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The study of various styrene–butadiene copolymers as compatibilisers in bulk blends of polystyrene/polybutadiene

Timothy J. Cavanaugh[a], **K. Buttle**[b], **J.N. Turner**[b] **and E. Bruce Nauman**[a,*]
[a] *The Isermann Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA*
[b] *Wadsworth Center, New York State Department of Health, Albany, NY 12221, USA*
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Bulk blends, produced by compositional quenching, were used to examine the effectiveness of different styrene–butadiene copolymers as interfacial agents in blends of polystyrene (PS) with polybutadiene (PB). Each polymer blend was compression molded for various times to allow particle ripening and was then tested for impact strength. The most effective compatibiliser proved to be a long, asymmetric diblock, which could entangle in both homopolymer phases. Diblocks with short PS segments were inadequate as interfacial agents, presumably because their short PS blocks were easily pulled from the matrix. Random copolymers with a composition near 50/50 were successful as interfacial agents, but the impact strength declined with a decrease in PS composition of the copolymer. A commercial multiblock copolymer, Phillips K-Resin®, also proved to be reasonably effective compatibiliser, giving better impact strength than the HIPS control. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: compatibiliser; adhesion; polymer blend)

INTRODUCTION

The blending of existing polymers is a successful means of creating new materials at a low cost. There are many advantageous reasons for blending[1,2]. The performance of an expensive resin can be extended by mixing it with a low cost polymer. A material with a full set of desired properties can be produced to meet a consumer's specifications. A brittle matrix can be modified to improve toughness by the addition of a rubbery polymer. In improving toughness, the blending of two immiscible polymers rarely results in a material with favourable properties. The polymer pairs typically separate into microscopic domains that have high interfacial tension and poor interfacial adhesion. Because rubber–matrix adhesion is an important factor in influencing toughness of a brittle polymer[2,3], the material will have poor mechanical properties.

The problem of poor interfacial adhesion can be alleviated with the addition of a compatibiliser or interfacial agent. The properly chosen compatibiliser will preferentially locate at the interface between the two immiscible polymers and will serve two functions. Besides promoting adhesion, the compatibiliser acts as a surfactant to stabilise the microstructure of the blend. Ideally, this component should be a block or graft copolymer, the segments of which are chemically identical to the two phases.

From recent studies[4–12], the reinforcement of the interface depends on the molecular weight of each block (M_A and M_B), the areal chain density (the number of chains per unit area) at the interface, Σ, and the entanglement molecular weights (M_{eA} and M_{eB}) of the two homopolymers. The deformation mechanisms can be summarised as follows:

(1) Chain pull-out, where the shorter block pulls out from one of the homopolymer phases, occurs if either $M_A < M_{eA}$ or $M_B < M_{eB}$.

(2) When $M_A \gg M_{eA}$ and $M_B \gg M_{eB}$ and when the areal chain density of the block copolymer is small, chain scission of the block copolymer, where the block copolymer breaks near the joint in the block, occurs before any significant amount of plastic deformation takes place.

(3) At higher Σ and when $M_A \gg M_{eA}$ and $M_B \gg M_{eB}$, the interface fails by large-scale plastic deformation. The interface first fails by forming a craze in the homopolymer that has the lower crazing stress, and subsequent failure occurs by chain scission, disentanglement, or by both mechanisms.

The most important regime is (3). The fracture toughness of a material is markedly enhanced when large-scale plastic deformation occurs.

Recently, random copolymers have received substantial attention as possible interfacial agents. Theoretical work by Balazs and co-workers[13,14] studied the behaviour of a single random copolymer chain at a liquid–liquid interface. From numerical simulations, they determined that the random copolymer forms large loops as it weaves back and forth across the interface, and that the maximum interfacial strength should be obtained for a random copolymer containing an equal number of A and B units[13]. Gersappe and Balazs[15] then examined a finite volume fraction of copolymer at the homopolymer–homopolymer interface, as opposed to a single chain. Using a mean field model, they determined that the random copolymer was localised at the interface and reduced interfacial tension. However, the block copolymer was most efficient in reducing the interfacial tension, with 50/50 random and alternating copolymers showing nearly identical results.

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[*] To whom correspondence should be addressed

Table 1 Materials used in this study

Polymer	Abbreviation	Source	Characteristics	Maximum Izod ft-lb$_f$ in^{-1} (J m^{-1})
Polystyrene	PS	Novacor Chemicals Ltd.	$M_n = 82\,000$ $M_w = 202\,000$	—
Polybutadiene	PB	Firestone Diene® 55NF	$M_n = 130\,000$ $M_w = 320\,000$ 40% *cis* 50% *trans* 10% vinyl	0.63 (35)
SB Diblock	D730A	Firestone Stereon® 730A	$M_n = 148\,000$ $M_w = 182\,000$ 30% bound PS 23% block PS	5.91 (315)
SB Diblock	D210	Firestone Stereon® 210	$M_n = 31\,000$ $M_w = 35\,000$ 25% bound PS 23% block PS	0.67 (36)
SB Diblock	D142	Enichem Europrene® Sol S142	$M_n = 77\,000$ $M_w = 89\,000$ 70% bound PS 46% block PS	8 wt% 2.38 (127) 6 wt% 2.88 (154) 4 wt% 2.00 (107)
SB Diblock	D183	Enichem Europrene® Sol S183	$M_n = 95\,000$ $M_w = 109\,000$ 10% bound PS 5% block PS	0.70 (38)
SB Multiblock	MB5	Phillips 66 K-Resin® KR05NW	$M_n = 86\,000$ $M_w = 155\,000$ 75% PS	2.19 (117)
SB Random	R706	Firestone Duradene® 706	$M_n = 106\,000$ $M_w = 365\,000$ 23.5% Bound PS 11% vinyl	0.75 (40)
SB Random	R715	Firestone Duradene® 715	$M_n = 121\,000$ $M_w = 406\,000$ 23.5% Bound PS 42% vinyl	0.88 (47)
SB Random	R740	Firestone Duradene® 740	$M_n = 146\,000$ $M_w = 328\,000$ 17% Bound PS 46% vinyl	0.82 (44)
SB Random	R7627	Firestone Duradene® SR-7627	$M_n = 294\,000$ $M_w = 592\,000$ 40% Bound PS 36% vinyl	1.60 (85)
SB Random	R1028	Goodyear Tire and Rubber Plioflex® 1028	$M_n = 140\,000$ $M_w = 415\,000$ 48% bound PS	2.42 (129)
HIPS	HIPS	Dow Chemical Styron® 484		1.50 (80)

Experimentally, random copolymers have strengthened polymer interfaces. Brown and co-workers[7,8] investigated the fracture energy, using a spun cast PS/PMMA random copolymer layer between homopolymer sheets of PS/PMMA as well as PMMA/poly(phenylene oxide) (PPO). The joined samples were fractured using an asymmetric fracture toughness test that forces a crack to form along the interface[4]. Brown and co-workers[7,8] determined that the random copolymer was not nearly as effective at reinforcement of the interface as the block copolymers. They hypothesised that the random copolymer organised itself at the interface and formed loops in both phases.

In another study, Kramer and co-workers[16,17] examined the effectiveness of deuterated-PS$_f$/poly(2-vinylpyridine)(PVP)$_{1-f}$ random copolymers, where f is the monomer fraction of styrene, as interfacial agents. They found, using films, that extremely long random copolymers, where $f = 0.48$, were more effective in strengthening the interface than a long symmetric block copolymer. Also, for the case of $f = 0.48$, 50% of the dPS was found to be on the PS side of the

Table 2 Diblock lengths

Polymer	Total M_n	PS Block M_n	PB Block M_n
D730A	148 000	35 000	113 000
D142	77 000	35 000	42 000
D183	95 000	5000	90 000
D210	31 000	7000	24 000

fracture. As f increased from 0.48 to 0.77, the effectiveness decreased considerably.

Russell and co-workers[18,19] studied the distribution of a random copolymer at the interface between two homopolymer phases, as a function of f and as a function of the Flory–Huggins interaction parameter, χ. Using Monte Carlo simulations, they found a symmetric distribution of the copolymer at the interface for a compositionally symmetric copolymer ($f = 0.5$), when χ was not a function of concentration. For the case of an asymmetric copolymer ($f = 0.67$), a symmetric distribution of copolymer at the interface can only exist when χ is a function of composition. Their predicted results showed agreement with experiments performed with PS/PMMA systems strengthened with PS/PMMA random copolymers.

Here, we examine the impact strengths of bulk blends produced by compositional quenching[20]. PS, a brittle matrix, is blended with PB to produce a microdispersion of rubber particles. We also add their corresponding copolymer (diblock, multiblock, or random) in an attempt to improve interfacial strength. We believe that the multiblock possesses short block lengths that will 'weave' back and forth across the interface similar to the model for the random copolymer. The focus of this work is on the relationship between the molecular structure of the copolymer and its effectiveness as a compatibiliser, which is measured in terms of Izod impact strength. The Izod impact test is a widely used method of measuring fracture resistance in toughened polymers. It is a high-speed test that is particularly sensitive to the degree of adhesion in polymer blends.

EXPERIMENTAL

Materials

Table 1 summarises the materials and their abbreviations used here. The homopolymers and copolymers used in this study were all commercial products. The PS is a general purpose grade supplied by Novacor Chemicals Limited. The polybutadiene rubber, Diene® 55NF, was acquired from Firestone. The compatibilisers used in this study were based on styrene–butadiene. The overall fraction of PS in the diblock is given as bound PS, while block PS is the fraction of PS block in the copolymer. The difference between bound PS and block PS is caused by a tapering zone between the PS and PB blocks. The *cis*, *trans*, and vinyl percentages refer to the PB portion of the polymer. As shown in *Table 2*, the diblock copolymers have different block lengths. The PB block lengths may be smaller because of the presence of the tapering zone. Most random copolymers were supplied by Firestone. The R1028 was supplied by Goodyear. The R706, R715, and R740 contain < 25% PS while the R7627 and R1028 consist of 40% and 48% PS, respectively. The K-Resin® (KR05NW) is a multiblock S–B copolymer that is approximately 75% PS. For comparison, we obtained a high-impact PS(HIPS) from Dow Chemical.

Blends preparation and characterisation

Homogeneous mixtures of different components were made by dissolving the polymers in xylene. The total concentration of polymers was 3%–5% by weight. To remove the solvent, the mixture was heated and then flashed into a vacuum chamber at a pressure of approximately 5 Torr[20,21]. The resulting polymer blend contained a small amount of solvent that was removed by further devolatilisation. The dried blend was ground into a powder and charged into a hot mold in a Carver hydraulic press. The powder was molded into Izod bars at 200°C and 200 p.s.i. for various times. The molding time began when the press was closed and ended when the sample was quenched into an ice bath. Following ASTM 256[22], the bars were then notched and tested for impact strength. Similarly, the HIPS pellets were compression molded and tested.

The specimens having no compatibiliser or block copolymers as the compatibiliser were immersed for 2 weeks in 4% aqueous solution of osmium tetraoxide (OsO_4)[23]. The sections were cut to approximately 0.75 μm in thickness using a Reichert-Jung Ultracut E ultramicrotome with a diamond knife. Samples containing a random copolymer as a compatibiliser were cryomicrotomed, at a temperature of − 120°C, to a thickness of approximately 0.75 μm using an RMC CR-X cryoultramicrotome. These sections were stained for 3 min with OsO_4 vapour. The morphologies of the blends were examined using an AEI Mark IV high-voltage electron microscope (HVEM) at 1.2 MeV. The negatives from the HVEM were digitised and processed to produce photographic quality images.

For the purpose of measuring particle size, the blends containing D730A were cut to 90 nm in thickness. The specimens were examined at 1.0 MeV in the HVEM. The negatives were digitised, and an observed particle size distribution was then computed from the images. A corrected particle size distribution was ascertained from the observed particle size distribution using a variation of the histogram transformation method[24], which is a correction based on slice thickness. The average particle size was then calculated from the transformed distribution. The number of particles ranged from approximately 300 at early ripening times to roughly 125 at later ripening times.

RESULTS AND DISCUSSION

For comparison with HIPS, which is comprised of 23% occluded particles, all of the blends contained 23% rubber phase volume. To ensure adequate interfacial coverage, we maintained the amount of compatibiliser at a constant weight of 8%. Blends with lower copolymer concentrations, 6 and 4 wt%, were also run for the D142 copolymer.

In compositional quenching these blends, submicron rubber particles, typically < 0.5 μm, are dispersed in the PS matrix. However, these particles are too small to effectively initiate and terminate crazes in the material, and therefore do not provide optimum toughness. Since the rubber particles are uncrosslinked, they can grow upon molding by Ostwald ripening or by coalescence mechanisms. The material will have proper toughening only when the particles have ripened to the optimum particle size[2]. The molding process does not damage the material, as can be seen in the HIPS data in *Figure 1*. The impact strength remained constant over long molding times.

The impact results of the blends containing block copolymers as interfacial agents are shown in *Figure 1*.

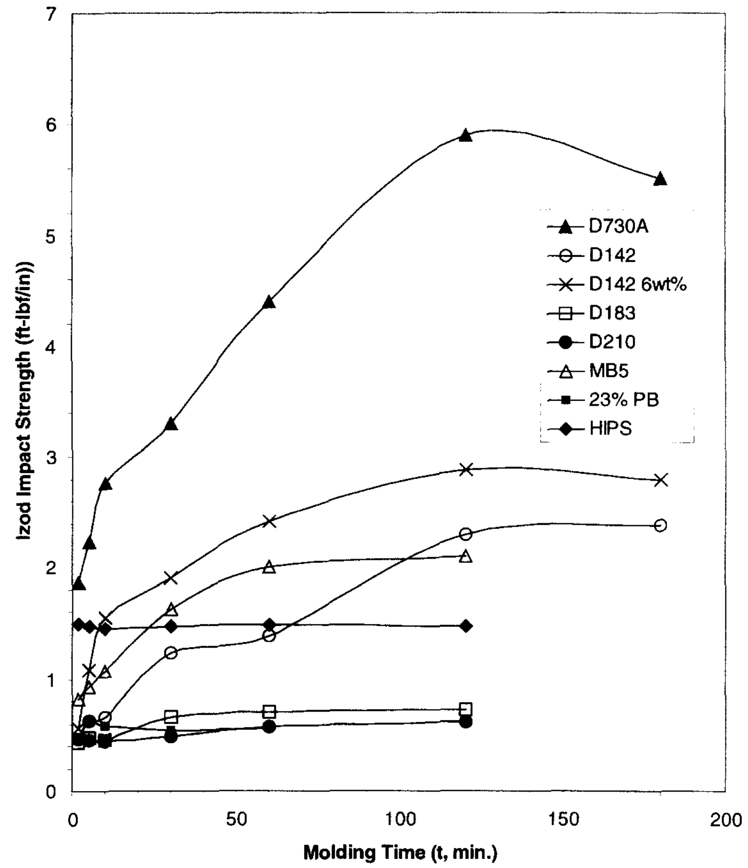


Figure 1 Impact strengths of blends containing block copolymers as interfacial agents

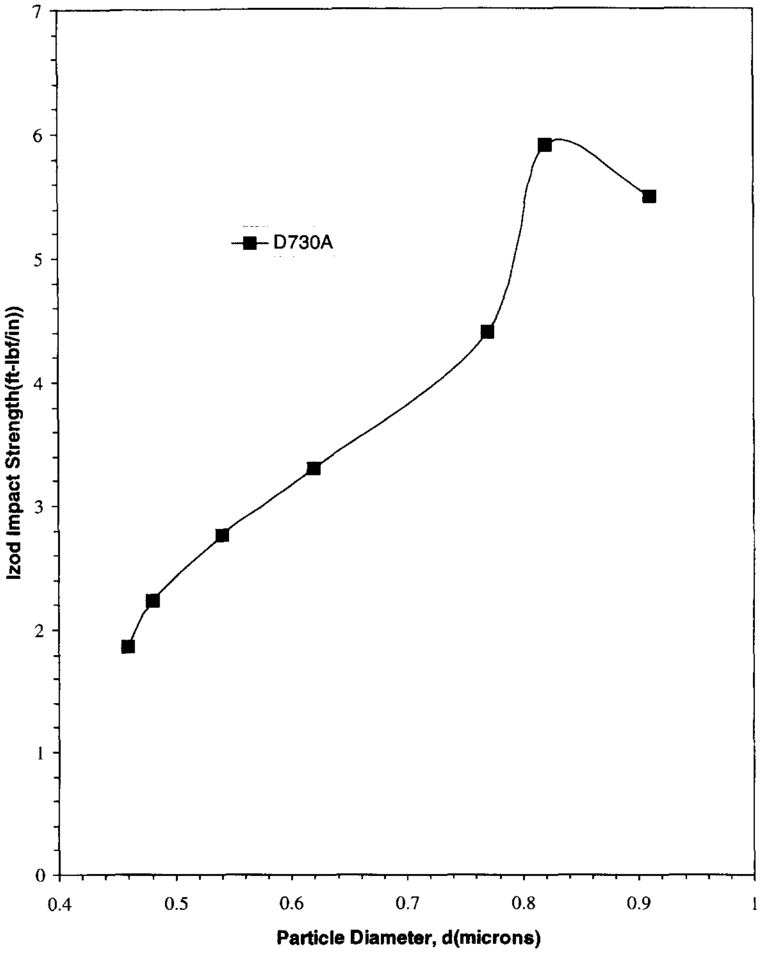
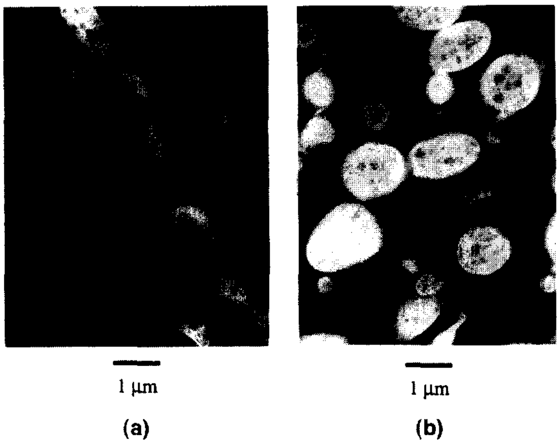


Figure 2 Impact strength *versus* particle diameter for PS/PB/D730A blends



(a) (b)

Figure 3 Micrographs of PS/PB/B730A at a molding time of 120 min (a) 90 nm thick section (b) 0.75 μm thick section

Figure 4 Lamellar interface of PS/PB/D142 blend

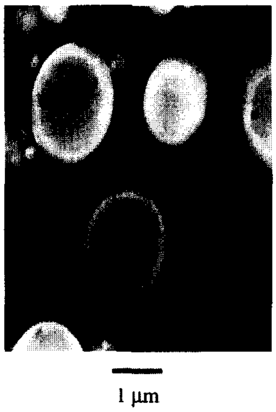


Figure 5 Micrograph of PS/PB/MB5 blend

The materials containing D730A and D142 were molded for longer times in order to reach a maximum impact strength. The blend with D730A as the compatibiliser has the greatest impact strength with a maximum at 5.9 ft-lb$_f$ in^{-1} (315 J m^{-1}). A summary of the maximum impact strengths is provided in *Table 1*. The fact that this diblock provided adequate adhesion is not surprising since both block molecular weights are greater than their corresponding homopolymer entanglement molecular weights, 31 000–35 000 for PS and 5900 for PB[25].

The maximum impact strength corresponds to an average particle diameter of approximately 0.8 μm, as seen in *Figure 2*. This value agrees with previous work[26]. However, in *Figure 3*, the particles in the thick specimen appear larger than the calculated average particle size from the thin section. This discrepancy between particle sizes in thick and thin sections has been shown previously for HIPS[27], where the average particle size in the thicker section was observed to be larger, by a factor of 2, than the thin specimen even after the transformation to account for cutting. In future work, we hope, using 3-D imaging techniques[28], to obtain an average particle size from stereopairs of thick specimens. It is important to note that, since the 0.75 μm section is much thicker than the conventional TEM samples, the rubber phase volume appears higher than 23%.

Ideally, we would like the interface to be exactly saturated with diblock and then obtain a relation between particle size and Izod strength. Since the interface is over saturated, micellisation occurs with the diblock in the PB phase, as seen in *Figure 3*. These micelles enlarge the dispersed phase volume which can increase the Izod strength. However, the presence of the PS, which is the core of the micelle, in the rubber phase can cause the modulus of the rubber particles to slightly increase and therefore may have a negative effect on impact strength.

The use of D142 as the interfacial agent showed some improvement in impact strength, with a maximum Izod of 2.4 ft-lb$_f$ in^{-1} (129 J m^{-1}), but not nearly as much as D730A. This is an unexpected result since both block lengths are long enough to entangle in their respected homopolymers. One explanation for this result can be seen in *Figure 4*. Some of the excess diblock formed lamella at the interface. Washiyama et al.[10] found that, for blends of PS/PVP, the lamellar interfaces were much weaker than the saturated homopolymer interface. After reducing the copolymer concentration to 6 wt%, the maximum Izod increased to 2.9 ft-lb$_f$ in^{-1} (154 J m^{-1}). A further reduction of copolymer concentration to 4 wt% show nearly the same results as the 8 wt% samples.

The remaining blends, which contain diblocks D210 and D183, show minimal improvement in impact strength. In both cases, the PS block is much shorter than the entanglement molecular weight and is believed to be pulled out of the PS homopolymer. These blends have similar impact strengths as the blend of uncompatibilised 23% PB in PS.

The material with the multiblock copolymer, MB5, as the compatibiliser did show some beneficial increase in impact strength, with a maximum Izod of 2.2 ft-lb$_f$ in^{-1} (117 J m^{-1}). *Figure 5* shows the rubber particles with the excess MB5 appearing as lamella structures in the matrix. Since there is some increase in impact strength, we believe that the multiblock did improve interfacial adhesion in weaving back and forth across the interface. The entanglements between the multiblock and the homopolymers are believed to be enough to allow large scale plastic deformation to occur.

Figure 6 displays the results of blends with random copolymers as the interfacial agent. The blends with R706, R715, and R740 show a minimal increase in impact strength compared to the binary blend of PB in PS. Since these copolymers are composed predominantly of PB, we believe the copolymer did not adequately entangle in the PS phase. The impact strength of blends with random copolymers increases as the composition of the random copolymer becomes closer to 50/50. The R1028 blend has a maximum Izod of 2.5 ft-lb$_f$ in^{-1} (129 J m^{-1}). *Figure 7* shows the random copolymer at the interface as a gray ring around the

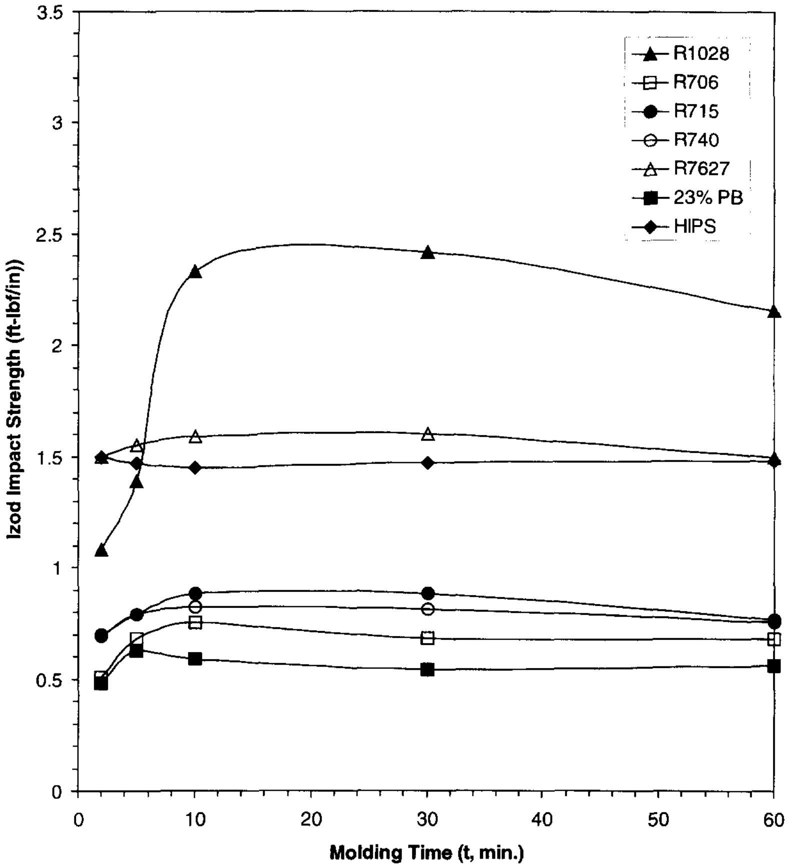


Figure 6 Impact strengths of blends with random copolymers as interfacial agents

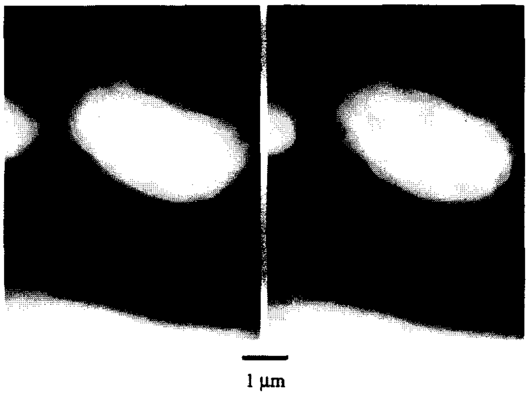


Figure 7 Stereopair of PS/PB/R1028 blend taken at ±8°

white particles. Viewing the stereopair properly, as described previously[29], the random copolymer appears at the interface as a gray ring around the white particles. From impact strength results, we believe that this random copolymer does entangle in both of the homopolymer phases, but it remains a significantly worse compatibiliser than the best block copolymer.

CONCLUSION

Using bulk blends produced by compositional quenching, we examined the effectiveness of various styrene–butadiene copolymers on the impact strength of blends of PS/PB. The long asymmetric diblock, which was capable of entangling in both homopolymer phases, was most effective in improving impact strength. The long symmetric diblock did improve adhesion, but it was not nearly as effective as the long asymmetric diblock. The short diblocks were ineffective compatibilisers presumably because of chain pull-out of the shorter PS block segment.

Most random copolymers proved to be inadequate as interfacial agents. The random copolymers which were composed predominantly of PB provided almost no interfacial strengthening and, therefore, the materials possessed impact strengths almost equivalent to a blend of 23% PB in PS. The R7627 and R1028 were successful as interfacial agents, with the R1028 random copolymer having the highest impact strength.

The last styrene–butadiene copolymer that we utilised as a compatibiliser was a multiblock copolymer. This copolymer was successful as an interfacial agent with results similar to the best random copolymers. Although the blocks are short, they are pure homopolymer and apparently penetrate deeply enough into their own phase to cause good entanglement.

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