

ORIGINAL ARTICLE

Effect of Organoclay and Blends on the Abrasion Resistance and Mechanical Properties of Poly(styrene-*block*-butadiene-*block*-styrene)

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Abstract

To investigate organoclay, high styrene resin masterbatch (HSR), high impact polystyrene (HIPS), and polystyrene (PS) as reinforcing materials for the improvement of the abrasion resistance of poly(styrene-*block*-butadiene-*block*-styrene) (SBS), SBS/organoclay nanocomposites, SBS/HSR, SBS/HIPS, and SBS/PS blends were prepared. The effect of organoclay and blends on the abrasion resistance and mechanical properties of SBS was investigated. Even though intercalations of organoclay are observed for SBS/Cloisite 20A nanocomposites and not for SBS/Cloisite 30B composites, the abrasion resistance of SBS/Cloisite 20A nanocomposites is worse than that of SBS/Cloisite 30B composites. When SBS was blended with HSR, HIPS and PS, the abrasion resistance of the blends increases with increasing of HSR, HIPS and PS content from 0 to 20 wt%.

Key words : Abrasion resistance, Organoclay, SBS

1. Introduction

Thermoplastic elastomers (TPEs) are materials that combine the processing characteristics of thermoplastics with the physical properties of vulcanized rubbers. Because of their ability to provide products with elastic behavior similar to that of vulcanized rubber without slow and costly process of vulcanization, some TPEs were used to replace vulcanized rubbers. Another advantage over vulcanized rubber is that they can be recycled. This advantage becomes important due to the strict environmental laws and increasing disposal costs, leading to many new products.

Because of these advantages, there has been strong demand to replace vulcanized rubbers with environment-friendly TPEs for the footwear outsole materials in the shoe industry. The possible solution for this is

using poly (styrene-*block*-butadiene-*block*-styrene) (SBS) for the outsole materials. Recently, SBS is used as an outsole material for the low-price footwears. However, SBS cannot replace vulcanized rubbers as an outsole material for most of footwears because of its poor abrasion resistance. Even though there have been a lot of research on miscibility behavior between SBS and other polymers (Chu et al., 1999; Han et al., 1992; Roe and Jin, 1984), there are few studies about the abrasion resistance of SBS.

In recent years, polymer/organophilic layered silicate (organoclay) nanocomposites have attracted considerable attention from both an academic and application point of view due to their improvement in material properties. Owing to the nanometer thickness and extremely high aspect ratio of silicate layers, the nanocomposites exhibit improvements in their

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mechanical, thermal and barrier properties (Alexandre and Dubois, 2000; Ataefard and Moradian, 2011; Giannelis, 1996; Lebaron et al., 1999; Maniar, 2004; Ray and Okamoto, 2003; Shafiee et al., 2010). Even though there have been studies about the mechanical properties and structure of SBS/organoclay nanocomposites (Chen and Feng, 2009; Laus et al., 1997; Liao et al., 2004), the systemic studies about the effect of organoclays on the abrasion resistance of SBS/organoclay nanocomposites have not been reported yet as best of our knowledge.

Therefore, in this study, SBS/organoclay nanocomposites were prepared using two kinds of organoclays. And the effect of organoclay on the abrasion resistance and mechanical properties of SBS was investigated. Also, to investigate high styrene resin masterbatch (HSR), high impact polystyrene (HIPS), and polystyrene (PS) as reinforcing polymers for the improvement of abrasion resistance of SBS, SBS/HSR, SBS/HIPS, and SBS/PS blends were prepared, and the relationship between the mechanical properties and abrasion resistance of the blends was studied.

2. Materials and Methods

2.1. Materials and preparation method

Organoclays were purchased from Southern Clay Products (U.S.A) under the trade name of Cloisite 20A and Cloisite 30B. Organic modifier of Cloisite 20A and Cloisite 30B is dimethyl dihydrogenated tallow quaternary ammonium and methyl tallow bis-2-hydroxyethyl quaternary ammonium, respectively. All the polymers used in this study were obtained from Kumho Petrochemical Co. (South Korea). The trade name of SBS is KTR 601 (33% styrene content). Its melt flow index is 6 g/10 min (200 °C, 5 kg), and hardness is 73 (Shore A). HSR is KHS 68 (68% total styrene content) and HSR was produced by mixing SBR 1502 of 23.5% styrene and high styrene resin latex at high temperature. HIPS is

HI425, and its melt flow index is 9 g/10 min (200 °C, 5 kg). PS is GP125, and its melt flow index is 9 g/10 min (200 °C, 5 kg).

SBS and organoclays were mixed in an internal mixer PBV-03 (Irie Shokai Ltd., Japan) at 150 °C and at a rotor speed of 30 rpm for 15 min. SBS was first introduced and followed by the addition of organoclays. Then the composites were put in a mold, and the samples for various measurements were obtained by compression-molding at 14.7 MPa, in a hydraulic press at 150 °C for 5 min. SBS/HSR, SBS/HIPS and SBS/PS blends at different weight ratios were prepared in an internal mixer PBV-03 at 150 °C and at a rotor speed of 30 rpm for 15 min. Then the blends were put in a mold, and the samples for various measurements were obtained by compression-molding at 14.7 MPa, in a hydraulic press at 150 °C for 5 min.

2.2. Testing

X-ray diffraction (XRD) patterns were taken with a Rigaku D/max 2200H X-ray diffractometer (40 kV, 50 mA). The scanning rate was 0.5 °/min. The basal spacing of the organoclay layer, d , was calculated using the Bragg's equation, $n\lambda = 2d\sin\theta$. In NBS abrasion test, three samples were abraded across the surface of a rotating, abrasive drum until 2.54 mm of the sample was abraded. A rubber standard was tested before the test. The NBS abrasion resistance was then calculated based on the cycles to abrade the sample and the rubber standard. For example, if the test sample took twice the number of cycles to abrade 2.54 mm, compared with the rubber standard, the NBS abrasion resistance would be 200 %. In this test, higher NBS abrasion numbers indicate higher resistance to abrasion. After NBS abrasion test, the surface in the samples was investigated using optical microscopy (Model Camscope, Sometech Co, South Korea).

A Universal Testing Machine (Model 4466,

Instron Co., USA) was used to obtain the tensile properties of the samples at room temperature. The crosshead speed was 500 mm/min. All measurements were performed for five replicates of dumbbell-type specimens and averaged to get the final result. The dumbbell-type specimens were obtained from the compression molded samples. Also the tear strength was measured using unnicked 90° angle test pieces at a cross head speed of 500 mm/min in the Universal Testing Machine.

Calorimetry was carried out in a differential scanning calorimetry (TA instrument, DSC 2010). The DSC measurements were conducted under a nitrogen atmosphere. The heating and cooling rate was fixed at 10 °C/min. The second heating DSC traces were used for analysis.

3. Results and Discussion

3.1. SBS/organoclay Nanocomposites

The d_{001} spacing of organoclays and SBS/organoclay composites are given in Table 1. The peak at $2\theta = 3.5^\circ$ corresponding to (001) plane (interlayer spacing d : 2.5 nm) is observed for pristine Cloisite 20A. The peak at $2\theta = 3.5^\circ$ shifts to the lower angle at $2\theta = 2.5^\circ$ (d : 3.5 nm) for SBS/Cloisite 20A (2 wt%) and SBS/Cloisite 20A (5 wt%) nanocomposites. This result indicates the intercalations of SBS molecules into the

Table 1. d_{001} spacing of organoclays and the SBS/organoclay composites

Materials	Diffraction angle (2θ , degree)	d_{001} spacing (nm)
Cloisite 20A	3.5	2.5
Cloisite 30B	5.0	1.8
SBS/Cloisite 20A (2 wt%)	2.5	3.5
SBS/Cloisite 20A (5 wt%)	2.5	3.5
SBS/Cloisite 30B (2 wt%)	5.0	1.8
SBS/Cloisite 30B (5 wt%)	5.0	1.8

interlayer of organoclays, resulting in the expansion

of the silicate interlayer. For SBS/Cloisite 30B composites, the peak position nearly does not change compared with pristine Cloisite 30B (d : 1.8 nm). This indicates nearly no intercalations of polymers into the interlayer of Cloisite 30B. Therefore, SBS/Cloisite 30B composites cannot be regarded as nanocomposites.

Fig. 1 and 2 show the effect of organoclay content on tensile strength and elongation at break of SBS/Cloisite 20A nanocomposites and SBS/Cloisite 30B composites, respectively. For SBS/Cloisite 20A nanocomposites, tensile strength increases with increasing content of Cloisite 20A from 0 to 2 wt%, but further increase in content of Cloisite 20A leads to the approximately constant value in tensile strength.

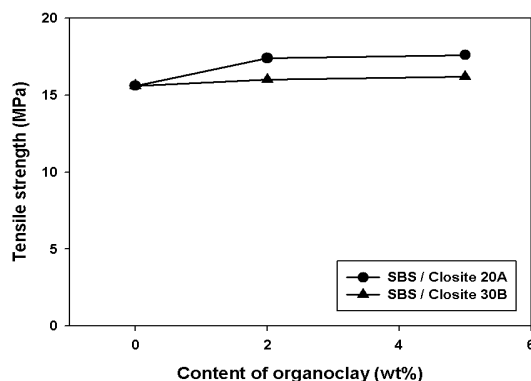


Fig. 1. Effect of organoclay content on the tensile strength of SBS/organoclay.

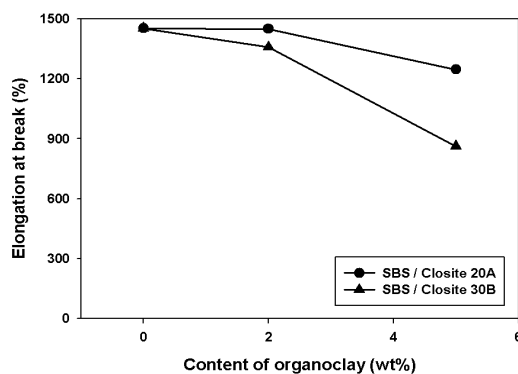


Fig. 2. Effect of organoclay content on the elongation at break of SBS/organoclay.

Properly dispersed organoclays restrict the mobility of polymer chains during tensile loading, resulting in the increase in tensile strength. No further increase in tensile strength for SBS/Cloisite 20A (5 wt%) from SBS/Cloisite 20A (2 wt%) nanocomposites could be caused by the premature failure starting at the filler aggregates. There was also a report that the decrease of tensile strength in high organoclay content could be attributed to aggregation of organoclay layers (Ahmadi et al., 2005). Elongation at break decreases with addition of organoclays. This is due to the decrease in ductility with increased stiffness. At the same content of organoclay, the tensile strength and elongation at break of SBS/Cloisite 20A nanocomposites is higher than those of SBS/Cloisite 30B composites. These results agree well with XRD results.

Fig. 3 shows the NBS abrasion resistance of SBS/Cloisite 20A nanocomposites and SBS/Cloisite 30B composites. With increasing content of organoclay, the NBS abrasion resistance decreases. Based on this result, it can be concluded that the addition of organoclays into SBS leads to decrease of abrasion resistance. At the same content of organoclay, the NBS abrasion resistance of SBS/Cloisite 30B composites is higher than that of SBS/Cloisite 20A nanocomposites, even though tensile strength and elongation at break of SBS/Cloisite 20A nanocomposites are higher than those of SBS/Cloisite 30B composites.

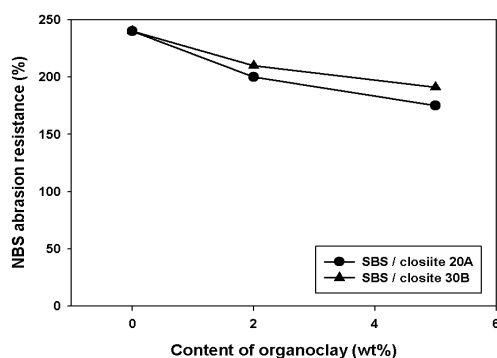


Fig. 3. Effect of organoclay content on NBS abrasion resistance of SBS/organoclay.

Yang et al. (1991) have shown that rigid fillers normally increase the abrasive wear loss of the filled silicone elastomers. The stress concentration introduced by the rigid fillers actually creates a damage zone surrounding the fillers. The damage zone is a location where microscopic damages that eventually lead to wear loss are more likely to take place. With increasing content of fillers, the volume of damage zones increases (Yang et al., 1991). In this study, since intercalations of organoclay are observed for SBS/Cloisite 20A nanocomposites but not for SBS/Cloisite 30B composites, the contact areas between organoclay and SBS are larger for SBS/Cloisite 20A nanocomposites than SBS/Cloisite 30B composites. As a result, volume of damaging zone surrounding the organoclay is larger for SBS/Cloisite 20A nanocomposites than SBS/Cloisite 30B composites. This may be the origin of worse abrasion resistance of SBS/Cloisite 20A nanocomposites than that of SBS/Cloisite 30B composites. Fig. 4 shows the tear strength of SBS/Cloisite 20A nanocomposites and SBS/Cloisite 30B composites. With increasing content of organoclay, tear strength slightly decreases. The decrease in tear strength may be due to the aggregates of organoclays. Weak SBS-organoclay interaction may lead to the organoclay aggregates in the matrix. The crack initiation or propagation is more likely in aggregation zone.

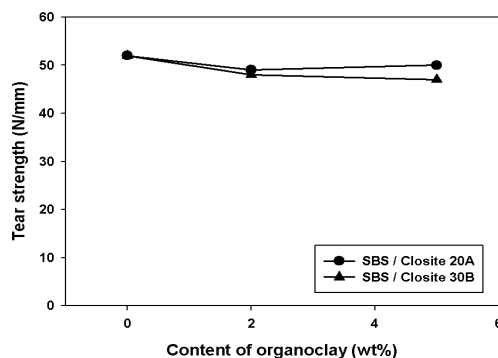


Fig. 4. Effect of organoclay content on the tear strength of SBS/organoclay.

3.2. SBS Blends

Table 2 shows the glass transition temperatures of SBS/PS, SBS/HIPS, and SBS/HSR blends determined by DSC measurements. SBS has a glass transition temperature (T_g) of the polybutadiene (PB) blocks at -84.6 °C, but T_g of the polystyrene blocks could hardly be detected due to the small PS content of this polymer. PS has T_g at 100.2 °C. For SBS/PS blends, there is no significant shift in T_g of SBS and T_g of PS. HIPS has T_g of the PS component at 101.6 °C, but T_g of the PB component cannot be detected. For SBS/HIPS blends, no significant change has been observed in T_g of SBS and T_g of HIPS. HSR has T_g at 66.8 °C. For SBS/HSR blends, there is also no significant change in T_g of SBS and T_g of HSR. Therefore, these results indicate the poor compatibility between SBS and the added polymers.

Fig. 5 shows the NBS abrasion resistance of SBS/HSR, SBS/HIPS and SBS/PS blends. With increasing content of HSR, HIPS and PS from 0 wt% to 20 wt%, the NBS abrasion resistance of the blends increases. However, with further increase of HSR, HIPS and PS content, the NBS abrasion resistance decreases. Because of their improvement in NBS abrasion resistance, the blends offer the potential to replace vulcanized rubbers for the footwear outsole materials in the shoe industry. Since vulcanized rubbers are irreversible cross-linked elastomers, they

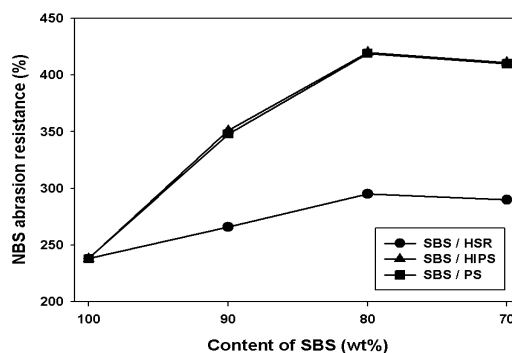


Fig. 5. NBS abrasion resistance of SBS/HSR, SBS/HIPS and SBS/PS blends.

cannot be remolded and recycled. Therefore, they are disposed to landfill or incinerated after being used. Disposing of the vulcanized rubbers to landfill is a serious environmental problem because rubbers do not decompose. Also, incineration has disadvantages. Incineration releases toxic air emissions (dioxines, chlorocompounds, etc.) (Pappa et al., 2001), damaging the environment and human health. And there is the Kyoto Protocol to consider, as many countries move towards their domestic goal of reducing carbon dioxide emissions. Because of their thermoplastic nature of SBS/HSR, SBS/HIPS and SBS/PS blends, they can be recycled and this is important to environmental protection. Also since the blends can be prepared without slow and energy-consuming vulcanization process, the use of the blends can lead

Table 2. Glass transition temperatures of SBS/PS, SBS/HIPS and SBS/HSR blends

Blends	T _g of SBS (°C)	T _g of PS (°C)	Blends	T _g of SBS (°C)	T _g of HIPS (°C)	Blends	T _g of SBS (°C)	T _g of HSR (°C)
SBS/PS (100/0)	-84.6	-	SBS/HIPS (100/0)	-84.6	-	SBS/HSR (100/0)	-84.6	-
SBS/PS (90/10)	-84.4	-	SBS/HIPS (90/10)	-85.5	-	SBS/HSR (90/10)	-85.6	68.3
SBS/PS (80/20)	-83.9	101.1	SBS/HIPS (80/20)	-86.0	103.1	SBS/HSR (80/20)	-85.8	68.2
SBS/PS (70/30)	-85.0	101.3	SBS/HIPS (70/30)	-85.5	102.8	SBS/HSR (70/30)	-84.5	67.9
SBS/PS (0/100)	-	100.2	SBS/HIPS (0/100)	-	101.6	SBS/HSR (0/100)	-	66.8

to the decrease of energy consumption.

To investigate the correlation between macroscopic mechanical properties and abrasion resistance, tensile properties and tear strength of the blends were investigated. Fig. 6 and 7 show the tensile strength and elongation at break of SBS/HSR, SBS/HIPS and SBS/PS blends, respectively. With increasing content of HSR, HIPS and PS, tensile strength and elongation at break of the blends decrease. Generally, when the molecular weight of PS homopolymer is low enough, it can be solubilized in the SBS block copolymer domains (Han et al., 1992). Otherwise added polymers form separated phases in the SBS blends. Since tensile strength of HSR, HIPS and PS is higher than that of SBS used in this study, decreased tensile

strength of the blends with increasing content of added polymers (HSR, HIPS and PS) indicates the poor adhesion between SBS matrix and the added polymer domains.

In many studies, the mechanical property to relate the abrasion resistance was the product of tensile stress and elongation at break. The approximately linear relationship between abrasion resistance and the product of tensile stress and elongation at break was observed for the twenty or so polymers studied by various authors (Briscoe, 1981). However, the improvement of tensile strength and elongation at break is not observed in this study as shown in Fig. 6 and 7.

After NBS abrasion test, the ridge patterns were

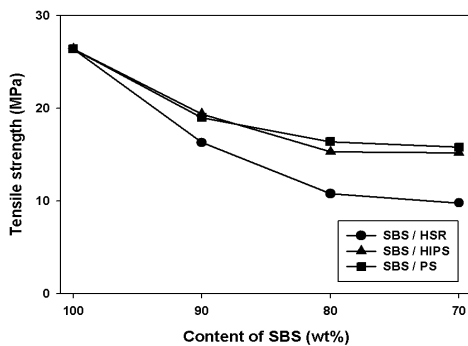


Fig. 6. Tensile strength of SBS/HSR, SBS/HIPS and SBS/PS blends.

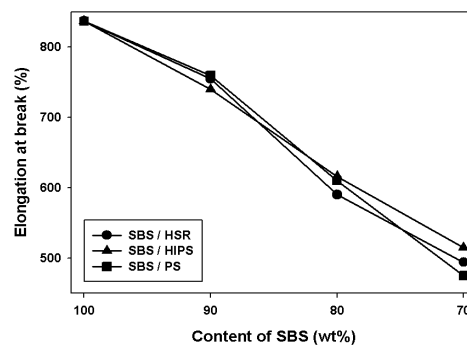


Fig. 7. Elongation at break of SBS/HSR, SBS/HIPS and SBS/PS blends.



Fig. 8. Optical microscopy image of the ridge on the surface of SBS/HSR (80/20) blend.

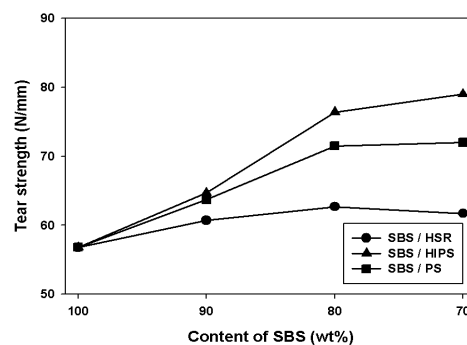


Fig. 9. Tear strength of SBS/HSR, SBS/HIPS and SBS/PS blends.

observed on the surface of all the blend samples. Fig. 8 shows an optical microscopy image of the ridge on the surface of SBS/HSR (80/20) blend as an example. Ridges are formed by microtearing mechanism (Zhang, 1981). These ridges were initiated by microtearing of the surface due to frictional forces between the abrasive and the surface. Therefore, the abrasion resistance of SBS/HSR, SBS/HIPS and SBS/PS blends may be related to the tear strength (Mukhopadhyay et al., 1991). Fig. 9 shows the tear strength of SBS/HSR, SBS/HIPS and SBS/PS blends. With increasing content of HIPS and PS, tear strength of the blends increases. For SBS/HSR blends, tear strength increases with increasing of HSR content from 0 to 20 wt%, but tear strength slightly decreases with further increase in content of HSR. Tear strength of the blends shows the similar behavior with abrasion resistance.

4. Conclusions

In this study, the addition of organoclays into SBS leads to deteriorated abrasion resistance. Even though intercalations of organoclay are observed for SBS/Cloisite 20A nanocomposites and not for SBS/Cloisite 30B composites, the abrasion resistance of SBS/Cloisite 20A nanocomposites is worse than that of SBS/Cloisite 30B composites. This might be related with larger volume of damaging zone surrounding the organoclays in SBS/Cloisite 20A nanocomposites than in SBS/Cloisite 30B composites.

When SBS was blended with HSR, HIPS and PS, the NBS abrasion resistance of the blends increases with increasing content of HSR, HIPS and PS from 0 wt% to 20 wt%. However, with further increase of HSR, HIPS and PS content, the NBS abrasion resistance decreases. Among the macroscopic mechanical properties, tear strength of the blends shows the similar behavior with abrasion resistance.

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