and, thus, our results may be confounded between particle size and surface coverage effects.

Figure 5 is a representative micrograph showing slightly occluded particles resulting from long ripening times. The occlusions are attributed to homopolystyrene having migrated to the core of the micelle in the rubber phase. Theoretically, these occlusions increase rubber phase volume and, hence, increase the Izod, but also increase the modulus of the rubber particles and, hence, are detrimental to impact strength. In practice, these complicating effects appear to be small. For a 1- μ particle the calculated rubber phase volume was 24.2%, based on the saturation density and the assumption that all the excess diblock went inside the particle to form micelles. If the content of diblock were adjusted to exactly saturate at the optimal particle size, it is possible that the optimal particle size for impact may be marginally lower than 1 μ .

Figure 6 shows the fracture surfaces as a function of ripening time and calculated areal chain density. The areal density calculations assumed that all the block went to the interface prior to saturation.³⁹ The interfacial area was based on the measured mean particle diameter. Figure 6(a) shows a fairly brittle fracture with a small amount of plastic deformation at a mean particle diameter of 0.3 μ and an areal chain density of 0.11 chains/nm². The holes correspond to the rubber particles. The increase in Izod due to increasing Σ and particle size correlates to increasing surface deformation as observed in Figure 6(a)– (d), which shows the fracture surfaces for blends ripened for 3, 30, 120, and 180 min with impact strengths of 3.01, 4.06, 5.82, and 6.2 ft.-lbf./in., respectively. Figure 6(d) shows a large amount of plastic deformation at a mean particle diameter of 1.08 μ and an areal density of 0.17 chains/nm², which is the saturation density.

Tensile tests were done for 730A blends ripened at 200°C. Table IV gives the detailed results for three test speeds. Figure 7 shows the stressstrain behavior at a test speed of 8.46×10^{-4} m/s for 730A ripened for 180 min and for the HIPS and PS controls. The dotted curve for 730A represents a test speed of 8.46×10^{-3} m/s. Higher speeds gave higher yield stresses for the blend than for the HIPS and PS controls. Surprisingly, the elongation at break increased with speed for the blend. This result is consistent with the fact that the 730A blend performed well under the high speed Izod test.

The lower elongation to failure for the 730A blend, compared to the HIPS standard, is attributed to nonuniform craze formation in the gauge length, as shown in Figure 8. Figure 8 is an optical photograph where crazing corresponds to the dark regions. Uniform crazing throughout the gauge was observed for HIPS. The 730A blend showed intense but localized crazing. The reason for the localization is unclear. If the blend sample could be made to craze more uniformly, higher elongations to break should be possible.

Diblock Loading

The amount of block at the PB particle interface depends on two parameters: the amount of diblock in the blend, and the particle size of PB. The results in the previous section were confined to a single composition, 74.5/16.4/9.1. In this section, the concentration of the 730A diblock is varied while keeping the total PB content constant at 23%. Figure 9 shows the effect of copolymer concentration as a function of ripening time. The maximum Izod was obtained for the 9.1% diblock. When more than a 9.1 vol % diblock was added, the maximum notched Izod was lower, and the ripening time to obtain the maximum value increased. For the 9.1, 12.7, and 18.1% diblock copolymers, the maximum Izods were 6.2, 5.2, and 4.1 ft.-lbf./in., and the corresponding ripening times were 180, 300, and 360 min. The particle sizes for saturation were calculated to be 0.48, 0.27, and 0.13 μ . These calculations assumed a saturation density of 0.17 chains/nm².³⁸ Thus, for

(b)



2μ



Figure 6 SEM of fracture surfaces at 25°C for PS/PB/730A molded at 200°C for: (a) 3 min, (b) 30 min, (c) 120 min, (d) 180 min.

all these runs, pure micelles or micelles with occluded homopolystyrene would be formed before the optimal particle size of 1 μ was achieved. It is postulated that the secondary structures are detrimental to high impact strength, despite the increase in rubber phase volume due to occlusions. A further improvement in impact strength should be possible using less than the 9.1% diblock so that saturation directly coincides with the optimal particle size. Assuming the optimal size is 1 μ , the appropriate diblock concentration would be 4.8%. The experiment at the 4.0% diblock concentration showed a much lower Izod of 3.6 ft.-lbf./in.

(c)

(a)

The particle size at which saturation occurs for this case is 1.3 μ , too large for optimal strength.

(d)

Other Results

A maximum strength of 7.2 ft.-lbf./in. (Table III) was obtained with the 730A copolymer when all the rubber in the blend came from the diblock, 68.5/0/31.5. However, the tensile modulus was 1.75 GPa, much lower than HIPS. Interacting micelles may have formed so that the morphology was no longer particulate. In any event, this blend is a far different material than conventional HIPS.



Figure 7 Stress–strain curves for: (a) PS molded at 200°C for 30 min for a tensile speed of 8.46×10^{-4} m/s, (b) HIPS molded at 200°C for 30 min for a tensile speed of 8.46×10^{-4} m/s, (c) PS/PB/730A molded at 200°C for 180 min for a tensile speed of 84.66×10^{-4} m/s, and (d) PS/PB/730A molded at 200°C for 180 min for a tensile speed of 8.46×10^{-4} m/s.

For a blend of PS/E142 (30/70), where all 23% rubber was obtained from this block copolymer, the Izod samples did not break. The tensile modulus was low, 0.59 GPa, suggesting that PS was not the continuous phase, and that lamella had formed. However, a tensile modulus of 2.4 GPa was obtained for PS/PB/E142 (71.6/20.3/8.1), which compared favorably to the other blends and the HIPS standard. When a blend composition of PS/PB/E142 (66.8/18.0/16.2) was tested, a lower maximum Izod value of 4.4 ft.-lbf./in. was obtained. Again, lamella due to excess diblock are suspected. Cavanaugh et al. have shown that excess E142 diblock forms lamella at the interface.⁴⁰ Washiyama et al. found that, for blends of PS/PVP, the lamellar interfaces were much weaker than the saturated homopolymer interface.⁴¹

The results in Figure 1 include quaternary blends of two different copolymers with PS and PB. When a 50/50 9.1% blend of F411 and F502 diblock copolymer was prepared, the Izod values were higher for each ripening time compared to the individual block copolymers, as shown in Figure 1. Also, when the 4.2% 730A diblock was blended with an equal amount of low MW diblock 183, the Izod strength was quite high (5.7 ft.-lbf./ in.). This suggests a possible synergism in blends of high and low molecular weight diblocks, allowing high Izods and lower ripening times. It also illustrates the effectiveness of compositional quenching in producing bulk blends with different compatibilizers.

CONCLUSIONS

Using a combination of compositional quenching and ripening, independent control of particle size and interfacial diblock concentrations is possible. This study showed the following:

Diblock copolymers provide good interfacial adhesion when block lengths are larger than their respective entanglement molecular weights. Super high-impact strengths are possible when $M_{PB} >> M_{ePB}$. In fact, all the strengths were higher than commercial HIPS (>1.5 ft.-lbf./in.), except for blends made with S183 and D210. These diblocks had a segment length shorter than M_e .

The optimal particle size for maximum impact strength with 730A diblock copolymer was found



Figure 8 Tensile bars pulled to failure for: (a) HIPS, (b) PS/PB/730A blend ripened for 180 min at 200°C.



Figure 9 Impact strength as a function of ripening time at 200°C for different 730A diblock concentrations.

to be $\sim 1 \mu$. This is much smaller than the optimal size of $\sim 2 \eta$ commonly cited for HIPS.

To achieve maximum impact strength, there are optimal molecular weights for the blocks in a diblock copolymer. The blocks must be long enough to entangle, but not so long as to lower the areal chain density due to stearic effects. For PB at least, the optimal block length is much longer than M_e , as determined by solution viscosity measurements.

The medium molecular weight, asymmetric, tapered diblock, 730A, which was capable of entangling in both homopolymer phases, was most effective in improving impact strength. The untapered diblock F502, and the symmetric diblock E142, were less effective.

The authors would like to thank Dr. G. N. Mathur of the Defense Materials Stores Research and Development Laboratory (DMSRDE), Kanpur, India, for use of their image analysis laboratory and S. K. Pandey for help with the SEM equipment. This research was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

REFERENCES AND NOTES

 Nauman, E. B.; Ariyapadi, M. V.; Balsara, N. P.; Grocela, T. A.; Furno, J. P.; Liu, S. H.; Mallikarjun, R. Chem Eng Commun 1988, 66, 29.

- Barensten, W. M.; Heikens, D.; Piet, D. Polymer 1974, 15, 119.
- Fayt, P.; Jerome, R.; Teyssie, Ph. J Polym Sci Polym Lett Ed 1981, 19, 79.
- Fayt, P.; Jerome, R.; Teyssie, Ph. J Polym Sci Polym Phys Ed 1981, 19, 1296.
- Folkes, M. J.; Hope, P. S. Polymer Blends and Alloys; Blackie Academic and Professional: Glasgow, UK, 1993.
- 6. Meier, D. J. J Polym Sci Part C 1969, 26, 81.
- Manson, J. A.; Sperling, L. H. Polymer Blends and Composites; Plenum Press: New York, 1976.
- Riess, G.; Jolivet, Y. In Copolymers, Polyblends, and Composites, Platzer, N. A. J., Ed.; Advances in Chemistry Series 142; American Chemical Society: Washington, DC, 1975.
- Crenton, C.; Kramer, E. J.; Hui, C.-Y.; Brown, H. R. Macromolecules 1992, 25, 3075.
- Crenton, C.; Kramer, E. J.; Hadziionnou, G. Macromolecules 1991, 24, 1846.
- Riew, C. K. Rubber Toughened Plastics; Advances in Chemistry Series 222; American Chemical Society: Washington, DC, 1989.
- Behan, P.; Thomas, A.; Bevis, A. J Mater Sci 1976, 11, 1207.
- Paul, D. R.; Newman, S. Polymer Blends; Academic Press: New York, 1978.
- Bucknall, C. B. Toughened Plastics; Applied Science: London, 1977.
- Donald, A. M.; Kramer, E. J. J Mater Sci 1982, 17, 2351; J Appl Polym Sci 1982, 27, 3729.
- 16. Larengood, R. E. USP 4,214,056, 1980 (Monsanto).
- 17. Hobbs, S. Y. Polym Eng Sci 1986, 26, 74.
- Cook, D. G.; Plumtree, A.; Rubin, A. J Appl Polym Sci 1993, 48, 75.
- Durst, R. R.; Griffith, R. M.; Urbanic, A. J.; VanEssen, W. J. Advances in Chemistry Series 154; American Chemical Society: Washington, DC, 1976.
- 20. Moore, J. D. Polymer 1971, 12, 478.
- Liu, N. C.; Baker, W. E. Polym Eng Sci 1992, 32, 1969.
- Yokouchi, M.; Uchiyama, H.; Kobayashi, K. J Appl Polym Sci 1980, 25, 1007.
- Bucknall, C. B.; Davies, P.; Partridge, I. K. J Mater Sci 1987, 22, 1351.
- Dağli, G.; Argon, A. S.; Cohen, R. E. Polymer 1995, 36, 2173.
- Cook, D. G.; Plumtree, A.; Rudin, A. Plastics Rubber Compos Process Applic 1993, 20, 219.
- Grocela, T. A. Doctoral Thesis; Rennselar Polytechnic Institute: Troy, NY (1992).
- 27. Nauman, E. B.; He, D. Q. Polymer 1994, 35, 2243.
- 28. Brown, H. R. Macromolecules 1989, 22, 2859.
- Shull, K. R.; Kramer, E. J. Macromolecules 1990, 23, 4769.
- Annual Book of ASTM Standards, 8.01, D-256, 1996.

- 31. Annual Book of ASTM Standards, 8.01, D-638, 1996.
- Adams, R.; Johnson, J. R.; Wilcox, C. F. Laboratory Experiments in Organic Chemistry; The Macmillan Co.: New York, 1970.
- 33. Kato, K. J Electron Micorsc 1965, 14, 219.
- 34. Porter, R. S.; Johnson, J. F. Chem Rev 1966, 66, 1.
- 35. Fayt, R.; Jerome, R.; Teyssie, Ph. J Polym Sci Polym Phys Ed 1982, 27, 2209.
- 36. Cavanaugh, T. J.; Nauman, E. B. J Polym Sci B Polym Phys, 1998, to appear.
- Kandasamy, S.; Nauman, E. B. Comput Theor Polym Sci 1997, 7, 183.
- Mathur, D.; Hariharan, R.; Nauman, E. G. Polymer, 1998, submitted.
- Beck, N. C.; Tai, S.-K.; Briber, R. M. Polymer, 1996, 37, 3509.
- 40. Cavanaugh, T. J.; Buttle, K.; Turner, J. N.; Nauman, E. B. Polymer 1998, 39, 4191.
- Washiyama, J.; Crenton, C.; Kramer, E. J.; Xiao, F.; Hui, C.-Y. Macromolecules 1993, 26, 6011.