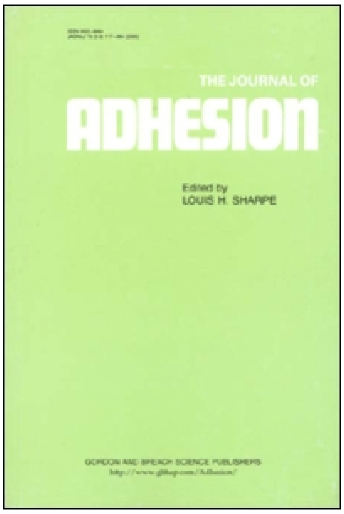

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Lap Shear Adhesion of Styrenic Triblock Copolymers to Polypropylene and Polystyrene

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Shear mode adhesive strength of several styrenic triblock copolymers to Polypropylene (PP) and Polystyrene (PS) was examined as a function of midblock structure, styrene content, and molecular weight. A modified lap shear test was designed to allow adhesive strength measurement in strongly adhering adhesive joints where, in the conventional lap shear test, tensile failure in one of the adherends occurred before the adhesive strength was attained. To both substrates, the adhesive strength was highest for poly(ethylene-butylene) midblock (S-EB-S), followed by polyisobutylene midblock (S-IB-S), polybutadiene midblock (S-B-S), and finally polyisoprene midblock (S-I-S). For the S-IB-S copolymers, as the styrene content and molecular weight increased the adhesive strength increased to the PS substrate but remained nearly constant to the PP substrate. Lap shear adhesive strength was related to the nanoscale block copolymer morphology. Adhesive strength increased as the adhering phase of the triblock, styrene when bonding to PS and the rubber midblock when bonding to PP, became more continuous.

Keywords: Adhesion; lap shear; triblock copolymers; domain morphology; effect of midblock structure; effect of molecular weight; effect of polystyrene content

INTRODUCTION

The unique nanoscale phase-separated morphology and good processing characteristics of styrenic block copolymers have enabled

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widespread use of these materials as both structural adhesives and polymer modifiers. Blends of immiscible polymers have coarse domain morphologies and poor mechanical properties. Block copolymers can effectively compatibilize immiscible blends if one block component can adhere to each of the blended materials. The interfacial tension is lowered and the resulting blend has a finer phase dispersion, good adhesion between phases and, consequently, much better mechanical properties. In each of these applications the adhesion between components is important, and numerous studies have investigated the adhesion of these materials [1–5].

The adhesive strength achieved depends on the number of chains traversing the interface and the depth of penetration of the chains [6–8]. Reichert and Brown [4], in a study of the adhesion of polystyrene–polyisoprene diblock copolymers to polyisoprene, found that maximum adhesion was achieved when the molecular weight was low enough that the chains could easily diffuse across the interface, yet high enough for the chains to penetrate sufficiently to create chain entanglement.

Block copolymers organize into spherical, cylindrical, and lamellar domain morphologies depending on the chemical structure, amount, and molecular weight of the block components. Green *et al.* [9] found that diffusion of homopolymer into block copolymer can be much slower than into the respective homopolymer because the phase-separated block copolymer morphology places physical constraints on the volume into which homopolymer chains can diffuse. Similarly, morphology is expected to influence adhesion, but there has been little attention in the prior literature to identifying the relation between nanoscale morphology and macroscale adhesion properties.

The lap shear test is a common test geometry because of the practical joint design and ease of testing. Paul *et al.* [2, 3] used the lap shear test to quantify adhesion of a styrene/poly(ethylene-butylene)/styrene triblock copolymer (S-EB-S) to polypropylene and polystyrene substrates. Adhesion to both substrates was good because of the affinity of one of the components of the block copolymer to each substrate. The lap shear test has an upper limit on joint strength for which an adhesive failure strength can be measured before tensile failure occurs in the substrate. In the present work a modified lap shear test was designed to allow adhesive strength measurement of high strength adhesive bonds.

The goal of this study was to examine the effects of midblock structure, styrene content, and molecular weight on the lap shear adhesion of styrenic triblocks to polypropylene (PP) and polystyrene (PS) substrates. Four different midblocks, polyisobutylene (S-IB-S), polyisoprene (S-I-S), polybutadiene (S-B-S), and poly(ethylene-butylene) (S-EB-S), were studied. The effect of styrene content was examined in S-IB-S by holding the molecular weight (M_n) constant at 80,000 and varying the styrene content from 20 to 60%. The effect of molecular weight was examined in S-IB-S by holding the styrene amount constant at 40% and varying the molecular weight between 40,000 and 167,000.

EXPERIMENTAL

Materials

Experimental S-IB-S materials were provided by the Amoco Chemicals Company. The matrix of S-IB-S copolymers included styrene contents of 20, 30, 40, 50 and 60% with the same triblock molecular weight (M_n) of 80,000, and four molecular weights of 40,000, 80,000, 120,000 and 167,000 with the same styrene content of 40%. The other triblocks were commercial Kraton® materials from the Shell Chemical Company. The S-EB-S (Kraton G1652) had a styrene content of 28% and a molecular weight of 52,000; the S-B-S (Kraton D1102) had 29% styrene and a 72,000 molecular weight; and the S-I-S (Kraton D1107) had 14% styrene and a 157,000 molecular weight. A summary of the different triblocks, molecular weights, and compositions is given in Table I.

Sample Preparation

Lap shear specimens were made by compression molding a sheet of triblock copolymer between two adherend plaques. The two adherends were individually compression-molded into plaques by placing the PS or PP pellets into a 150 × 150 × 4.5 mm mold between two steel plates

TABLE I Thermoplastic elastomer triblocks

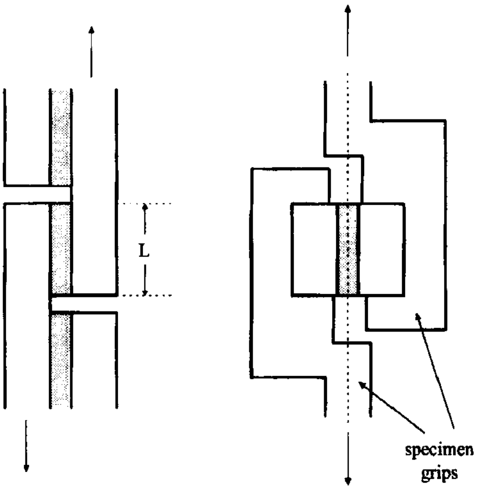
Triblock Copolymer	*Molecular Weight (M_n)* PS Endblock	Midblock	Total	*PS Content* %
S-B-S (Kraton® D 1102)	9, 940	51, 120	71, 000	28
S-I-S (Kraton D 1107)	10, 990	135, 020	157, 000	14
S-EB-S (Kraton G 1652)	7, 540	36, 920	52, 000	29
S-IB-S	8, 000	64, 000	80, 000	20
S-IB-S	12, 000	56, 000	80, 000	30
S-IB-S	16, 000	48, 000	80, 000	40
S-IB-S	20, 000	40, 000	80, 000	50
S-IB-S	24, 000	32, 000	80, 000	60
S-IB-S	8, 000	24, 000	40, 000	40
S-IB-S	24, 000	72, 000	120, 000	40
S-IB-S	33, 500	100, 000	167, 000	40

with a mirror finish. The mold was preheated in the press for 10 minutes at 175°C for PS or 210°C for PP. A pressure of 1,000 psi (6.9 MPa) was applied at this temperature for an additional 10 minutes, and then the mold was cooled under pressure to room temperature at about 10°C/min. The triblock copolymer was compression-molded under the same conditions at 175°C, except the molding was done against Teflon sheets to prevent sticking. The thickness was about 0.5 mm, but tended to vary between 0.8 mm in the center of the plaque and 0.3 mm near the plaque edge.

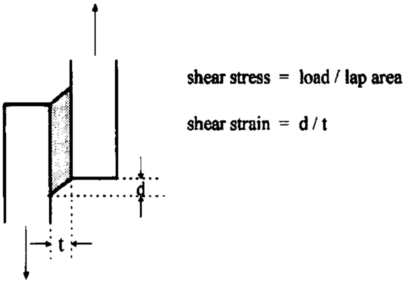
The triblock copolymer sheet was placed between the two adherend plaques in a 9 mm thick mold, and the sandwich was preheated for 20 minutes in the compression molder at 175°C. The adherend plaques were either both polystyrene or both polypropylene. A pressure of 1,000 psi (6.9 MPa) was applied for 10 minutes, and the mold was cooled to room temperature at about 10°C/min. Once at room temperature, the mold was left under pressure for an additional 30 minutes to ensure that the center of the plaque had cooled to room temperature. For the S-EB-S the effects of temperature were further examined by molding sandwich specimens at 75, 100, 125, 150, 175, 200 and 225°C.

Testing

The sandwich specimens were cut with a band saw into strips 25.4 mm wide and the sides were smoothed with a router. For the conventional lap shear test (ASTM D 3165), Figure 1a, strips were notched with a



(a) Conventional lap shear **(b) Modified lap shear**



(c) Calculation of shear stress and shear strain

FIGURE 1 Schematics of the conventional lap shear test, the modified lap shear test, and the calculation of shear stress and shear strain.

band saw to produce a lap length of 12.7 mm. For the modified lap shear test (MLS), Figure 1b, the strips were cut into 12.7 mm sections and smoothed with a router. Tests were done at ambient temperature and the strain rate in all the lap shear tests was 100%/min. Shear modulus was measured from the shear stress *vs.* shear strain curves, which were linear up to about 20% strain. Fracture surfaces of the failed MLS specimens were examined by Optical Microscopy (OM) and photoacoustic FTIR. The Attenuated Total Reflectance (ATR) mode was attempted but the fracture surfaces were too rough to achieve good contact between the surface and the crystal.

The compression-molded triblocks were cut into ASTM D 1708 microtensile specimens 5 mm wide and with a 22.5 mm gauge length. Tests were performed at ambient temperature with a strain rate of 200%/min. Tensile modulus was measured directly from the initial linear portion, up to about 4% strain, of the stress *vs.* strain curve. An Instron Model 1123 was used for all tensile and lap shear testing.

Transmission Electron Microscopy (TEM)

The morphology of compression-molded and solution-cast triblock copolymers was examined by TEM. Compression-molded specimens were embedded in an epoxy, trimmed at −90°C, and vapor stained with a 2% solution of RuO_4. Sections were wet cryo-microtomed with an RMC MT6000-XL ultramicrotome with a CR-2000 cryo-sectioning unit. The temperatures were −90°C for the specimen and −50°C for the freshly-cut glass knife. The sectioning direction was perpendicular to the plane of the compression-molding platens. The 90 nm thick sections were examined in a JEOL 100SX transmission electron microscope. For the solution-cast specimens 0.2 g of triblock copolymer was dissolved in 100 ml of toluene. One drop of the solution was deposited on a 300-mesh hexagonal copper TEM grid and stained in RuO_4 vapor for 15 minutes before viewing in the TEM.

RESULTS AND DISCUSSION

Lap Shear Testing

The lap shear test, illustrated in Figure 1a, requires pre-notching, which may induce defects along the notch edges that initiate failure. Several notching techniques were compared using a PS/S-EB-S/PS specimen. Shear failure stresses of about 1.1 MPa, similar to the value obtained by Paul *et al.* [3] in a similar system, were measured when the notch was machined with an end mill. Notching with a band saw, rotating low speed diamond saw, or a rotating staggered tooth metal blade all increased the shear failure stress to between 2.2 and 2.8 MPa. This variation in lap shear strength indicated that damage to the substrate and the adhesive bond during notching could significantly affect the lap shear measurement. For consistency, all notches were subsequently machined with a band saw.

There was an even more serious difficulty with the conventional geometry. The shear failure stress of strongly adhering specimens, i.e. those failing above 3–4 MPa, could not be measured due to tensile failure of one of the adherends prior to shear failure of the adhesive bond. It might appear that higher shear stress values could have been measured by simply decreasing the lap length. However, because of the complex stress distribution along the lap length [10, 11] and the tendency for fracture to occur along the notch edges [12], there is a significant effect of lap length on measured shear failure stress [1, 13]. In order to measure shear failure stress of some of the high-strength adhesive bonds in this study, the lap length would have to be decreased up to four times less than the ASTM D 3165 recommended lap length of 12.7 mm. Edge effects in a lap length this small would render shear stress measurements nearly meaningless.

Consequently, we chose to modify the conventional lap shear geometry to measure shear failure stresses in high-strength adhesive bonds while maintaining the ASTM recommended 12.7 mm lap length. A Modified Lap Shear test (MLS), shown schematically in Figure 1b, was developed to achieve shear loading without requiring notches. By eliminating the notches, deformation and tensile failure of the adherends and the edge effects due to notching were avoided. The shear stress and shear strain were calculated according to the expressions in Figure 1c. Test results from the two lap shear geometries are compared in Figure 2. One of the lower adhesive strength samples, PS/S-EB-S/PS, exhibited comparable shear stress *vs.* shear strain curves in both configurations, which confirmed the validity of the MLS test for measuring shear strength of adhesive joints. The advantage of the MLS for measuring high-strength adhesive bonds is shown by comparing a high-strength PS/S-IB-S (50% PS)/PS joint in each geometry. The lap shear specimen experienced tensile failure of an adherend at 2.5 MPa; in comparison, the MLS specimen failed adhesively at 8.7 MPa. Thus, the MLS test gave results in accordance with the conventional lap shear test for low-strength adhesives and enabled shear failures to be obtained for high-strength adhesives.

The shear stress distribution through the thickness of the adhesive layer produced the highest stresses at the interface, so failure always

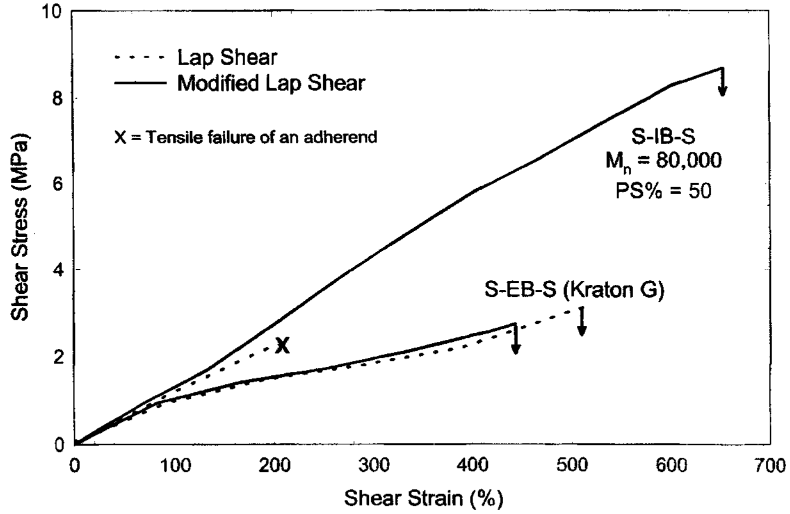


FIGURE 2 Comparison of conventional and modified lap shear tests of S-EB-S and S-IB-S (50% PS) bonded to PS which shows the advantage of the modified lap shear test in measuring adhesive strength in high-strength adhesive bonds.

occurred at or near one of the interfaces. Three failure modes, adhesive, mixed, and cohesive, were distinguished. Adhesive failure was defined as fracture at one of the interfaces with no residual adhesive remaining on the substrate as determined by OM and photoacoustic FTIR. Macroscale tearing through the adhesive layer was called cohesive failure. In this case, a thin layer of adhesive material coated the detached substrate. The failure was termed mixed mode if patches of adhesive material were detected on the detached substrate by OM and photoacoustic FTIR.

The effects of molding temperature on adhesion to PP and PS were examined with S-EB-S as the adhesive. In S-EB-S molded to PP below 150°C the adhesion was so poor that specimens failed while being machined into the test geometry. At a molding temperature of 150°C specimens failed adhesively at 0.5 MPa. A large increase in adhesive strength was observed when the molding temperature was raised to 175°C. The shear failure stress of most specimens molded at this temperature was greater than 3.5 MPa, the stress at which the PP adherends began to slip in the shear grips. The one exception was a joint that failed in mixed mode at 3.5 MPa. Specimens molded at 200°

and 225°C also had shear failure stresses above 3.5 MPa, and slipped in the grips. The large jump in adhesive strength between 150° and 175°C coincided with the 165°C T_m of PP.

Two adhesion mechanisms were responsible for the large jump in adhesive strength at the melting temperature of PP. First, melting of the PP allowed diffusion of the PP chains into the EB domains of S-EB-S. Second, adhesion was promoted by the drawing of influxes of adhesive between spherulites during recrystallization of PP. This type of mechanical interlocking has been observed to enhance interface strength in polyethylene/PP bonds [14-16].

Figure 3 shows the shear failure stress of S-EB-S to PS over a range of molding temperatures from 75° to 225°C. In all cases the failure mode was adhesive. At 75°C the shear failure stress was less than 1 MPa. Between 75° and 150°C the failure stress increased to about 3 MPa. Increasing the molding temperature above 150°C did not change the shear failure stress further. As with PP, increasing the molding temperature above the transition temperature of the adherend, for PS the T_g at 100°C, increased adhesive strength. Because PS is non-spherulitic no mechanical interlocking could have occurred. The

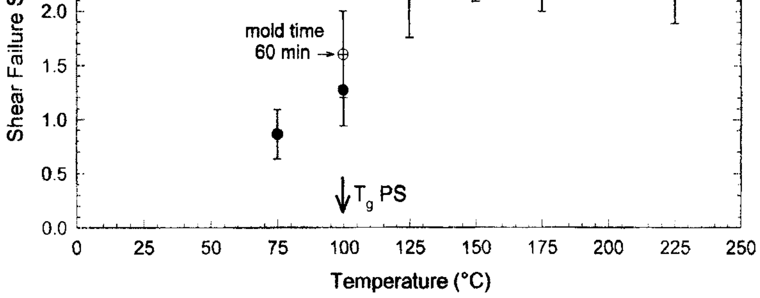


FIGURE 3 Effect of molding temperature on lap shear strength of S-EB-S bonded to PS for a strain rate of 100%/min. At least five specimens were tested for each temperature.

increase in strength at molding temperatures above T_g was due to interdiffusion between the increasingly mobile PS chains in the adherend and the PS domains in S-EB-S. Interestingly, the increase in adhesion with temperature was more rapid for PP, which passed through a primary transition (T_m), than for PS, which underwent a secondary transition (T_g).

The gradual increase in adhesive strength with temperature in PS indicated a time dependence, which could mean high adhesive strength at lower molding temperatures could be obtained by increasing the molding time, t. When t was increased from 10 to 60 minutes, the shear failure stress increased from 1.27±0.33 MPa to 1.60±0.40 MPa. A linear increase in lap shear strength with $t^{1/4}$ has been demonstrated for welded PS interfaces [7, 17]. Based on the measured lap shear strength for t = 10 minutes, a lap shear strength for t = 60 minutes can be calculated for a lap shear strength that is proportional to $t^{1/4}$. If the total molding time is taken as the preheating time, 20 minutes, plus the time molded under pressure, 10 or 60 minutes, then the calculated lap shear strength for the 60-minute molding time under pressure is 1.62 MPa. The measured value at 60 minutes was 1.60±0.40 MPa, which is in accord with a lap shear strength proportional to $t^{1/4}$.

The results for both PP and PS showed that in each material a good adhesive bond was obtained with a molding temperature of 175°C. For this reason 175°C was chosen as the molding temperature for all subsequent experiments. The large scatter in Figure 3 was typical for most materials because the adhesive bond in the lap shear geometry was very sensitive to flaws. Sometimes, prior to final separation, cracks initiated from the free edges at the top and bottom of the adhesive joint and propagated along the adhesive bond as the load continued to increase. These cracks then coalesced to cause final separation.

Effect of Midblock Structure on Lap Shear Strength

The effect of midblock on shear mode adhesion was examined by comparing S-I-S, S-B-S, S-EB-S and S-IB-S. The latter three materials each contained about 30% PS, and had M_ns of 72,000, 51,000 and 80,000, respectively. The S-I-S contained 14% PS and had an M_n of 157,000. Even though the S-I-S had a much higher molecular weight than the other materials, the PS content was lower and, consequently, the molecular weight of the PS endblocks was similar in all four block copolymers, ranging from 7,500 in S-EB-S to 12,000 in S-IB-S. These endblock molecular weights were well below the critical entanglement molecular weight for PS of 32,000 [18] and the midblock molecular weights were well above the critical entanglement molecular weights for the corresponding rubbers [19].

A summary of the shear and tensile properties is presented in Table II. The shear modulus was independent of the substrate to which the adhesive was bonded and, therefore, was taken as the shear modulus of the adhesive. The values were 0.22, 0.76, 0.45 and 1.85 MPa for S-I-S, S-B-S, S-IB-S and S-EB-S, respectively. The ratio of tensile to shear modulus, E_t/E_s, should be 3 for an isotropic morphology of PS spheres dispersed in the rubber matrix. A value greater than 3 would indicate that the PS domain morphology was not spheres, but rather cylinders or lamellae. Thus an E_t/E_s value of 4.4 in S-I-S suggested that the morphology was almost spherical; 7.8 in S-B-S suggested short

TABLE II Effect of midblock on adhesion and mechanical properties of block copolymers

Triblock Copolymer	*S-I-S*	*S-B-S*	*S-IB-S*	*S-EB-S*
PS%	*14%*	*28%*	*30%*	*29%*
M_n	*157, 000*	*72, 000*	*80, 000*	*51, 000*
Morphology	*Spheres*	*Short Cylinders*	*Long Cylinders*	*Lamellae*
Modulus (MPa)				
Tensile	0.96 (0.42)[a]	5.9 (1.0)	11.3 (0.5)	32 (10)
Shear to PP	– [b]	0.81 (0.10)	0.44 (0.04)	1.9 (0.3)
Shear to PS	0.22 (0.02)	0.71 (0.10)	0.46 (0.03)	1.8 (0.4)
Tensile/Shear	4.4	7.8	25	17
Failure Stress (MPa)				
Tensile	> 4	> 10	23 (5.3)	21 (5.7)
Shear to PP	– [b]	0.71 (0.09)	1.7 (0.2)	> 3.5
Shear to PS	0.37 (0.11)	1.6 (0.14)	2.8 (0.7)	2.8 (0.8)
Failure Strain (%)				
Tensile	>1000	>1000	570 (60)	520 (30)
Shear to PP	– [b]	150 (10)	480 (20)	>400
Shear to PS	290 (65)	440 (110)	525 (40)	460 (120)
Shear Failure Mode				
to PP Substrate	Adhesive	Adhesive	Adhesive	Mixed
to PS Substrate	Mixed	Adhesive	Adhesive	Adhesive

[a] Standard deviations shown in parentheses.

[b] Specimen failed during machining.

cylinders; and 25 in S-IB-S and 17 in S-EB-S suggested longer cylinders or lamellae. This interpretation is consistent with previous direct observations that found the PS domain morphology of triblocks, with styrene contents and molecular weights comparable with the ones in this study, to be spherical in S-I-S [20], cylindrical in SBS [21, 22] and S-IB-S [23, 24] and lamellar in S-EB-S [25].

The tensile stress *vs.* strain curves of the triblocks in Figure 4 showed two types of behavior. Two of the triblocks, S-EB-S and S-IB-S, exhibited a stress upswing at higher strains with a relatively high fracture stress. Strain hardening may have been related to the reinforcing effect of the highly-anisotropic domains of S-EB-S and S-IB-S. Strain hardening was absent from the tensile stress *vs.* strain curves of S-B-S and S-I-S; both drew to high strains with low stresses.

The MLS curves for each material bonded to PP are shown in Figure 5. The S-EB-S had the highest shear failure stress bonded to PP, greater than 3.5 MPa. Of the specimens tested, one failed in mixed mode failure at 3.5 MPa and the remainder began to torque in the shear grips before failure so the tests were stopped. The S-IB-S failed

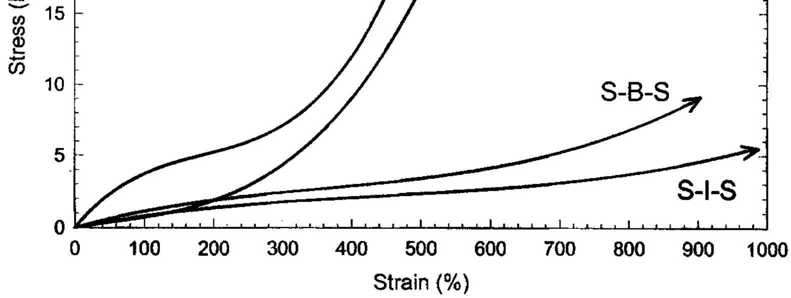


FIGURE 4 Effect of midblock on tensile stress *vs.* strain curves at a strain rate 200%/min for S-EB-S, S-IB-S, S-B-S and S-I-S.

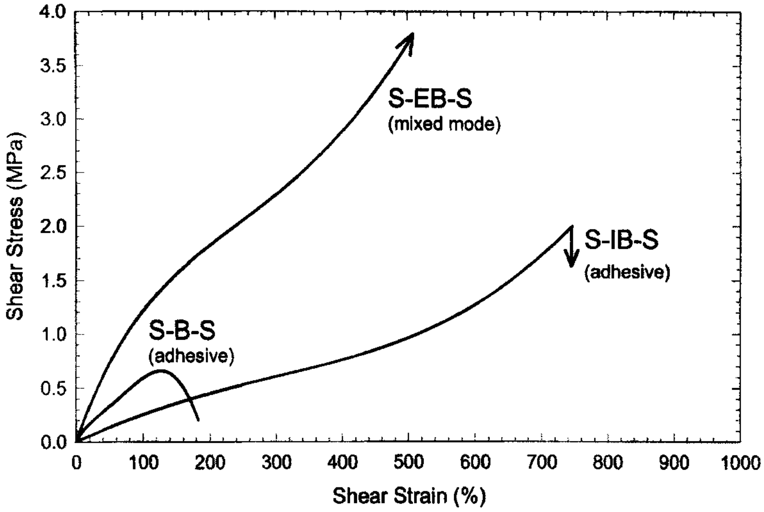


FIGURE 5 Effect of midblock on shear stress *vs.* strain curves for S-EB-S, S-IB-S and S-B-S, each containing about 30% PS, bonded to PP. S-I-S (14% PS) failed during machining of the test specimens.

adhesively at 1.9 MPa and a shear strain of 700–800%. The S-B-S failed adhesively at a much lower stress, 0.7 MPa, and a much lower shear strain, less than 200%. The adhesive strength of S-I-S was so poor that specimens failed while being machined into the test geometry.

Cohesive failure would have occurred if the shear strength of the adhesive material was reached before the adhesive bond to PP was broken. The mixed mode failure of the one S-EB-S specimen indicated that, in this case, the adhesive strength was comparable with the cohesive strength of the adhesive. The other three adhesives reached the adhesive strength of the bond to PP. Of the three, S-IB-S formed the strongest bond to PP, S-B-S was intermediate, and S-I-S formed the weakest bond.

The MLS curves for each material bonded to PS are shown in Figure 6. The S-EB-S, S-IB-S and S-B-S all failed adhesively at approximately the same shear strain, 400–600%. The shear stress *vs.* shear strain curves qualitatively resembled the tensile stress *vs.* strain behavior of the triblocks by exhibiting a stress upswing for S-EB-S and S-IB-S, but not S-B-S. Correspondingly, the shear failure

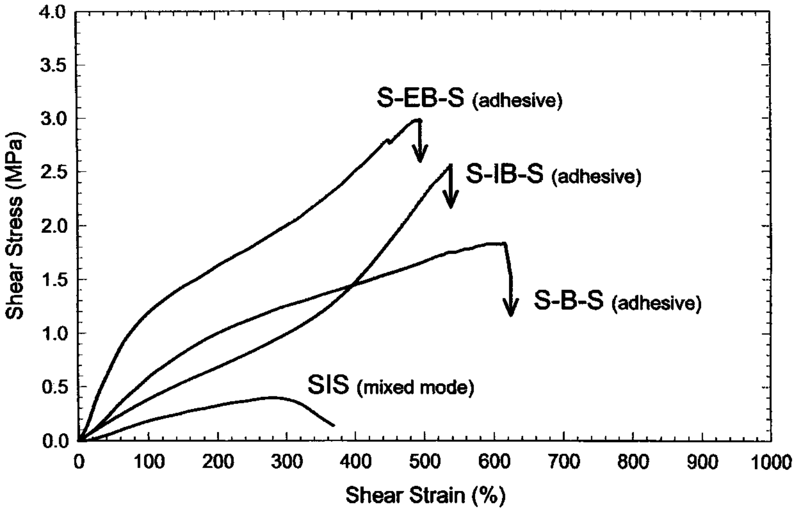


FIGURE 6 Effect of midblock on shear stress *vs.* strain curves of S-EB-S, S-IB-S and S-B-S, each containing about 30% PS, and for S-I-S (14% PS), bonded to PS.

stress was much higher for S-EB-S and S-IB-S than for S-B-S. The S-I-S specimens failed in mixed mode at low shear stress and strain. Comparing adhesion to the two substrates, S-EB-S had a higher adhesive strength to PP(greater than 3.5 MPa) than to PS (2.8 MPa). Conversely, S-IB-S had a higher adhesive strength to PS (2.6 MPa) than to PP (1.9 MPa). The S-B-S and S-I-S also had higher adhesive strength to PS than to PP. However, for both substrates, adhesive strength decreased in the order of S-EB-S > S-IB-S > S-B-S > S-I-S.

Although the styrene content and molecular weight of the PS blocks were similar in S-B-S, S-IB-S and S-EB-S, the adhesive strength to PS was quite different. A schematic showing the effect of morphology on adhesion is presented in Figure 7 for copolymers bonded to both PS and PP. The differences were explained by considering the morphology of the triblocks. The surface morphology of block copolymers can differ from the bulk morphology [25] and, furthermore, diffusion in block copolymer systems depends on morphology [9]. Block copolymers with dispersed PS domains in the bulk are likely richer in PS segments near a PS substrate. As the bulk PS domain morphology becomes increasingly continuous, for example from S-I-S to S-B-S to

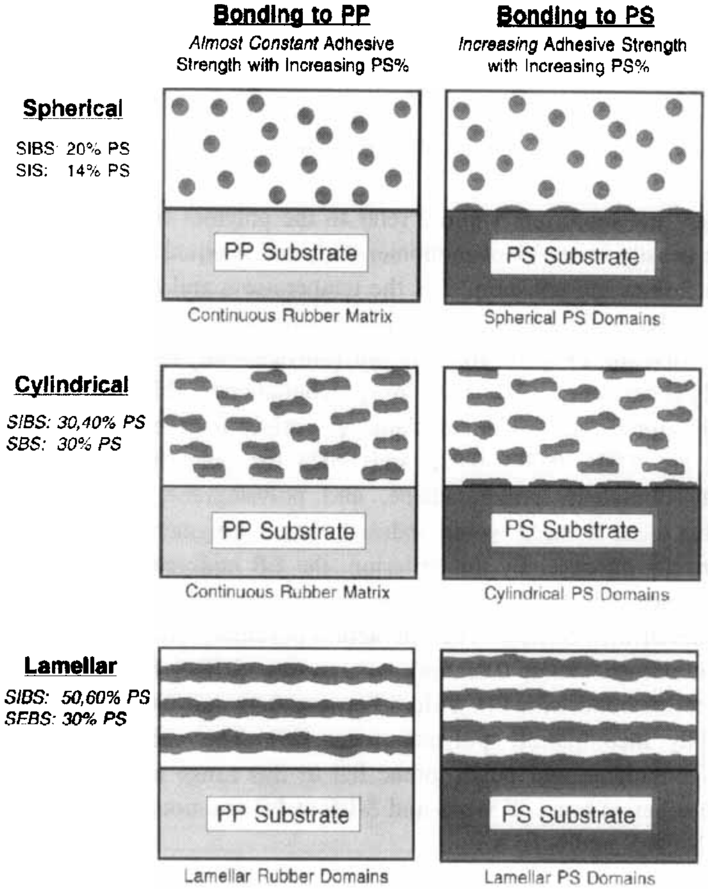


FIGURE 7 Schematic of the proposed block copolymer morphology at the interface and the relation to adhesive strength.

S-IB-S to S-EB-S, the amount of PS at the interface can increase. Consequently, the extent of diffusion increases and the adhesive strength increases correspondingly.

Domain morphology was not expected to control adhesion to PP if the rubber phase was continuous. It was more likely that adhesive strength to PP depended on the interaction of the rubber midblock with PP. The Flory-Huggins interaction parameter, χ_{12}, for the midblocks with PP was estimated from the Hildebrand solubility parameter, δ, using the relationship proposed by Helfand [26] for immiscible polymer pairs:

$$\chi_{12} = \frac{(\delta_1 - \delta_2)^2}{\rho_o kT}$$

where the subscripts 1 and 2 refer to the polymer components; ρ_o is the density in moles of monomer/cm^3, and is equal to $(\rho_1\rho_2)^{1/2}$; k is the Boltzmann constant; T is the temperature; and δ_1 and δ_2 are the solubility parameters. The solubility parameters in units of MPa$^{1/2}$ are 16.0 for PP [27], 16.2 for poly(ethylene-butylene) [28], 16.5 for polyisobutylene [27], 17.0 for polybutadiene [27], and 17.0 for polyisoprene [27]. The calculated χ_{12} values for the midblocks with PP are 0.001, 0.006, 0.022 and 0.024 for poly(ethylene-butylene), polyisobutylene, polybutadiene, and polyisoprene, respectively. A value close to zero would indicate that a polymer pair is at least partially miscible. By this criterion, the EB midblock was closest to miscible with PP. Correspondingly, the best adhesion to PP was achieved with S-EB-S. The interaction parameter for polyisobutylene was also less than 0.01 and, as a result, S-IB-S formed a strong adhesive bond with PP. Values between 0.01 and 0.03 are typical of mildly incompatible polymer pairs [29]. The values of χ_{12} for polybutadiene and polyisoprene fell in this range and, accordingly, the adhesive bond of S-B-S and S-I-S to PP was not as strong as that of S-EB-S and S-IB-S.

Effect of PS Content on Lap Shear Strength of S-IB-S

The effect of PS content on lap shear adhesion was examined using S-IB-S materials ranging from 20 to 60% PS with constant molecular weight of 80,000. A summary of the shear properties, tensile properties, and morphology is shown in Table III. Morphological changes with increasing PS content were observed in TEM micrographs of thin sections cut from compression-molded adhesive, or from thin films solution-cast from toluene, Figure 8. Over the entire composition range the morphology of the solution-cast films mimicked the morphology of the compression-molded adhesives. Three morphologies were distinguished: spherical, cylindrical, and

TABLE III Effect of polystyrene content on adhesion and mechanical properties of S-IB-S (M_n = 80,000)

PS%	*20%*	*30%*	*40%*	*50%*	*60%*
Morphology	*Spheres*	*Short Cylinders*	*Long Cylinders*	*Lamellae*	*Lamellae*
Modulus (*MPa*)					
Tensile	3.9 (1.3)[a]	11 (0.5)	30 (8.0)	95 (7.0)	160 (6.0)
Shear to PP	0.19 (0.01)	0.44 (0.04)	0.78 (0.03)	1.2 (0.3)	1.3 (0.3)
Shear to PS	0.16 (0.02)	0.46 (0.03)	0.86 (0.41)	1.3 (1 trial)	1.6 (0.4)
Tensile/Shear	20	25	37	79	110
Failure Stress (*MPa*)					
Tensile	3.7 (0.7)	23 (5.3)	23 (2.0)	23 (2.1)	19 (0.8)
Shear to PP	0.8 (0.3)	1.7 (0.2)	2.6 (0.5)	2.7 (0.5)	2.3 (1.1)
Shear to PS	3.4[a] (0.1)	2.8 (0.7)	4.6 (0.7)	8.7 (1 trial)	10.1 (1.9)
Failure Strain (%)					
Tensile	810 (140)	570 (60)	550 (35)	390 (45)	160 (10)
Shear to PP	735 (40)	480 (20)	405 (50)	305 (35)	125 (45)
Shear to PS	1100 (140)	525 (40)	645 (10)	650 (1 trial)	750 (70)
Shear Failure Mode					
to PP Substrate	Cohesive	Adhesive	Adhesive	Adhesive	Adhesive
to PS Substrate	Cohesive	Adhesive	Adhesive	Adhesive	Adhesive

[a] Standard deviations shown in parentheses.

[b] Cohesive damage initiated around 1 MPa.

lamellar. The 20% composition had spherical PS domains dispersed in the polyisobutylene matrix, Figure 8a. Increasing the PS content to 30% resulted in a cylindrical morphology, Figure 8b, and in the 40% composition the cylinders increased in length. The morphology became lamellar in the 50% and 60% compositions, Figure 8c. These lamellae were thicker and less regular than those of S-EB-S, Figure 8d.

The tensile stress *vs.* strain curves of the copolymers in Figure 9 reflected the effect of changing composition and morphology. Increasing PS content resulted in a modulus increase from 1 MPa (20%, spherical) to 160 MPa (60%, lamellar). Failure strain decreased from 1,000% (20%, spherical) to 160% (60%, lamellar). Failure stress increased from 4 MPa (20%, spherical) to a maximum of 23 MPa in the 30 to 50% range (cylindrical and lamellar), and then decreased slightly to 19 MPa in the 60% composition (lamellar). These values are higher than those previously reported in the literature for S-IB-S [23, 24, 30, 31]. Lower molecular weight species such as diblock and homopolystyrene are known to reduce the tensile properties, so the

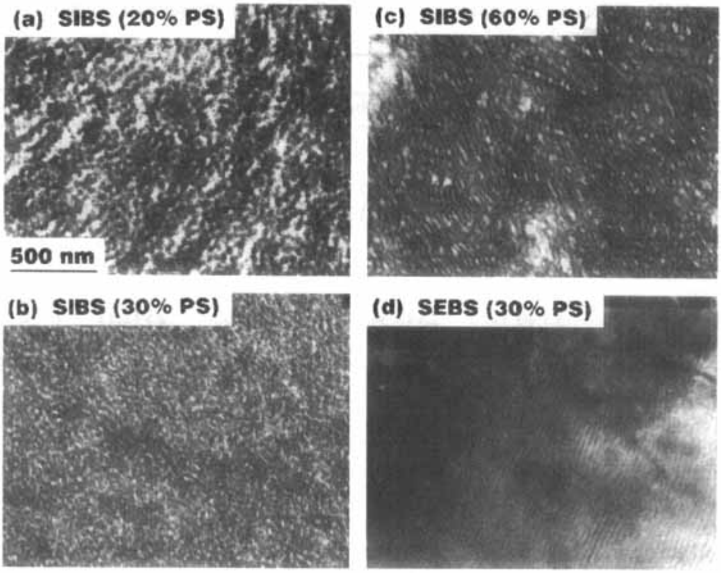


FIGURE 8 TEM micrographs showing domain morphology of S-IB-S with M_n= 80,000: (a) 20%, (b) 30% and (c) 60% PS. The micrograph, (d), is S-EB-S, 30% PS. The dark-stained phase is PS.

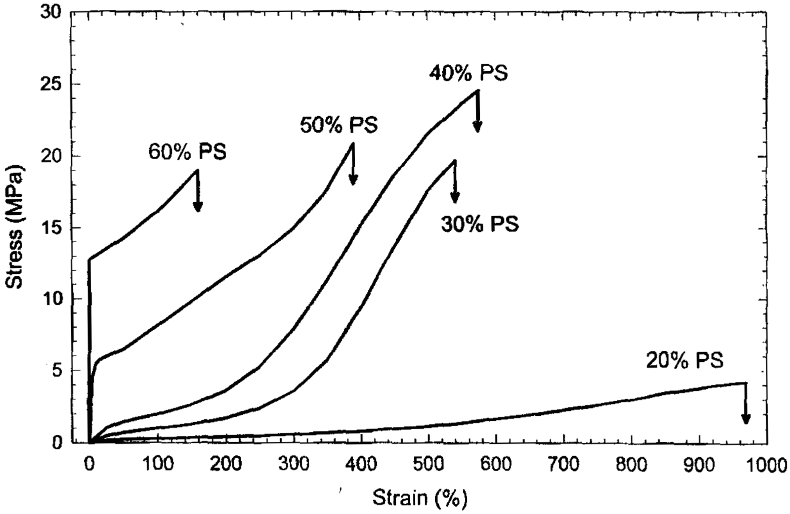


FIGURE 9 Effect of styrene content on the tensile stress *vs.* strain curves of S-IB-S with M_n= 80,000.

higher values in this study may have been a consequence of higher purity materials.

The largest change in properties occurred between 20% and 30% PS, which corresponded to an increase in PS block length from 8,000 to 12,000. This transition was observed in the previous studies of S-IB-S triblocks and was found to occur between 6,000 and 12,000 PS block molecular weight [24, 31]. A transition in mechanical properties between 20% and 30% PS content was also observed in S-I-S and S-B-S copolymers of similar molecular weight [32]. The large increase in tensile strength was attributed to a critical PS molecular weight necessary to achieve good phase separation; without good separation in the 20% composition rubber segments remaining in the PS phase acted as a plasticizer.

The MLS curves of S-IB-S bonded to PP and PS are shown in Figures 10 and 11, respectively. The effect of styrene content on adhesive strength is shown in Figure 12. Over the composition range the shear modulus increased modestly from 0.2 MPa (20%) to 1.5 MPa (60%) with increasing PS content, Table III. Shear modulus increased much more slowly with PS content than the tensile modulus.

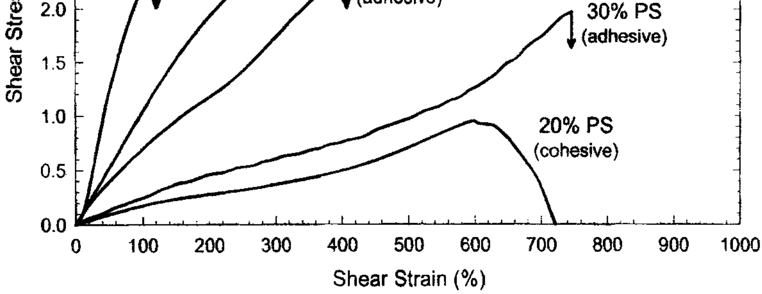


FIGURE 10 Effect of styrene content on the shear stress *vs.* strain curves and failure modes of S-IB-S with $M_n = 80{,}000$ bonded to PP.

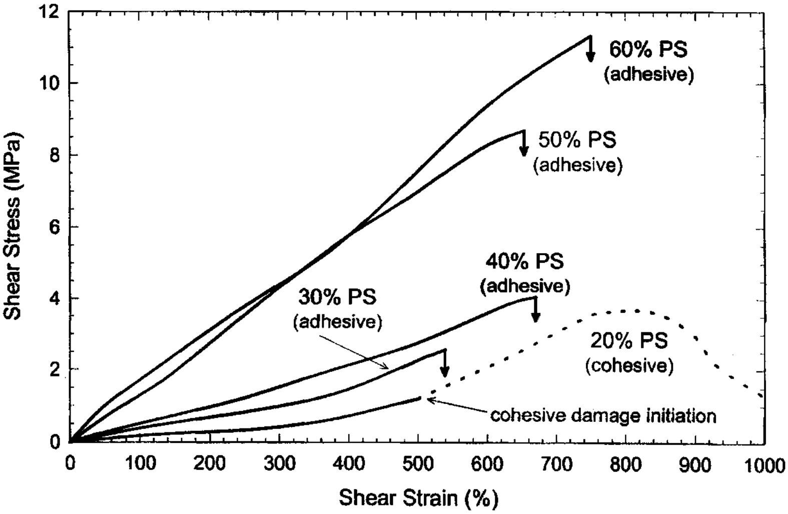


FIGURE 11 Effect of styrene content on the shear stress *vs.* strain curves and failure modes of S-IB-S with M_n = 80, 000 bonded to PS.

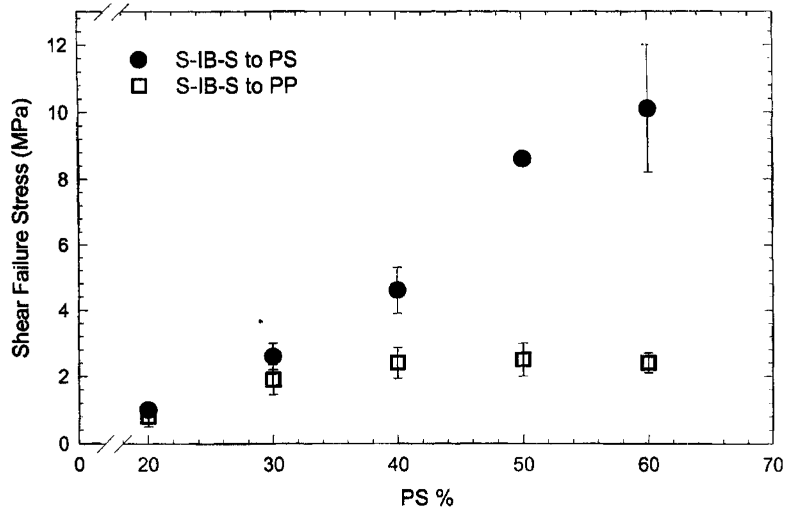


FIGURE 12 Effect of styrene content on adhesive strength of S-IB-S with M_n = 80,000 bonded to PP and PS. Five specimens for each composition were tested, except the 50% composition bonded to PS which is a single test.

The corresponding increase in E_t/E_s reflected the increasingly anisotropic domain morphology.

Failure of S-IB-S bonded to PP was adhesive except for the 20% composition which failed cohesively at a low shear stress, 0.8 MPa, and a high shear strain, 750%. The adhesive strength increased from 1.7 MPa in the 30% composition to a constant value of about 2.5 MPa in the 40, 50 and 60% compositions. The shear failure strain decreased with increasing PS content.

Failure to PS was also adhesive with the exception of the 20% composition. In this composition, failure initiated at about 1 MPa and 500% shear strain; however, the load continued to increase as more cohesive damage accumulated in the adhesive layer. Slow cohesive tearing finally began around 3.5 MPa shear stress and 800% shear strain. The other compositions failed adhesively and, unlike the case of bonding to PP, the shear failure stress increased over the composition range from 2.6 MPa in the 30% composition to 11.1 MPa in the 60% composition. Also, in contrast to bonding to PP, the shear failure strain was nearly constant or increased slightly with increasing PS content.

For the adhesive failures, the 30%–60% PS composition range in S-IB-S, the shear failure stress increased nearly linearly with increasing PS content in bonding to PS; in contrast, the shear failure stress remained fairly constant in bonding to PP, Figure 12. This behavior was again explained by considering the morphology of the adhesive according to the model in Figure 7. The adhesive strength to PP remained constant over the 30% to 60% composition range because the midblock morphology was continuous, so diffusion into the block copolymer was independent of styrene domain morphology. The adhesive did become stiffer, so shear failure strain decreased. In bonding to PS, however, the adhering phase was PS, which changed from spherical to cylindrical to lamellar with increasing PS content. Thus, the layer contacting the interface became increasingly rich in PS, and the extent of diffusion of PS chains into the block copolymer increased. Consequently, adhesive strength increased.

Effect of Molecular Weight on Lap Shear Strength of S-IB-S

The effect of molecular weight on lap shear adhesion was examined with four S-IB-S copolymers with constant PS content of 40% and different molecular weights ranging from 40,000 to 167,000. A summary of the shear properties, tensile properties, and morphology is presented in Table IV. The MLS curves for bonding to both PP and PS are shown in Figures 13 and 14, and the uniaxial tensile curves are shown in Figure 15. The shear modulus increased from 0.4 MPa in the 40,000 molecular weight to 0.9 MPa in the 80,000 molecular weight, and then increased slightly to 1.0 MPa and 1.2 MPa in the 120,000 and 167,000 molecular weights. Tensile modulus increased from 10 MPa in the 40,000 molecular weight to 30 MPa in the 80,000 molecular weight, and remained constant between 20 and 30 MPa in the 120,000 and 167,000 molecular weights. The ratio of tensile to shear modulus, E_t/E_s, showed almost no dependence on molecular weight. In all cases, TEM of thin films solution cast from toluene revealed cylindrical PS domains, although the length of the cylinders appeared to increase with molecular weight. Because the rubber was always the continuous phase, the tensile modulus remained almost constant with increasing molecular weight.

A large increase in tensile failure stress from 2.2 to 23 MPa was observed in the 40% PS composition when the M_n increased from

TABLE IV Effect of molecular weight on adhesion and mechanical properties of S-IB-S (30% PS)

M_n	*40,000*	*80,000*	*120,000*	*167,000*
Morphology	*Spheres*	*Short Cylinders*	*Long Cylinders*	*IPN-like*
Modulus (MPa)				
Tensile	10.4 (3.3)[a]	30 (8.0)	22 (1.0)	29 (3.3)
Shear to PP	–[b]	0.78 (0.3)	0.82 (0.06)	1.2 (0.4)
Shear to PS	0.36 (0.09)	0.86 (0.4)	0.99 (0.21)	1.2 (0.2)
Tensile/Shear	29	37	24	24
Failure Stress (MPa)				
Tensile	2.2 (0.5)	23 (2.0)	27 (1.6)	29 (0.2)
Shear to PP	–[b]	2.6 (0.5)	2.9 (0.5)	1.6 (0.3)
Shear to PS	0.80 (0.12)	4.6 (0.7)	5.3 (2.2)	6.8 (1.8)
Failure Strain (%)				
Tensile	315 (15)	550 (35)	590 (60)	530 (10)
Shear to PP	–[b]	405 (50)	380 (60)	200 (30)
Shear to PS	240 (10)	645 (10)	460 (140)	610 (60)
Shear Failure Mode				
to PP Substrate	Adhesive	Adhesive	Adhesive	Adhesive
to PS Substrate	Mixed	Adhesive	Adhesive	Adhesive

[a] Standard deviations shown in parentheses.

[b] Specimen failed during machining.

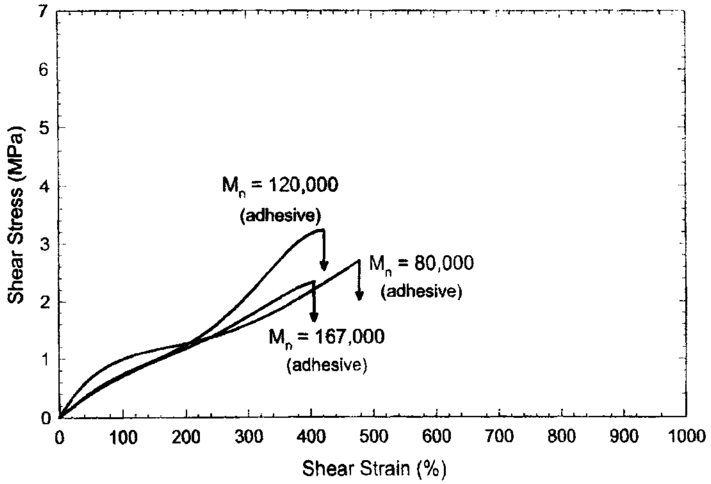


FIGURE 13 Effect of molecular weight on the shear stress *vs.* strain curves and failure modes of S-IB-S with 40% PS bonded to PP.

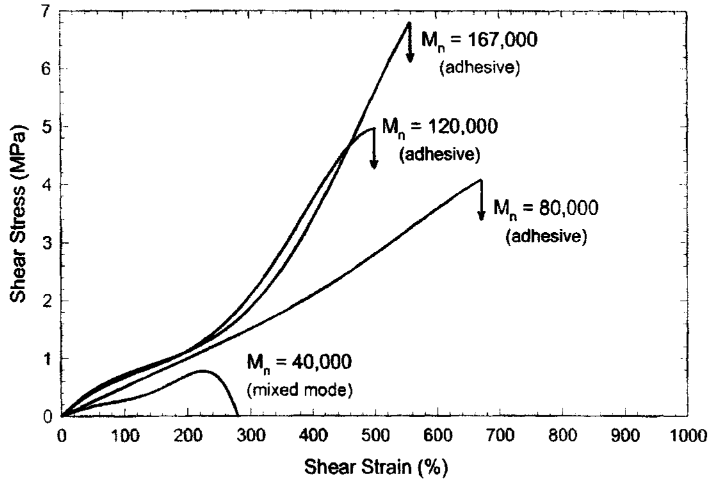


FIGURE 14 Effect of molecular weight on the shear stress *vs.* strain curves and failure modes of S-IB-S with 40% PS bonded to PS.

40,000 (M_n of each PS block = 8,000) to 80,000 (M_n of PS = 16,000). Again, this transition was attributed to a critical PS block molecular weight necessary to achieve good phase separation and to prevent

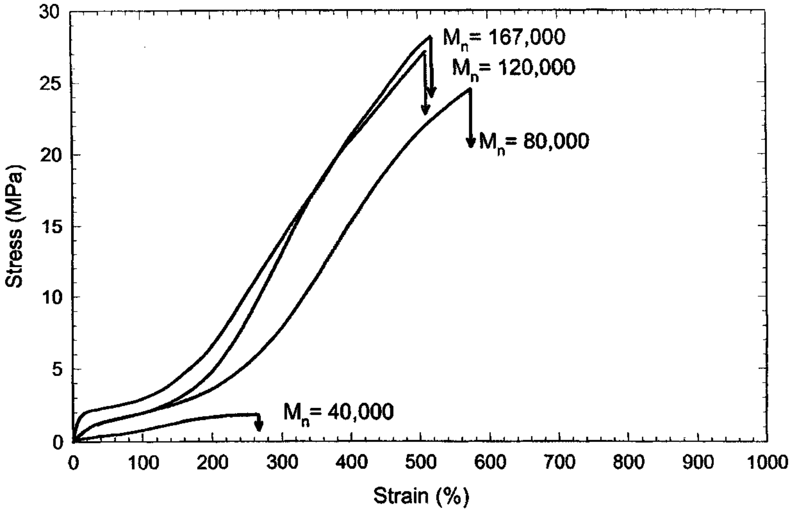


FIGURE 15 Effect of molecular weight on the tensile stress *vs.* strain curves of S-IB-S with 40% PS.

plasticization of the PS domains by the rubber phase. A similar transition was observed between the 20% (M_n of PS = 8,000) and 30% (M_n of PS = 12,000) compositions when the total molecular weight was 80,000. In the two compositions where tensile strength was poor the PS block molecular weight was 8,000. High tensile strength was observed when the PS block molecular weight increased to 12,000 and 16,000. Therefore, the critical PS domain molecular weight necessary for high tensile strength in S-IB-S was experimentally found to be between 8,000 and 12,000.

The shear failures in bonding to PP were all adhesive and the failure strains were between 400 and 500%. The 40,000 M_n material had such poor adhesion that test specimens failed while being machined into the test geometry. The shear failure stresses were 2.7, 2.9 and 1.9 MPa in the 80,000, 120,000 and 167,000 M_n specimens, respectively. The effect of PS content on adhesive strength to both PP and PS is shown in Figure 16. The 2.9 MPa shear failure stress of the 120,000 molecular weight was the highest of any of the S-IB-S materials, and approached the value of S-EB-S.

In bonding to PS the failures were all adhesive except the 40,000 M_n which failed in mixed mode at low shear stress and shear strain. The

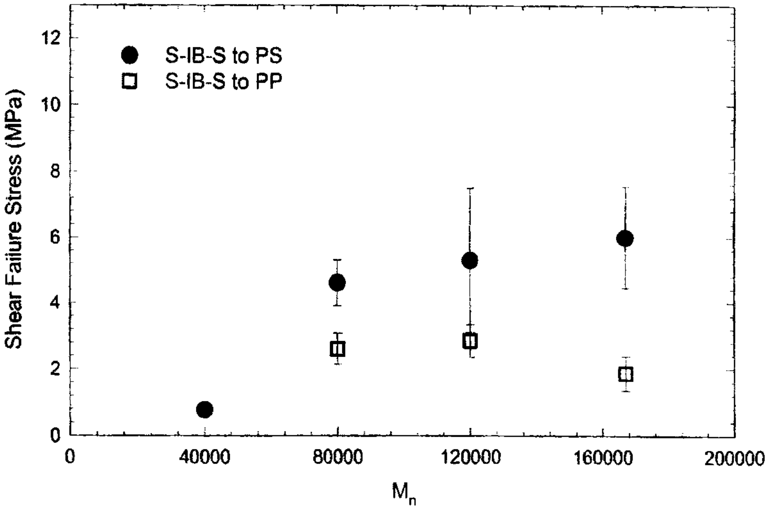


FIGURE 16 Effect of molecular weight on the adhesive strength of S-IB-S with 40% PS bonded to PP and PS. Five specimens for each molecular weight were tested.

adhesive shear failure stress increased with molecular weight from 4.6 to 5.3 to 6.8 in the 80,000, 120,000 and 167,000 molecular weights, respectively. The shear failure strain was between 500 and 650%. Although the PS domains were cylindrical for all molecular weights, the increase in cylinder length with increasing molecular weight corresponded to an increasingly anisotropic morphology. It followed that the adhesive strength to PS increased somewhat with increasing molecular weight. Conversely, the rubber phase, the component responsible for adhesion to PP, remained continuous so adhesion to PP did not change significantly. The decrease in adhesive strength of the 167,000 M_n material bonded to PP may have been due to slower diffusion.

Increasing the anisotropy of the PS endblock domain morphology was shown to increase shear strength in bonding to the PS substrate, but increasing molecular weight may also have affected adhesion. These two factors were differentiated by comparing S-IB-S materials with the same PS block length, but with different midblock lengths and different morphologies. The 120,000 M_n specimen with 40% PS (cylindrical) and the 80,000 M_n with 60% PS (lamellar) each had a PS block length of 24,000, but the adhesive strength was 5.3 MPa in the former and 11.1 MPa in the latter. Therefore, as long as the PS molecular weight was above a certain value, the effect of PS block molecular weight was secondary to the effect of domain morphology in determining lap shear adhesive strength.

CONCLUSIONS

1 A modified lap shear test was developed to examine shear stress *vs.* strain properties for high strength adhesive bonds where in the conventional lap shear geometry failure occurred in one of the adherends.
2 The adhesive strength of triblocks with 30% PS was highest for S-EB-S, followed by S-IB-S and then S-B-S. The S-I-S, with 14% PS, had the lowest adhesive strength.
3 The adhesive strength of S-IB-S bonded to PS increased with both increasing styrene content and molecular weight because the increasingly anisotropic PS domain morphology allowed for a layer richer in PS to contact the substrate. Adhesive strength of the S-IB-S materials with high styrene content exceeded the strength of other triblock copolymers.
4 The adhesive strength of S-IB-S bonded to PP remained nearly constant over the ranges of styrene content and molecular weight examined because the continuous rubbery midblock phase was able to wet the PP substrate completely.

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