Impact Strength of Bulk PS/PB Blends: Compatibilization and Fracture Studies

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ABSTRACT: The effect of rubber phase content on notched Izod for polystyrene (PS) and polybutadiene (PB) blends compatibilized with PS-PB diblock and PS-PB-PS triblock copolymers has been studied. The effectiveness of various PS-PB-PS triblock copolymers in improving the impact strength of PS/PB blends has been studied. The effect of blending PS-PB diblock with commercial HIPS has been explored. Studies were done for bulk blends produced by compositional quenching. It was observed that a minimum rubber phase volume of 7% was required for significant impact modification. This volume fraction corresponds to a interparticle distance of one particle diameter. The increase in impact strength was attributed to stress field overlap. HIPS blends showed no synergistic impact behavior, previously attributed to particle size bimodality. Atomic Force Microscope studies performed on fracture surfaces showed that energy dissipation is not associated with creation of surface area. A notched Izod of 5.6 ft.-lbf./in. combined with a modulus of 2.17 GPa was obtained using a medium molecular weight triblock, having a block molecular weight of 40,000-24,000-40,000. The triblock results were marginally worse than the best results obtained with diblocks²⁷ (Mathur and Nauman, J Appl Polym Sci, 1999), but were significantly better than results obtained with multiblock and random copolymers¹ (Cavanaugh et al., Polymer, 1998). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1151-1164, 1999

Key words: impact strength; polystyrene blends; rubber content; HIPS; triblocks

INTRODUCTION

Blending of two immiscible polymers to produce a phase-separated microstructure is now a well-established procedure for altering polymer properties.^{2,3} Polymers may be blended to obtain products that potentially offer desirable combinations of characteristics, i.e., impact strength. Thermodynamic incompatibility may not be a problem because it is often desirable to have a two-phase structure. However, low adhesion at the interface due to high interfacial tension may lead to poor mechanical properties. Compatibilization by copolymers may alleviate this problem. $^{\rm 4}$

When a rubbery polymer is combined with another polymer, particularly one that is normally brittle, a marked rise in fracture energy occurs.^{5,6} A well-known example is high impact polystyrene (HIPS), in which the addition of a relatively small amount of polybutadiene gives a considerable increase in elongation to failure. The failure mechanism for such polymers is crazing. The theory of multiple crazing in rubber was proposed by Bucknall and Smith.⁷ According to the theory, crazes are initiated at points of maximum principal strain, which are usually near the equator of the rubber particles, and then propagate outward along the plane of maximum principal strain. The process is terminated when the stress concentra-

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tion falls below the critical level for propagation, or when a large particle or an obstacle is encountered. Adhesion between the rubber particle and the PS matrix is critical. If the bond between rubber and PS were not a strong one, a void would form at the interface, and a crack would be initiated, lowering the toughness.^{2,8} In a previous study,²⁷ for quenched blends with a constant phase volume rubber, it was found that diblock copolymers were effective in impact modification provided both block lengths were near or above the entanglement molecular weight. This article studies the effect of triblocks as compatibilizers for bulk blends, and the effect of rubber phase volume on the high speed Izod test. Also, fracture surfaces have been studied and the role of compatibilization and rubber content have been qualitatively defined. Finally, blends of diblock compatibilized PS/PB with commercial HIPS have been prepared and their impact strength reported.

It has been observed that the impact strength increases with increasing rubber phase volume. However, the increase in not linear. Wang, Matsuo, and Kwei⁹ performed a study of crazing using balls of various materials. They tested polystyrene with rubber and steel balls, and found that, consistent with Goodier's analysis,¹⁰ crazes initiated at points of maximum stress concentration. The stress concentration for the rubber balls was confined to small angles around the equator, perpendicular to the direction of the applied stress. More importantly Matsuo, Wang, and Kwei¹¹ found that the interaction of the stress fields between two balls was not additive, but of a higher order. When the balls were placed close together (L/d < 1.45), where L is the center to center distance, and d is the diameter of the balls), crazes were initiated at even lower stress levels than before. The initiation stress decreased linearly as the balls were moved close together. In

other words, stress field interaction helped to make the material tough by formation of a large number of crazes, thereby releasing the external load in the form of strain energy. Wu¹² also investigated stress field interactions and stated that, when rubber particles are sufficiently close, the stress field is no longer simply additive. Grocela and Nauman¹³ showed that a critical interparticle distance was needed for toughening in high speed impact tests. Grocela and Nauman,¹⁴ based on the work of Matsuo, Wang, and Kwei¹¹ and Wu,¹² explained that this was the nearest neighbor distance in a plane of thickness d/2. The distance found by numerical simulations was 1.003 d. Thus, at a minor phase volume above 7%, the nearest neighbor distance in a plane is less than one particle diameter. This results in a stress field interaction with the neighboring particles and as a consequence, the rubber particles provide good impact modification in high speed tests such as Izods.

Cook, Rudin, and Plumtree¹⁵ showed that, with increasing rubber, and hence, decreasing interparticle distance, and increasing particle size, the impact strength went up. Earlier Hall¹⁶ calculated an interparticle distance for HIPS, and found that reduced distance and higher minor phase volume correlated to increased Izod impact. Turley and Keskkula¹⁷ found that impact strength was a linear function of the phase volume. However, these studies were conducted for phase volumes between 20-45%. Wu¹² showed that the tough-brittle transition occurred at the interparticle distance of 0.304 μ m, based on experiments for rubber phase volumes between 12.8 and 40.8%. Grocela and Nauman¹³ showed that 7% phase volume rubber was the critical value to achieve impact modification in the Izod test. Their results were based on extrapolations for three different rubber-modified PS blends with varying phase volumes.

| Material | Manufacturer | Molecular Weight (M_w) | | |
|-----------------------------|--------------------------|--------------------------|--|--|
| Polystyrene GP Polystyrene | Novacor Chemical Company | 202,000 | | |
| Polybutadiene Diene® 55NF | Firestone | 320,000 | | |
| HIPS Styron® 484 | Dow Chemical Company | | | |
| PS-PB Diblock Stereon® 730A | Firestone | 154,000 | | |
| PS-PB Triblock Kraton® 1101 | Shell Chemicals | 246,000 | | |
| PS-PB Triblock 530A | Fina Oil and Chemical | 120.000 | | |
| PS-PB Triblock 520A | Fina Oil and Chemical | 110,000 | | |

| | Table I | Materials | Used |
|--|---------|-----------|------|
|--|---------|-----------|------|

| Polymer | ${\rm Total} \\ M_n$ | $\begin{array}{c} \text{PS Block} \\ M_n \end{array}$ | PB Block M_n |
|---------|----------------------|---|----------------|
| 730A | 140,000 | $33,000 \ 2	imes 27.000$ | 98,000 |
| 1101 | 223,000 | | 155.000 |
| 530A | 104,000 | $2 \times 40,000$ | 24,000 |
| 520A | 96,000 | $2 \times 35,000$ | 25,000 |

Table II Block Segment Lengths

EXPERIMENTAL

Materials

Table I gives the various starting polymers used, their molecular weights, and their manufacturers. All the materials 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 40% *cis*, 50% *trans*, and 10% *vinyl* contents. The triblocks (PS-PB-PS) and diblocks (PS-PB) obtained are fairly monodisperse, ~ 1.1 . Table II gives the block lengths of these copolymers. 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 a common solvent, xylene, and a homogeneous solution was obtained. This single phase solution was heated to a temperature of 230–260°C, and quenched under a vacuum of 5 Torr to remove the solvent. The total minor phase (PB) volume was varied from 3–23%. The various blends produced are listed in Table III, with their compositions, modulus, and maximum Izod obtained. After the quench, the blend contained a small amount of

| Table III | Maximum | Izod | Strengths, | and | Modulus | for ` | Various | Blend | Com | ositions |
|-----------|---------|------|---|-----|---------|-------|---------|-------|-----|----------|
| | | | ···· · · · · · · · · · · · · · · · · · | | | | | | | |

| Blend | %PS | % PB | % Block | %HIPS | Modulus (GPa) | Maximum Izod (ftlbf./in.) |
|----------------------------|------|---------|------------|-------|------------------|------------------------------|
| PS | 100 | | | | 3.73 | 0.4 |
| PS/PB | 77 | 23 | | | 2.37 | 0.6 |
| HIPS | | | | 100 | 2.18 | 1.5 |
| PS/PB/730A | 96.7 | 2.1 | 1.2 | | 3.34 | 0.4 |
| (variable rubber) | 92.2 | 5.0 | 2.8 | | 3.12 | 0.4 |
| ((allabic lassel) | 83.4 | 10.6 | 6.0 | | 2.62 | 2.65 |
| | 74.5 | 16.4 | 9.1 | | 2.21 | 6.2 |
| PS/PB/1101 | 96.7 | 2.1 | 1.2 | | na | 0.5 |
| (variable rubber) | 92.2 | 5.0 | 2.8 | | na | 0.47 |
| (, | 83.4 | 10.6 | 6.0 | | na | 1.2 |
| | 74.5 | 16.4 | 9.1 | | 2.11 | 3.8 |
| PS/PB/1101 | 75.8 | 20.2 | 4.0 | | na | 2.9 |
| (23% rubber) | 74.5 | 16.4 | 9.1 | | 2.11 | 3.8 |
| | 73.6 | 13.7 | 12.7 | | na | 3.2 |
| | 72.1 | 9.8 | 18.1 | | na | 3.2 |
| HIPS/PS/PB/7 | 74.5 | 16.4 | 9.1 | 0.0 | 2.21 | 5.82 |
| 30A | 67.1 | 14.8 | 8.1 | 10.0 | 2.27 | 5.25 |
| (HIPS/PS) | 55.9 | 12.3 | 6.8 | 25.0 | 2.37 | 4.50 |
| (23% rubber) | 37.3 | 8.2 | 4.5 | 50.0 | 2.48 | 3.23 |
| | 18.6 | 4.1 | 2.3 | 75.0 | na | 2.76 |
| | 7.5 | 1.6 | 0.9 | 90.0 | 2.49 | 2.41 |
| | _ | | | 100.0 | 2.50 | 2.40 |
| PS/PB/520A (23% rubber) | 69.7 | 20.3 | 10.0 | — | na | 2.67 |
| PS/PB/530A | 73.7 | 22.3 | 4.0 | | 2.20 | 5.2 |
| (23% rubber) | 71.2 | 21.3 | 7.5 | | 2.17 | 5.6 |
| | 65.6 | 19.4 | 15.0 | _ | na | 1.5 |
| | 54.0 | 15.5 | 30.5 | _ | 1.81 | 0.75 |

solvent that was removed by further devolatilization. After drying, the blend was ground to a powder. The final solvent content was 600–1000 PPM. The mean particle size and the concentration of the copolymer at the interface was varied at this stage by ripening at 200°C and 10,000 psi for various times in a Carver press. The reference HIPS sample was also molded for various times, although no growth in particle size was detected.

Characterization

At least six Izod bars obtained from the Carver press were notched and tested with a 3 lb. hammer at 25°C.¹⁸ Samples were prepared in accordance with ASTM-256 standards, with dimensions of $2.5 \times 0.5 \times 0.125''$. The blends were notched on a TMI model 22-05 and impact tested on a TMI 43-1, both from Testing Machines Inc., Amityville, NY. The tensile modulus was measured using an Instron 4204 tensile testing machine with a 0.5 in. extensometer attachment and a 5 kN load cell.¹⁹

A JEOL 35 CF JSM scanning electron microscope (SEM) was used to examine the morphology of the fracture surface of the molded blends. The



Figure 1 Impact strength as a function of ripening time at 200°C for varying rubber content with the 730A diblock copolymer.



Figure 2 Impact strength as a function of ripening time at 200°C for varying rubber content with the 1101 triblock copolymer.

broken sample was carefully removed from the vice of the impact tester so that the surface was not altered. A thin layer (~ 100 Å) of gold was sputtered onto the surface to minimize charging. The fracture sample was attached to the SEM sample holder with silver paint and left in the vacuum oven for 45 min before imaging. Surface scans of fractured surfaces were also done using an Autoprobe CP Atomic Force Microscope, from Park Scientific Instruments, Sunnyvale, CA. Contact mode scanning with sharpened Type A microlevers was used.

Molded samples were cut, shaped to form a pyramid, and stained for 2 weeks in 4% aqueous osmium tetraoxide.²⁰ Thin sections were cut to 800 and 7,500 Å using a Reichert-Jung UltracutE Ultramicrotome with a diamond knife. Morphologies were examined under a 100 KeV beam using a Philips CM12 TEM and AEI Mark IV HVEM at 1.2 MeV.

Solvent in the final blend was measured using a Perkin-Elmer Thermogravimetric Analyzer, TGA 7, interfaced to an automatic computer-controlled data acquisition system by a thermal analysis controller, TAC 7/DX.

RESULTS AND DISCUSSION

Effect of Rubber Content

Blends were prepared with varying total rubber content while maintaining the same ratio of block-to-pure rubber (see Table III). Figure 1 shows the impact strength of the PS/PB/730A blends for various ripening times as a function of rubber content. The impact strength is unchanged from that of the PS reference until 7% volume fraction of the rubber phase is reached. Figure 2 shows the data for the PS/PB/1101 triblock blend for various ripening times as a function of rubber content. Again, no improvement in impact strength is observed until approximately 7% rubber phase volume. Schwier, Argon, and Cohen²¹ found that the elongation to fracture dropped precipitously when the rubber content fell below 6% for tensile tests. They attributed it to the lack of cavitation below 6% phase volume rubber. Previously, Grocela, and Nauman¹³ found similar results for impact for three different blend systems. The current results confirm their conclusion that 7% minor phase volume is required for impact modification as measured in a high speed



Figure 3 Impact strength as a function of ripening time at 200°C for various block copolymer blends with 23% overall rubber phase volume.



Figure 4 Impact strength as a function of ripening time at 200°C for different 1101 triblock concentrations.

test. The increase in Izod after 7% rubber content is attributed to overlapping stress fields. Low speed tests, and particularly the integral under the stress–strain curve of a tensile test can show improvements in toughness at lower rubber concentrations.^{13,22}

Effect of Compatibilization

Figure 3 shows the impact strength as a function of ripening time for various experimental blends and for PS, PS/PB, and HIPS references. All the experimental blends in this section contained 23% rubber phase volume with the polybutadiene coming from the pure rubber, or the rubber portion of the diblocks and triblocks. The experimental blends were all compositionally quenched. The PS and HIPS references were molded from the pellets as received.

For comparison with triblocks and other blends in this article, results are included for the PS/PB/ 730A (74.5/16.4/9.1) system, which gave the highest notched Izod previously.²⁷

A lower impact strength of 3.8 ft.-lbf./in. was obtained for PS/PB/1101 (74.5/16.4/9.1), even though the block lengths were substantially higher than the entanglement molecular weights.²³ Lower





Figure 5 TEM micrograph of PS/PB/1101 blend containing excess triblocks. Scale bars represent: (a) 250 µm, (b) 250 µm, (c) 100 µm, (d) 500 µm.

Izods, compared to the 730A blend, are attributed to the very high molecular weight of the 1101 block, which may result in low interfacial concentration due to steric hindrance, and the fact that 1101 is a triblock.²⁴

Figure 4 shows the effect of varying D1101 triblock concentration as a function of ripening time for blends containing 23% total PB. The maximum Izod was obtained for the 9.1% triblock. Figure 5 shows some representative micrographs of secondary structures that are formed when an excess triblock is present. Because the PB block is much longer than PS block, all the secondary structures are formed within the PB particles. Figure 5(a) and (b) shows internal phase separation in the bulk PB particle. A mixture of cylindrical domains and alternating la-

mella seems to have been formed. These are similar to morphologies obtained by Matuso using SBS copolymers solution cast from toluene.²⁵ Figure 5(c) and (d) are lamella formed at the interface with TEM cuts vertical and horizontal to the direction of the block. Washiyama et al. found that, for PS/PVP blends, the lamellar interfaces were much weaker than the saturated homopolymer interface.²⁶ Thus, the lower maximum strength of the high copolymer blends (12.7 and 18.1%) is attributed to the formation of secondary structures, while the poor results found at the 4% triblock concentrations is attributed to the lack of interfacial saturation. Similar results have been obtained for diblock copolymers, and were the subject of an earlier study.²⁷

Figure 6 shows the effect of varying the 530A triblock concentration as a function of ripening time for blends containing 23% total PB. The best results were obtained for PS/PB/530A (71.2/21.3/ (7.5) containing a (7.5) triblock, with an impact strength of 5.6 ft.-lbf./in. and a modulus of 2.17 GPa. When more than a 7.5% copolymer was added, the Izod strengths were poor. Similar trends have been previously obtained for varying the diblock amount.²⁷ With increasing the copolymer amount, the ripening times to obtain maximum Izod value decreased. For 4, 7.5, 15, and 30.5%, the corresponding ripening times were 420, 360, 240, and 120 min. A marginally lower molecular weight triblock, 520A, was also used with a composition of PS/PB/520A (69.7/20.3/ 10.0), and a reasonable impact strength was obtained.

The results in Figure 3 include a quaternary blend of two different copolymers with PS and PB homopolymers. The maximum Izod value for a 50/50 blend of 730A diblock and 1101 triblock was achieved at a lower time, and was equivalent to that of the 730A diblock. This suggests possible synergism in blends of various compatibilizers allowing high Izods and lower ripening times.



Figure 6 Impact strength as a function of ripening time at 200°C for different 530A triblock concentrations.





Figure 7 SEM of fracture surface at 25°C for PS molded at 200°C for 3 min. Scale bar: (a) 50 μ , (b) 2μ .

Fracture Studies

The fracture surfaces for the various blends have been studied to provide an insight into the difference in toughness. Figures 7, 8, and 9 are the fracture surfaces for the reference materials. Figure 7(a) and (b) shows the fracture surface for unmodified polystyrene. Figure 7(a) shows large plane areas with sharp, brittle fractures in various planes. Figure 7(b) is a magnified cleaved surface. No deformation is observed. The impact strength was 0.4 ft.-lbf./in. Figure 8(a) and (b)



(a)



Figure 8 SEM of fracture surface at 25°C for HIPS

molded at 200°C for 3 min. Scale bar: (a) 50 μ , (b) 2 μ .

shows the fracture surface for HIPS. Both figures show a fairly intricate fracture pattern resulting in the high impact strength of 1.5 ft.-lbf./in. Figure 9(a) shows the fracture surface for PS/PB (77/23). A surface similar to 8(a) is observed. However, when magnified, a different pattern appears. Figure 9(b) and 9(c) shows holes corresponding to the rubber particles. The number of holes on the fracture surface is higher than would be expected for 23% rubber phase volume. This is attributed to the fact that the crack preferentially propagates through regions of high stress caused by the rubber particles. Because no adhesion exists between the particle and the matrix, the crack changes direction upon coming in contact with a rubber particle. Judging by the fracture surface, it appears that the crack propagates around the rubber particles through the PS matrix in the shortest possible distance. The lack of



(a)





(c)

Figure 9 SEM of fracture surface at 25°C for uncompatibilized PS/PB (77/23) molded at 200°C for 3 min. Scale bar: (a) 50 μ , (b) 10 μ , (c) 2 μ .

adhesion at the interface of the homopolymers leads to the low impact strength of 0.6 ft.-lbf./in.

Figures 10 and 11 show fracture surfaces of compatibilized blends containing 23% rubber. Figure 10(a) shows small bands of fracture for PS/PB/730A (74.5/16.4/9.1). Almost all the area has an intricate fracture pattern, with no large brittle area observed. Higher magnification [Fig. 10(b)] shows the number of holes to be lower than in Figure 9(b), and approximately equal to the number expected for the 23% rubber phase. The holes are also approximately six times smaller in size. This is attributed to a reduction in ripening rate caused by the block copolymer, and is consistent with TEM particle size measurements.²⁷ Fig-





Figure 10 SEM of fracture surface at 25°C for PS/ PB/730A containing 23% molded at 200°C for 3 min. Scale bar: (a) 50 μ , (b) 2 μ .



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Figure 11 SEM of fracture surface at 25°C for PS/ PB/730A containing 23% molded at 200°C for 240 min. Scale bar: (a) 50 μ , (b) 2 μ .

ure 11 shows the surface structure when the blend was ripened for a higher time of 240 min. Figure 11(a) shows an intricate fracture pattern, and Figure 11(b) reveals a large amount of plastic deformation with a highly developed fracture surface. A high-impact strength of 5.9 ft.-lbf./in was attributed to the large particles and higher copolymer chain density at the interface compared to the blend ripened for 3 min.²⁷

Figure 12 shows scans of fracture surfaces obtained with the atomic force microscope. Table IV gives the associated statistical data. The mean height is the average of all the data points with reference to the lowest point on the surface. The peak-to-valley ratio gives the depth between the single highest and lowest points on the fracture surface. The ratio between the actual area of the rough fracture surface to the surface area assuming a flat plane is the projected area ratio. The root-mean-square roughness is given by the stan-



Figure 12 AFM of fracture surface area of 2.5 \times 2.5 μm at 25°C for: (a) PS/PB (77/23) molded for 3 min, (b) PS/PB/730A (74.5/16.4/9.1) molded for 3 min, (c) PS/PB/730A (74.5/16.4/9.1) molded for 240 min.

dard deviation of the data. The most striking aspect of the results in Table IV is the strong negative correlation between Izod and surface roughness, as characterized by mean height, peak-to-valley or root-mean-square distances. The fracture surfaces for the uncompatibilized blend has a substantial vertical range, and as observed in Figure 9(b), contacts many more particles than would lie in a single plane. The observations reinforce the view that uncompatibilized rubber particles, and presumably even voids, are good craze initiators but poor craze terminators. In the absence of termination, the crazes grow to cracks, creating a large surface area but absorbing little energy. The projected area is marginally higher for the compatibilized blend and increases upon ripening. A higher projected area, combined with a low roughness value, would imply that more, finer features are present on the surface on a microscopic scale. Presumably, these represent the effects of plastic deformation and craze termination in the region near the PS/PB interface. Figure 12 qualitatively confirms this conclusion, as do the lower magnification scans in Figure 13.

The effect of varying rubber content is illustrated in the next two figures and in Figure 10. Figure 14(a) shows the very plain SEM fracture surface for a PS/PB/730A (96.7/2.1/1.2) blend containing 3%

| | Uncompatibilized PS/PB (77/23) Ripened for 3 Min | PS/PB/730A (74.5/16.4/9.1) Ripened for 3 Min | PS/PB/730A (74.5/16.4/9.1) Ripened for 240 Min |
|----------------------------|--|--|--|
| Mean height | 10,900 Å | $4,\!253{ m \AA}$ | 3,427 Å |
| Peak to valley | 19,900 Å | 8,119 Å | 7,117 Å |
| Projected area ratio | 1.46 | 1.67 | 1.71 |
| Root mean square roughness | 2363 Å | 1142 Å | 870 Å |
| Observed izod (ftlbf./in.) | 0.6 | 3.0 | 5.9 |

Table IV AFM Surface Analysis Data



Figure 13 AFM of fracture surface area of $5 \times 5 \mu m$ at 25°C for: (a) PS/PB (77/23) molded for 3 min, (b) PS/PB/730A (74.5/16.4/9.1) molded for 3 min.

rubber. There are bands of brittle fracture, but higher magnification [Fig. 14(b)] reveals that there is also some crazing. The crazes typically encircle a hole. They sometimes bifurcate. They typically have a free end within the matrix polymer. The holes correspond to the expected number and size of rubber particles. Even though the adhesion is good between the rubber particles and the matrix, the number of particles is too low to give stress field interactions. Thus, propagating crazes are not channeled between particles, but either terminate in the matrix or become cracks before significant energy is absorbed. As a result, an impact strength of 0.4 ft.-lbf./in. was obtained, which is equivalent to unmodified PS. Figure 15 shows the same rubber blend system but with 15% total rubber. The fracture surface in Figure 15(a) also exhibits bands of brittle fracture; however, the surface is more highly developed with a higher fracture density compared to Figure 14(a). The holes observed in Figure 15(b)correspond to the expected number and size of the rubber particles. The onset of plastic deformation is also observed. A few areas in the matrix appear to have yielded and pulled out, but there is also a large number of surface cracks. The Izod is only marginally higher than that of unmodified PS. Figure 10 shows the SEM fracture surface for the PS/PB/730A blend with 23% total rubber. The particle size is suboptimal, but the Izod has increased to 3.0 ft.-lbf./ in. Significant plastic deformation is observed. Again, the sample shows holes that correspond to the expected number and size of rubber particles as observed in TEM studies.²⁷

HIPS Blends

Figure 16 shows the impact strength as a function of ripening time at 200°C for various HIPS

blends. The quenched blends in this section contain 23% minor phase volume overall, and can be





Figure 14 SEM of fracture surface at 25°C for PS/ PB/730A containing 3% rubber molded at 200°C for 3 min. Scale bar: (a) 50 μ , (b) 2 μ .





(b)

Figure 15 SEM of fracture surface at 25°C for PS/ PB/730A containing 15% rubber molded at 200°C for 3 min. Scale bar: (a) 50 μ , (b) 2 μ .

considered as binary mixtures of a pure HIPS and the PS/PB/730A (75.5/16.4/9.1) blend that performed best on the Izod test. Note that the minor phase in HIPS consists of a continuous PS phase, and a second phase, which is possibly also continuous, of occluded PS (see Fig. 17). The occluded PS is counted as part of the minor phase volume.

No synergistic effects of blending or particle bimodality were observed. The quenched HIPS had a impact strength of 2.4 ft.-lbf./in. and a modulus of 2.50 GPa. The higher modulus and impact strength of the quenched HIPS compared to 1.5 ft-lbf./in. and 2.18 GPa for the virgin pellets is surprising and unexplained. Also surprising is the minimum in impact strength for the blend containing 10%HIPS ripened for 3 min. At higher ripening times, the impact strength was a monotonically decreasing function of the HIPS content. Figure 17 shows a HVEM micrograph for a blend containing 75%HIPS ripened for 3 min. Because the sections are thicker than conventional TEM samples, the particle overlap is quite extensive, and the minor phase volume appears higher than 23%. The figure shows one large, highly occluded HIPS particle with many solid rubber particles that are smaller by a factor of about 10. Figure 18 shows a representative TEM micrograph for a blend containing 50% HIPS ripened for 2 h. The solid rubber particles are much larger, but remain somewhat smaller than the HIPS particles.

CONCLUSIONS

For effective impact modification, the minimum phase volume of rubber was found to be 7% using notched Izod tests. This result was independent of particle size, type of compatibilizer, and amount of compatibilizer at the interface. This confirms the theory that stress field interactions result in controlled craze formation leading to high toughness of the blend.

It was found that triblocks were effective in improving impact strength, but not as good as



Figure 16 Impact strength as a function of ripening time at 200°C for various HIPS/copolymer blends with 23% overall rubber phase volume.

diblock copolymers. The maximum strengths were higher than commercial HIPS (>1.5 ft.-lbf./ in.). It was observed that the blocks must be long enough to entangle, but not so long as to lower the interfacial chain density due to steric effects. A higher PB block length for rubber in the 530A triblock may yield higher impact strengths, consistent with the results for 730A diblock. Based on previous works of Cavanaugh et al.,¹ and Mathur and Nauman²⁷ for rubber-modified polystyrene blends in bulk, the following general conclusions can be drawn for the effectiveness of various compatibilizers of medium molecular weight (80,000–300,000 total):

Diblocks > Triblocks > Multiblocks > Randoms.

No synergy was observed for the HIPS blends prepared with the 730A blends and pure HIPS. This was surprising, because previous works have indicated that particle size bimodality gives impact strengths higher than the starting, individual blends.^{28,29} Hobbs²⁸ obtained a maximum impact strength for a blend containing 20% small particles. Okamoto et al.²⁹ further stated that the greater the difference is between particle sizes of blends, the higher the Izod impact strength. Our results show no such trend. It was observed that for increasing particle size difference (3-min ripening time), detrimental results were obtained for blends rich in small particles, 0 < % HIPS < 50.

The fracture surfaces showed that a high amount of plastic deformation was necessary for high-impact strengths. The high RMS roughness



Figure 17 TEM of a HIPS/PS/PB/730A (75/18.6/4.1/ 2.3) blend molded at 200°C for 3 min. Scale bar is 1 μ m.



Figure 18 TEM of a HIPS/PS/PB/730A (50/37.3/8.2/ 4.5) blend molded at 200°C for 240 min. Scale bar is 1 μ m.

for the uncompatibilized blend showed that the impact strength is not a function of roughness or amount of PS surface area created. The negative correlation with roughness serves as strong evidence that energy dissipation is not associated with creation of a surface area as such. Other mechanisms, like crazing and plastic deformation, are needed for tough blends.

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