The Mechanical Properties of Short Fiber–Styrenic Block Copolymer Composites

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SYNOPSIS

The effect of fiber loading, fiber length, matrix type, and interface adhesion on mechanical properties of PET short fiber–styrenic block copolymer TPEs, SIS, and SBS, was investigated. A strong bonding between PET fiber and TPE was obtained by surface treatment of TPE with isocyanate in toluene solution. The stress of the composites, filled with treated fiber, increased with increasing strain by two steps; the modulus for the first step was higher than the one for the second step, and the composites yielded obviously at about 50% strain, with higher stress than that of matrix TPE. With increasing fiber loading and fiber length, the modulus for the first step and the yield stress increased, but the yield elongation decreased. It seems that the matrix elastomer underwent most of the deformation and that the filled fiber underwent large internal stress with little deformation during extension of the composite, which may be an important phenomenon to influence short fiber reinforcement. The stress softening of composites showed a somewhat larger decreased rate than that of the matrix with repeated stress–strain cycles, and the stress softening in the first cycle increased linearly with increasing fiber loading and increased in an S shape with increasing fiber length. In comparison with the SIS elastomer, the hysteresis of the SBS elastomer showed a big residual strain after the first elongation of 30%, and its retraction and subsequent re-extension curves were obviously different from the extension curve, which was considered to be due to the destruction of parts of the styrene hard domain in SBS. The stress softening of the composites was influenced by the matrix elastomer, as well as by the loading fiber. The interface separation around the end of a fiber under large strain, and the breaking and restructuring of hard domain in the matrix, were considered to be important sources of softening of the composite. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Elastomer composites, reinforced with short fiber have many applications,[1] because they combine the elasticity of the matrix with the strength and stiffness of the loading fiber. Short fiber reinforcement of rubber composites shows strain hardening in the matrix during extension,[2] as does particulate fillers,[3-5] and therefore can be manifested as an increase in tensile strength and modulus, as well as a decrease in elongation and swelling, in comparison to the matrix rubber.[6,7] However, such composites exhibit considerable anisotropy in mechanical properties,

because the filled fibers orient along the flow direction during forming. The short fibers in composites produce considerable reinforcement[8-12] along their orientation direction for vulcanized rubber, which is reinforced isotropically with particulate filler, such as carbon black. According to Coran et al.,[13] the properties of cellulose fiber–elastomer composites depend on the type of elastomer used as the matrix, the fiber concentration, fiber aspect ratio, and fiber orientation. We have reported mechanical and dynamical properties of short fiber–rubber composites, such as PET fiber–chloroprene rubber (CR), nylon fiber–CR, PET fiber–urethane rubber (UR), and PET fiber–ethylene propylene dienes (EPDM).[14-16]

A thermoplastic elastomer (TPE) is a rubbery material with the fabrication characteristics of con-

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ventional thermoplastic and the performance properties of a conventional thermoset rubber.[17,18] Rubber products commonly contain a reinforcing agent, such as carbon black. In TPEs, the polymer system itself provides this reinforcement, which is commonly due to two or more intermingled polymer systems, each with its own phase. Thermoplastic elastomers offer a variety of practical advantages over conventional thermoset rubbers, as follows: little or no compounding, simpler processing with fewer steps, and recycling of scrap material. TPEs, however, have a practical disadvantage of melting at elevated temperatures. This inherent property prevents TPE applications requiring exposure to temperatures above the melting point. Styrenic block copolymers are typical thermoplastic elastomers, composed of hard domains of styrene segment and soft domains of diene segment. Because the styrenic block copolymer TPEs have components similar to vulcanized rubbers, their mechanical and thermal properties are expected to improve by loading with short fiber.

In this article, the effect of loading short fiber on the mechanical properties of styrenic block copolymers was investigated by using two styrene–isoprene–styrene copolymers and a styrene–butadiene–styrene copolymer.

EXPERIMENTAL

Materials

The thermoplastic elastomers used were styrenic block copolymers of two styrene–isoprene–styrene copolymers (SIS), with different styrene contents, and one styrene–butadiene–styrene copolymer (SBS) (Shell Co., Ltd.). Their properties are given in Table I. The short fiber used was polyethylene

Table I   Styrenic Block Copolymers and Short Fibers Materials

Elastomer	Density (g/cm³)	Hardness (Shore A)	Styrene/ Elastomer (wt %)
SIS(1) (TR1107)	0.92	37	14/86
SIS(2) (TR1111)	0.93	52	21/79
SBS (TR1024)	0.94	59	42/58

PET fiber: diameter = 0.028 mm; length = 0.5 mm, 2.0 mm, 4.0 mm, and 6.0 mm.
PET film: thickness = 0.025 mm.

terephthalate (PET), with various lengths, as given in Table I (Teijin Co., Ltd.).

Surface Treatment of PET Fiber

In order to achieve a strong bond between PET fiber and the TPE matrix, an adhesion test was carried out using PET films, which were treated with three kinds of solutions under conditions as follows: (1) dipping in a toluene solution containing 2 wt % isocyanate and baking at 175°C for 3 min, (2) dipping in a toluene solution containing 3 wt % SIS and baking at 175°C for 3 min, and (3) dipping in a resorcinol formaldehyde latex (RFL) solution, as described previously,[16] and baking at 200°C for 1 min. Each treated PET film was compressed together with a TPE film and the adhesion strength between them was measured by 180 degree peeling.

Processing

Styrenic block copolymer and PET short fiber were mixed directly in an open roll with a 2 mm opening. The mixture was always rolled along the same direction in order to orient fibers in sheets. Finally, each stock was passed through the mill and was then compressed at 150°C for 5 min to form sheets that were 2.0 in thickness for tensile tests.

Measurement

The stress–strain curves of the composites were obtained in the direction of the orientation of the fibers at a strain rate of 50 mm/min, using an Autograph (Shimazu Co., Ltd.). The section and fracture faces of the composites were coated with sputtered gold and were observed by a scanning electron microscope.

RESULTS AND DISCUSSION

Fiber Treatment

The surface treatment of PET films was carried out with various systems, presented in Table II. The adhesive strength between PET film and SIS film increased with the treatments and became greater using two treatment steps, such as Nos. 5 and 6. The highest adhesive strength was obtained by treatment in toluene solution containing isocyanate and SIS. On the basis of the results, PET fibers were dipped in toluene solution, containing 2 wt % isocyanate and 3 wt % SIS, and were baked at 175°C for 3 min.

Table II Surface Treatment Steps for PET Film and Their Adhesive Strength

No.	1st Solution	2nd Solution	Baking Temperature (°C)	Adhesive Strength (gf)
1	—	—	—	200
2	Isocyanate	—	175[a]	280
3	SIS	—	175[a]	300
4	RFL	—	200[b]	250
5	Isocyanate	RFL	200[b]	450
6	Isocyanate	SIS	175[a]	850
7	(Isocyanate + SIS)		175[b]	1100

[a] Baking for 3 min.
[b] Baking for 1 min.

For SBS composites, PET fibers were treated with the mixed solution of isocyanate and SBS in toluene solvent.

The effect of the fiber treatment on stress–strain curves is shown in Figure 1 for the composites filled with 10 vol % PET fiber that were 6 mm in length. The composites display almost the same stress for treated and untreated fibers at small strain (under 10%). The stress of the composites filled with untreated fiber yields at 10% strain and is invariant at greater elongations. The stress of composites filled with treated fiber increases linearly with increasing strain to yield at about 50% elongation. After the yield point, the stress of the composites falls down and the composites are broken down. This shows that the bonding agent of isocyanate in toluene solvent is useful for the PET fiber–styrenic block copolymer composites.

The fracture faces of the composites, filled with fiber that are 6 mm in length, are shown in Figure 2. The fracture face of the composites, filled with

Figure 1 Stress–strain curves for SIS(1), SIS(2), and SBS composites; 10 vol % fiber was 6 mm length, untreated and treated by isocyanate bonding agent.

untreated fiber, has a lot of holes on the surface, as shown in Figure 2(a), which indicates that the fibers are pulled out from the matrix due to the poor adhesion between the fiber and the matrix. In the case of composites filled with treated fiber, fragments of the matrix adhered on the fractured fiber and few holes on the surface are observed, as shown in Figure 2(b). It is obvious that the treatment with isocyanate and TPE can produce strong adhesion on the interface between TPE matrix and PET fiber. Cross sections of composites, filled with untreated and treated PET fiber, are shown in Figures 3(a) and (b), respectively. The figures indicate a uniform distribution of PET fibers in matrix elastomer, but Figure 3(a) shows that there are gaps between the fiber and matrix due to a lack of bonding.

Stress–Strain Behavior

Figure 4 shows the effect of fiber loading on tensile properties for the SIS(1) elastomer and composites filled with treated fiber that was 6 mm in length. The stress of the SIS(1) elastomer increases gradually with increasing strain, which is typical rubbery elasticity. The stress of the composites increases almost linearly with increasing strain, then falls rapidly above about 50% strain. The inflection point at the maximum stress is the yield point of these composites, which may correspond to adhesion failure between the fiber and the matrix, because such a yield point does not occur in the matrix alone. Figure 5 shows the yield point with respect to fiber loading and fiber length. The yield strength increases with increasing fiber loading and fiber length. The yield elongation decreases with increasing fiber length, but it is little dependent on fiber loading in the present range. A similar relationship between the yield point and fiber loading and fiber length was found in the SIS(2) and SBS composites. The yield
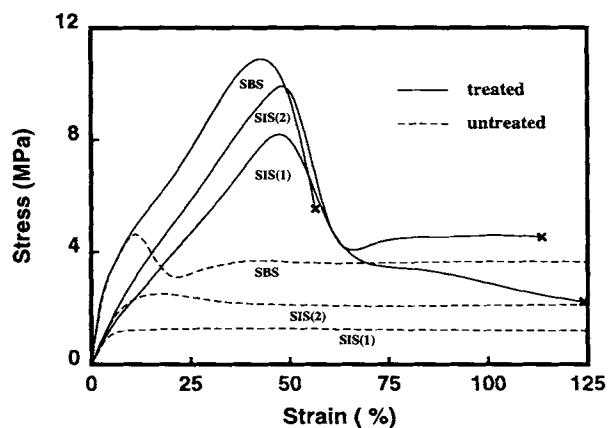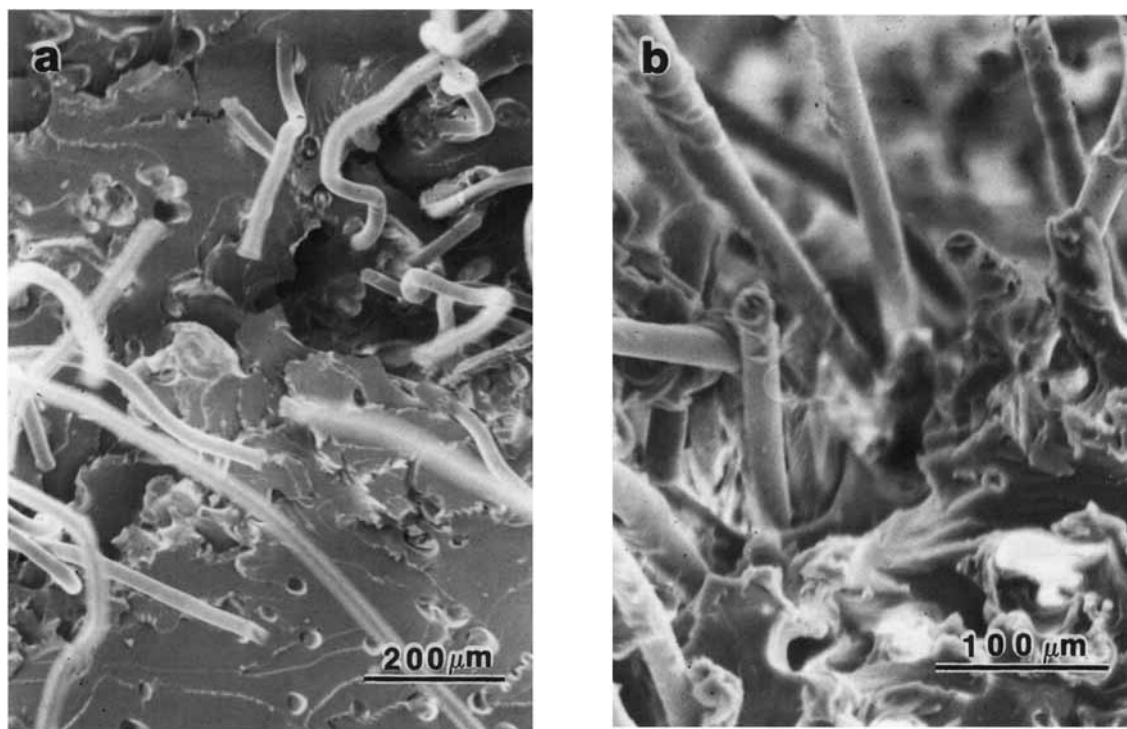
Figure 2   Fracture surfaces of SBS composites filled with 10 vol % PET fiber untreated (a) and treated by isocyanate (b).
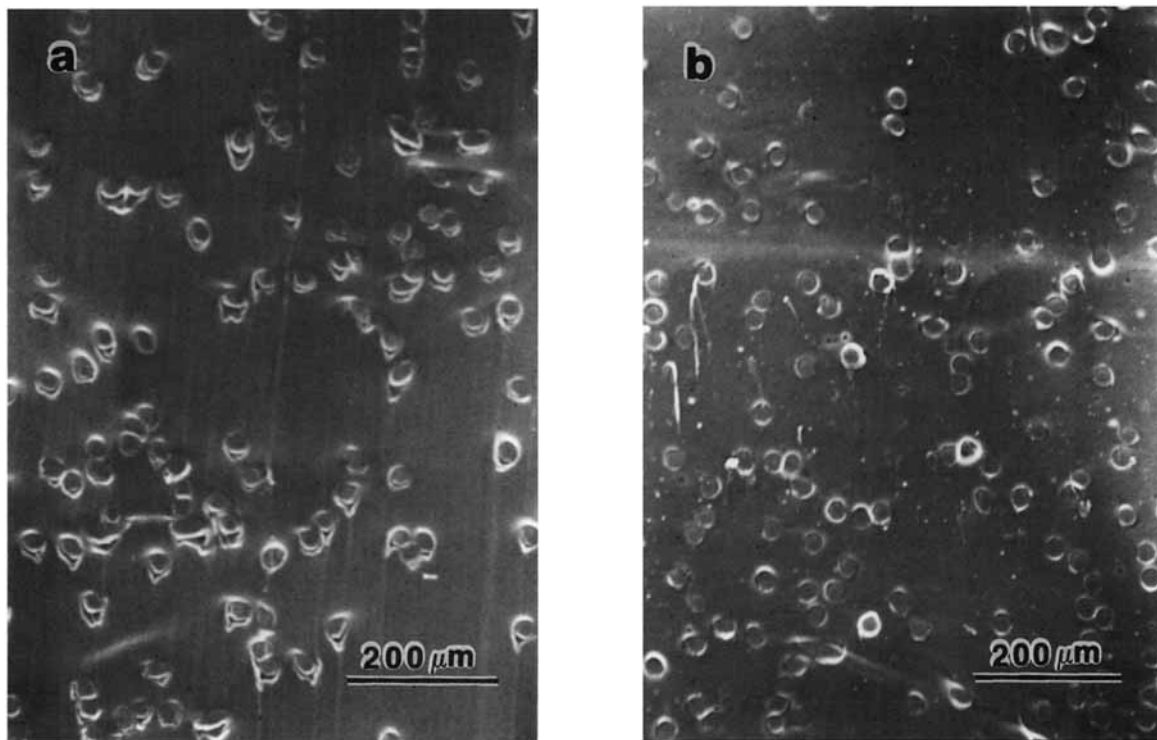

Figure 3   Cross sections of SBS composites filled with 10 vol % PET fiber untreated (a) and treated by isocyanate (b).
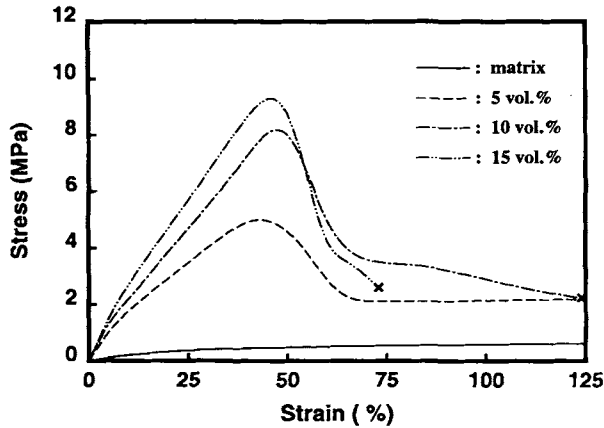
Figure 4 Effect of fiber loading on stress-strain curves for SIS(1) composites; treated fiber was 6 mm in length.

strength increased and the yield elongation decreased a little in the order of SIS(1), SIS(2), and SBS.

Figure 6 shows the dependence of the initial Young's modulus on fiber loading and fiber length for the SIS(1) composites with treated fiber. The composite filled with fiber that was 0.5 mm in length shows similar stress-strain behavior to the SIS(1) elastomer, though with a little higher stress for the former. The Young's modulus of the composite increases slightly with increasing fiber loading. In this
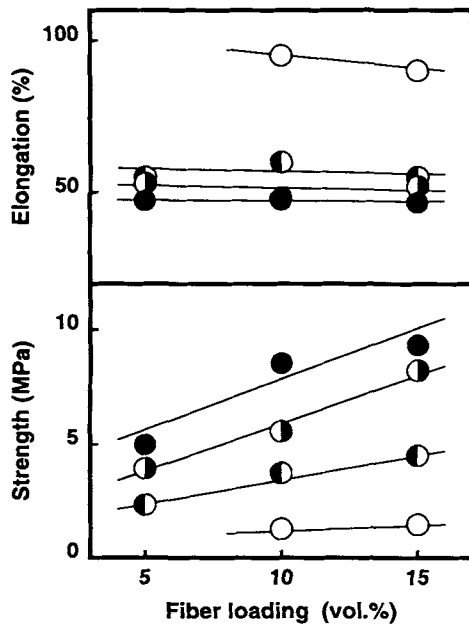

Figure 5 Effect of fiber loading on strength and elongation at yield point for SIS(1) composites; treated fiber was 0.5 mm, (O) 2 mm, (◐) 4 mm, (◑), and (●) 6 mm in length.
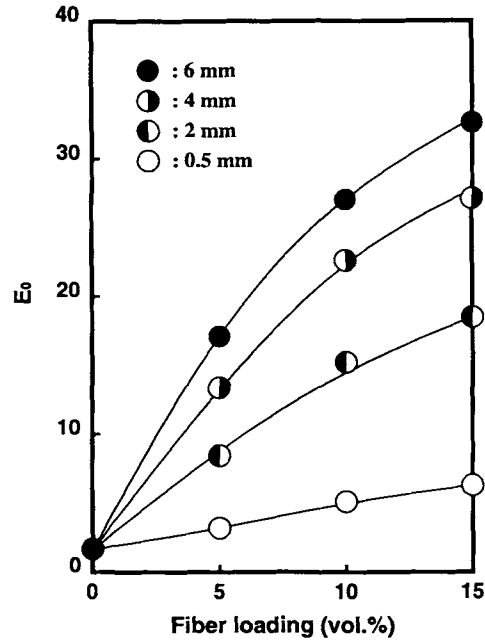

Figure 6 Effect of fiber loading and fiber length on Young's modulus E_0 of SIS(1) composites with treated fiber.

case, the fiber length is so short that fiber plays a role only as a particle with volume effect. When the fiber length is above 2.0 mm, the Young's moduli of the composites increase remarkably with increasing fiber loading and fiber length. The stress-strain curves of the SIS(2) composites are similar to those of the SIS(1) composites; the Young's modulus and the stress at yield point of the former are a little larger than those of the latter. This result is mainly due to the higher volume ratio of styrene block in SIS(2), because the styrene block has a higher modulus than the isoprene block.

Figure 7 shows the stress-strain curves of SBS composites filled with treated fiber that was 6.0 mm in length. The stress on the SBS elastomer rises steeply up to an elongation of about 3%, which indicates that SBS has a higher Young's modulus than that of the SIS elastomers. The stress-strain curve of the SBS elastomer shows a yield point at an elongation of about 3%, and follows with a plateau value of stress. It is noted that the stress of PET fiber-SBS composites increases by two steps with increasing strain. In the first step, under 3% elongation, the stress of the composites increases with a steep slope to the inflection point, corresponding to the yield point of the matrix elastomer, and in the second step, between 3% and 50% elongation, the stress increases with a moderate slope from the inflection point to the yield point of about 50%, with
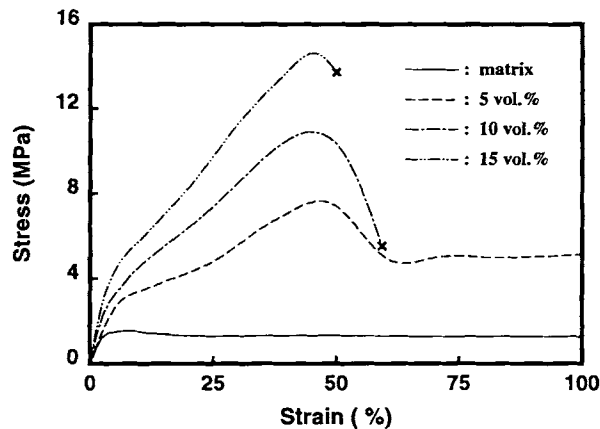
Figure 7 Effect of fiber loading on stress–strain curves for SBS composites; treated fiber was 6 mm in length.

increasing strain. When the strain is over the yield point, the PET fiber–SBS composites are broken down at a higher stress and at a lower elongation than those of PET fiber–SIS composites. The tangent moduli of the SBS composite for the initial step and for 15% elongation of the second step are shown in Figure 8, as compared with those of SIS(1) and SIS(2) composites. The modulus of SIS composites for the second step, E_{15}, have nearly the same values as those for the initial step, E_0. The modulus of the SBS composite for the initial step increases
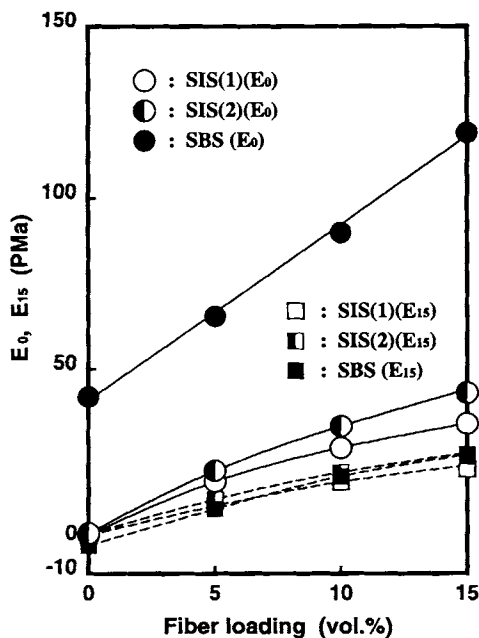

Figure 8 Effect of fiber loading on tangent modulus of at 0% and 15% elongation for SIS(1), SIS(2), and SBS composites; treated fiber was 6 mm in length.
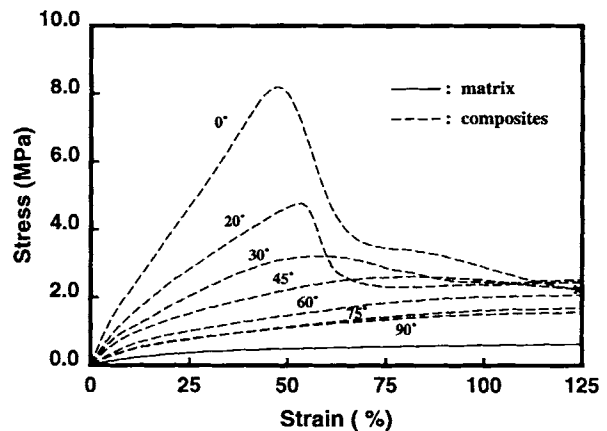

Figure 9 Stress–strain curves as a function of angle θ for SIS(1) composite; 10 vol % treated fiber was 6 mm in length.

steeply with fiber loading and the one for the second step increases with fiber loading as slowly as the SIS composites.

The effect of tensile angle θ to the fiber's direction of orientation is shown in Figure 9 for the SIS(1) composite, filled with 10 vol % treated fiber that was 6 mm in length. With increasing θ, the yield stress decreases markedly and the yield point shifts to a longer elongation. When θ is larger than 60°, the stress is so small that the yield peak disappears and the stress–strain curve takes on a similar shape to that of the matrix. On the other hand, the yield elongation increases slowly with increasing θ up to 30°. Therefore, the mechanical properties of short fiber reinforced composites are affected by tensile angle, as well as by fiber length.

From the tensile data above, the yield elongations (about 50%) for all the composites were greater than the break elongation of PET fiber (about 14%). This fact suggests that the matrix elastomer undergoes most of the deformation in the composite and that the filled fiber undergoes large internal stress with little deformation during extension. A reinforcement mechanism of short fiber–elastomer composites may be described as follows: the matrix elastomer, attached to the middle of fiber, is restrained to extend greatly and most of the deformation occurs in the matrix region surrounding the end of fibers, because short fibers, with large aspect ratios, are oriented along the direction of rolling.

Stress Softening

The effect of strain amplification and reinforcement of short fiber–elastomer composites is related with

tensile hysteresis, as shown by the area of the stress–strain cycle and the stress softening during extension. In the stress–strain cycle test, specimens were extended to constant strains of 30% or 55%, which were just under or beyond the yield point of the composites filled with treated fiber, respectively, and after resting for few seconds, they were retracted. For the next cycles, the specimens were extended to the same strain as the initial strain. The cycles were repeated eleven times. Figure 10 shows the first and second stress–strain cycles for the SIS(1) elastomer and its composites, filled with 10 vol % treated and untreated fibers that were 6 mm in length. For the SIS(1) elastomer, all the retraction and subsequent reextension curves show a close resemblance to the original stress–strain curve, so that the hysteresis loops are small. On the other hand, the SIS(1) composites, filled with treated and untreated fibers, show bigger hysteresis loops and residual strain after the first cycle, in comparison with those of the SIS(1) elastomer. The second hysteresis loops of the composites, filled with untreated fibers, are different from the first hysteresis loops, but they are similar in shape at 30% and 55% strains. This suggests that the breakage of weak bonds between fiber and matrix elastomer occurs at a low stress of about 1 MPa. The stress of the composite, filled with treated fiber, increases by two steps with increasing strain at the
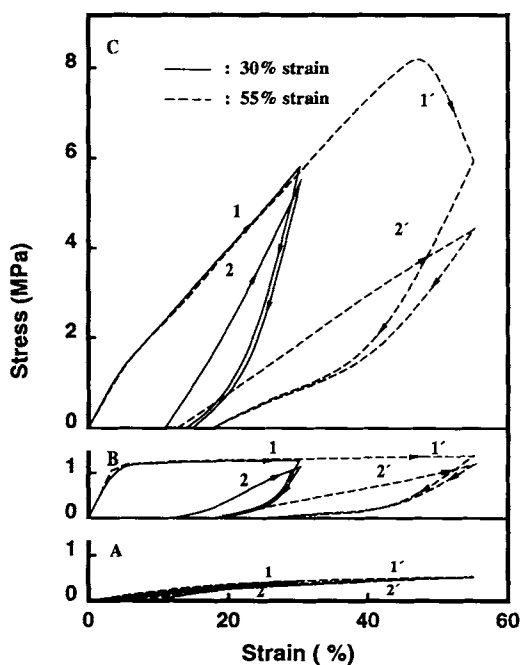
Figure 11   Stress softening at constant strains of 30% (circle) and 55% (square) vs. hysteresis cycle times for SIS(1) composites. (O, □) elastomer, (●, ■) treated, and (◐, ◧) untreated; 10 vol % fiber was 6 mm in length.

first cycle. Furthermore, the composite shows different loops under and beyond the yield point.

The effect of repeated cycles on stress softening is shown in Figure 11 for the SIS(1) composites. The relative stress is given as the ratio of the stress to the original stress at the same strain. The stress softening of the SIS(1) elastomer occurs mostly in the first cycle of stressing, similar to rubber and filler loaded vulcanizates,[19] and further stress softening increases only a little during subsequent cycles. The relative stress of the composites, filled with untreated fiber, decreases rapidly during the initial few cycles and shows a similar tendency between cycles at 30% and 55% strains. For the composite filled with treated fiber, the relative stress for the 30% strain decreases at a rate similar to that of the SIS(1) elastomer, but the one at 55% strain falls remarkably with each cycle so that the composite is broken down during repeated cycles. Such an obvious difference in the increase rate of stress softening between the composites, filled with treated and untreated fiber, may be due to different mechanisms under repeated deformation. The SIS(2) composites had behavior similar to the SIS(1) composites, although the relative stress of the SIS(2) elastomer decreases at a little higher rate than for the SIS(1) elastomer. Figure 12 shows the hysteresis loops of stretching for the SBS elastomer and com-

Figure 10   Hysteresis loops of the first and second circles of SIS(1) composites. (A) elastomer, (B) untreated, and (C) treated; 10 vol % fiber was 6 mm in length.
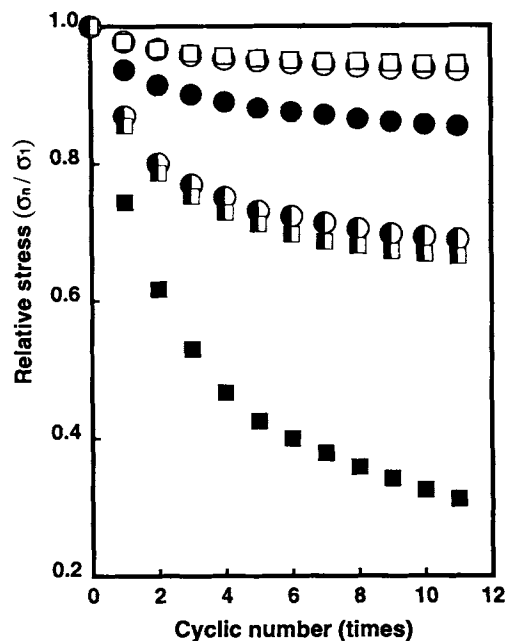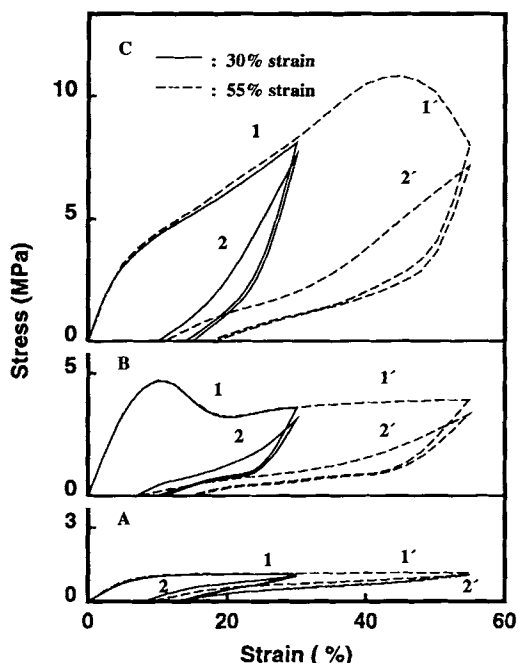
Figure 12 Hysteresis loops of the first and second circles of SBS composites. (A) elastomer, (B) untreated, and (C) treated; 10 vol % fiber was 6 mm in length.

posites. The hysteresis of SBS elastomer shows a big residual strain after the first elongation of 30%. It is noted that the hysteresis loops of the SBS elastomer are similar to those of the SIS(1) composite, filled with untreated fiber, as shown in Figure 11. The stress softening of the SBS elastomer decreases at a rate higher than the SIS elastomers, but the softening of the SBS composites is like that of the SIS composites. These findings suggest that the stress softening of composites is influenced by the matrix elastomer, as well as the loading fiber, and that the stress of composites depends on the hard domain of the matrix at the first step and on the soft domain at the second step.

Figure 13 shows the effect of fiber loading on stress softening at the first cycle for composites of SIS and SBS elastomers. The softening increases linearly with increasing fiber loading for all the TPE, and becomes greater in the order of SIS(1), SIS(2), and SBS. The difference among those composites increases with increasing fiber loading. Figure 14 shows the effect of fiber length on stress softening at the first cycle for SIS(1) composites. The softening increases in an S shape with increasing fiber length, and at the length of 2 mm, the increment is large. When fiber length is longer than 2 mm, the softening increases gradually.
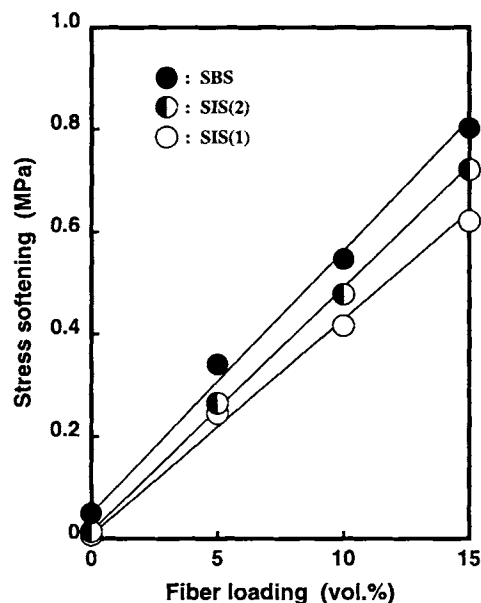

Figure 13 Effect of fiber loading on stress softening in the first hysteresis loop at 30% strain for SIS(1), SIS(2), and SBS composites; treated fiber was 6 mm in length.

The stress softening of carbon black filled rubber vulcanizates is mainly attributed to the breakage of carbon black chains or agglomerates, or to the breakage of weak bonds between the rubber and the carbon black surface.[19] According to Hardwood et
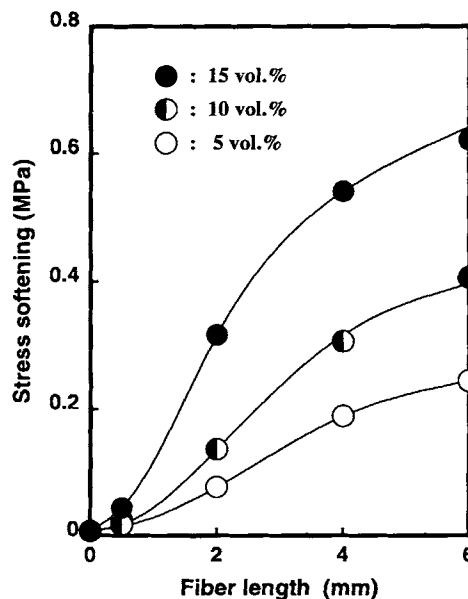

Figure 14 Effect of fiber length and fiber loading on stress softening in the first hysteresis loop for SIS(1) composites with treated fiber.

al.,[20,21] however, the softening process has mainly been due to change in the rubber phase alone, possible sources include breaking and remaking of crosslinks during extension, residual local orientation of network chains persisting after recovery, and breaking of network chains. For the styrenic block copolymer, the hard domains of styrene segment increase stiffness provide the restriction of flexibility in the crosslinked soft block. The stress softening in stretching results from a breakdown of some of the hard domains, and the recoverable elasticity is limited to low strain levels.

For composites filled with untreated fiber, the hysteresis for the first cycle includes energy loss from debonding of fiber in the composites. The stress softening from repeated cycles is mainly attributed to energy loss, due to friction between the free fiber and the matrix, and the stress softening of the matrix. On the other hand, composites filled with treated fiber, extended to strains smaller than 30%, have little stress softening, due to the strong bond. The stress softening at higher elongation beyond the yield point may be mainly due to the destruction of bonding between fiber and matrix, due to the large strain. Debonding cracks are produced at points where large stress is present and develop further during repeated cycles so that the composite is broken down. Thus, stress softening increases steeply with increasing numbers of cycle. Therefore, the possible softening sources of short fiber reinforced composites include (1) interface separation around the end of fiber under large strain, (2) breaking and restructuring of hard domains of styrene segments in the matrix where the stress is large, especially at the region surrounding the end of the fiber, (3) stress softening of matrix, and (4) stress softening of fiber.

CONCLUSION

The reinforcement of TPEs with short fibers results in composites with the elasticity of the matrix and the stiffness of the fiber. The performance and properties are a function of fiber–matrix adhesion, the properties of the TPE matrix, fiber loading, fiber length, and fiber orientation. The following facts were established by investigating the mechanical properties of the composites.

1. Fiber-to-matrix adhesion was poor when no bonding agent was present. In this case, stress–strain curves of composites showed low yield stress and large break elongation. The interaction between fiber and elastomer can be improved by a treatment of TPE with isocyanate in toluene solution. The stress–strain curve of the composites, filled with treated fiber, displayed a yield point at about 50% elongation, with higher stress and smaller break elongation. The uniformity of fiber dispersion for PET fiber-SIS and PET fiber-SBS composites was confirmed.

2. The stress on composites, filled with treated fiber, increased by two steps up to the yield point with increasing strain; the modulus for the first step was larger than the one for the second step. The modulus of SBS composites showed a similar value to the SIS composites at the second step and a larger value at the first step. The yield stress of composites increased with increasing fiber length, and the yield elongation decreased with increasing fiber length, but was little influenced by fiber loading. Furthermore, the stress–strain curve depended on the fiber orientation.

3. For the SIS elastomers, all the retraction and subsequent reextension curves in hysteresis loops showed a close resemblance to the original extension curve, so that the hysteresis loops were small. The hysteresis of SBS elastomer showed a bigger hysteresis loop and a greater residual strain after the first elongation of 30%, as compared with SIS elastomers. It seems that the stress softening in stretching is a result of a breakdown of some of the hard domains; the recoverable elasticity is limited to the low strain region.

4. The composites showed greater hysteresis and stress softening than the respective matrix elastomers, and the softening of composites increased a little more than the respective matrix with repeated cycles. The softening in the first cycle increased linearly with increasing fiber loading, and increased in an S shape with increasing fiber length.

5. These findings suggest that the stress softening of composites is influenced by the matrix elastomer, as well as the loading fiber, and that the stress of composites is dependent on the hard domain of the matrix in the first step and on the soft domain in the second step. The interface separation around the end of fiber under large strain, and the breaking and restructuring of hard domains in the matrix, might be important sources of softening of the composites.

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