

Effect of Polyethylene Glycol on the Properties of Styrene-Butadiene Rubber/Organoclay Nanocomposites Filled with Silica and Carbon Black

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ABSTRACT: Polyethylene glycol (PEG) is widely used as a dispersing agent and can also be used to prevent the adsorption of ingredients on the surface of silica. From the XRD results, PEG that was used as the dispersing agent on the SBR/organoclay compound filled with silica and carbon black (CB) was intercalated between the organoclay layer. Additionally, the interactions with the PEG differed depending on whether 3-aminopropyltriethoxysilane (APTES) or *N,N*-dimethyldodecylamine (DDA) were used as clay modifiers. When PEG was added, the T_g of the SBR/silica/APTES-MMT compound increased through the formation of hydrogen bonds between the ether linkages of PEG and the

hydroxyl groups of APTES. For the SBR/silica/DDA-MMT compound with PEG, slippage occurred between the silicate, and DDA because of the alkyl chain of DDA. The SBR/silica/APTES-MMT/CB compound with PEG exhibited the highest T_g value and the highest bound rubber content, with high modulus values at 100 and 300%. The SBR/silica/DDA-MMT/CB compound had the best properties in terms of the wet skid resistance and the rolling resistance. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1766–1777, 2011

Key words: SBR; organoclay; latex method; XRD; polyethylene glycol; carbon black; silica

INTRODUCTION

Around 70% of natural rubbers (NR) that are produced on the globe are used for tire production. Additionally, 30% of tire raw materials are manufactured using NR, while 20% are synthetic rubber.¹ In recent years, nano-fillers have been applied as reinforcing agents for styrene-butadiene rubber (SBR), NR, and isobutylene-isoprene rubber (IIR) to improve the properties of tires.^{2–8} Clay, a type of nano-filler, is constructed of multiple sheets of silicates that are piled up. The silicate has a layered structure with a thickness of 1 nm for each layer. Each side is typically 100–1000 nm in length with an aspect ratio of at least 100. If silicates are distributed in this layered formation within a matrix, the surface area and orientation are very great.⁹

When SBR/clay nanocomposites were manufactured using the latex method with 3-aminopropyltriethoxysilane (APTES) as a modifier, hydroxyl

groups formed on the surface of silicate through the hydrolysis reaction of the ethoxy group of the APTES. Additionally when bis(triethoxysilylpropyl)-tetrasulfide (TESPT) was added to the manufactured SBR/APTES-MMT compound, the 100 and 300% modulus values increased more than the SBR/APTES-MMT compound alone.^{4,10,11} These results were attributed to the improvement in the interfacial interactions between the rubber molecules and silicates through the form of covalent bonds between the ethoxy group of TESPT and the hydroxyl group that was generated on the surface of the silicate during the hydrolysis of APTES.^{4,10,11}

In recent studies, SBR/organoclay nanocomposites were prepared using APTES and the *N,N*-dimethyldodecylamine (DDA) as modifiers for Na⁺-montmorillonite (Na⁺-MMT), and the SBR/DDA-MMT nanocomposite exhibited better mechanical properties than the SBR/APTES-MMT nanocomposite because the degree of crosslinking and the better dispersion of the silicates within the rubber matrix for the DDA modifier even though the APTES modifier formed covalent bonds with TESPT.⁴ Additionally, the ethoxy group of APTES was replaced in the MMT-suspension with a hydroxyl group because of the hydrolysis reaction. Either the hydrogen bonding between the hydroxyl group and the oxygen atoms in the silicate caused a physical adsorption to occur,

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or an ion-dipole interaction between the hydroxyl group and the ions between the layers of the silicate.^{4,11} These results were critical to examination of the SBR/clay nanocomposite using the latex method. A previous study examined the properties of SBR/organoclay nanocomposites that were manufactured using APTES-MMT and DDA-MMT.

Some recent studies on tire tread compounds reported that during the manufacturing process for the SBR compound, the rolling resistance and the wet skid resistance were better when a dual phase filler system was applied using silica and carbon black (CB) compared to CB alone as the filler.^{12–14} The rolling resistance is related to the fuel efficiency of automobiles, while the wet skid resistance deals with the braking power on the surface of a wet road.^{14,15}

Silica has a large quantity of hydroxyl groups on its surface, and thus, filler–filler interactions occur between the silica through hydrogen bonding. These interactions reduce the dispersion of silica within the rubber matrix and cause the adsorption of polar accelerators on the surface of silica. Therefore, some accelerators do not participate in the crosslinking reaction, and the degree of crosslinking is reduced for the rubber/silica compounds.^{16–19} Therefore, poly(ethylene glycol) (PEG; HO—(CH₂CH₂O)_{*n*}—H) has widely been used to prevent the loss of the accelerators due to polar groups in silica, which improves the silica dispersion.^{17,21} PEG has a large number of ether linkages (—CH₂—O—CH₂—), which form hydrogen bonds with the silanol groups on the silica. Therefore, PEG is used to reduce the filler–filler interactions in silica, preventing the accelerator loss.^{8,20} According to the results from a study on the application of PEG in NR/clay nanocomposites, PEG was intercalated between the layers of the silicate, which reduced the hydrophilic properties of the silicate and improved the dispersion of the silicates within the NR matrix.⁸ Additionally, the existence of the PEG chains between the exchangeable cations between the clay layers prevented the adsorption of the vulcanizing agents, improving the degree of crosslinking. As a result, the 100% modulus, the 300% modulus and the tensile strength of the NR/clay nanocomposites were enhanced.⁸

For a SBR compound that is filled with 20 phr of CB (HAF) and 10 phr of organoclay, the 100% modulus, the elongation at break and the tensile strength showed more than doubled in comparison with SBR/CB (20 phr) compounds. In this case, the network structure due to the bound rubber of CB contributed to the improved modulus. Furthermore, the macromolecule chains slippage on the surface of the nanoclay contributed to the improved elongation at break and tensile strength, leading to synergistic effects between CB and the organoclay in the SBR

nanocomposites.²² Silica has a large quantity of silanol groups on its surface, while CB contains many functional groups, such as phenol, ketone, carboxyl, and quinone groups.²³ As a result, the interactions between the rubber molecules and the fillers were different when silica and CB were used together for the SBR/organoclay nanocomposites. Also, the properties were different depending on whether or not PEG was added.

In this study, the SBR/organoclay nanocomposites were prepared with APTES and DDA as the modifiers using the latex method. For the SBR/organoclay nanocomposites that were filled with silica and CB, the effects of the presence of PEG between the modified silicates on the layer-to-layer structure of the silicate, the swelling ratio, the dynamic viscoelastic properties, the bound rubber contents, and the mechanical properties were studied.

EXPERIMENTAL

Materials

In this experiment, SBR 1502 (bound styrene contents: 23.5% in styrene-butadiene rubber; 25 wt % of solid contents in the latex; Kumho Petrochemical Co., Korea) was used for the SBR latex and KUNIPIA-F (cation exchange capacity; 115 mequiv./100g; Kunimini Co., Japan) was used for the sodium montmorillonite (Na⁺-MMT). 3-Aminopropyltriethoxysilane (APTES, 99%) and *N,N*-dimethyldodecylamine (DDA, 97%) were purchased from Aldrich, and bis(triethoxysilylpropyl)tetrakisulfide (TESPT) was used as the coupling agent. Zeosil-175 (Rhodia-Korea, Korea) and Carbon black ISF N220 (Corax N220, Evonik Carbon Black Korea Co., Ltd., Korea) were used as the fillers, and poly(ethylene)glycol (PEG-4000F, average molecular weight of $M_n = 3180\text{--}3520\text{ gmol}^{-1}$, Greensoft Chem., Ltd., Korea) was the dispersion agent. Additionally, zinc oxide (ZnO), stearic acid, antioxidant (BHT; 2,6-di-*tert*-butyl-4-methyl-phenol), sulfur and accelerator (TBBS; *N-tert*-butyl-2-benzothiazol sulfonamide) were used as additives.

Modifier-MMT suspension solutions

First, 7 g of Na⁺-MMT was stirred in 700 mL of distilled water for 24 h at 65°C. Then 2 g each of APTES and DDA were added to the MMT-suspension solution and stirred at 500 rpm using a hot plate stirrer for 15 h at 65°C.

Cocoagulation of SBR latex/modifier-MMT

The modifier-MMT suspension and 420 g of SBR latex were intensively stirred at 1500 rpm using a high speed stirrer for 30 min at room temperature to

TABLE I
The Formulation of Various SBR Compounds; Without PEG(Amounts; Weight Parts Per 100 Weight Parts of Rubber (phr))

No.	Materials	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8
1	SBR 1502					100			
2	Clay	7	7	–	7	7	–	7	7
3	DDA	2	–	–	2	–	–	2	–
4	APTES	–	2	–	–	2	–	–	2
5	PEG-4000	–	–	–	–	–	–	–	–
6	Silica(zeosil-175)	–	–	25	18	18	25	18	18
7	TESPT					2			
8	Carbon Black(N220)	–	–	–	–	–	35	35	35
9	Zinc Oxide					3			
10	Stearic Acid					1			
11	BHT					1			
12	TBBS					1			
13	Sulfur					1.75			
The optimal vulcanization time (t_{90} ; min:sec)		21 : 18	26 : 00	26 : 49	20 : 43	26 : 41	24 : 27	17 : 44	25 : 49

prepare the SBR/organoclay compound. A coagulation solution was prepared by mixing 1.5 mL of sulfuric acid (latex coagulant) with 300 mL of distilled water. Then this solution was added to the mixed solution of SBR latex and the modifier-MMT suspension, thus coagulating the latex. The prepared SBR/organoclay compounds were washed until a pH value of 7 was reached, and then the compounds were dried in an oven for 20 h at 50°C.

Manufacturing of SBR nanocomposites

Each of the SBR and SBR/organoclay compounds shown in Table I and Table II were mixed in an 8-in. two-roll mill (rotor speed ratio; 1 : 1.4) for 3 min at 50°C and mixed in a banbury type kneader for 2 min at 110°C. Additionally, silica, TESPT, and PEG (variable) were added to the kneader for 4 min, and then CB was mixed in the kneader for 3 min. The primary additives, including ZnO, stearic acid and BHT, were added with mixing for 3 min. At this

time, the dump temperature ranged from 130 to 135°C. Additionally, the secondary additives, including sulfur as the crosslinker and TBBS as the accelerator, were added, and the compound was mixed for 3 min at 40°C using a two-roll mill to prevent any scorching that could be caused by the viscous heat generation of the compound.

The optimal vulcanization time (t_{90}) was determined by measuring the torque value of the rubber compound at 160°C using an oscillating disk rheometer (ODR, MYUNG-JI Tech, Korea, Model; ODR 2000). Then the mixed compounds were pressed at 2000 psi and 160°C using a hydraulic press for the optimal vulcanization time to manufacture the SBR nanocomposites.

Layer-to-layer structure analysis of organoclay

The layer-to-layer distance of the organoclay was measured using an X-ray diffraction (XRD) test at room temperature with a Rigaku D/MAX 2200

TABLE II
The Formulation of Various SBR Compounds; with (Amounts; Weight Parts Per 100 Weight Parts of Rubber (phr))

No.	Materials	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8
1	SBR 1502					100			
2	Clay	7	7	–	7	7	–	7	7
3	DDA	2	–	–	2	–	–	2	–
4	APTES	–	2	–	–	2	–	–	2
5	PEG-4000					2			
6	Silica(zeosil-175)	–	–	25	18	18	25	18	18
7	TESPT					2			
8	Carbon Black(N220)	–	–	–	–	–	35	35	35
9	Zinc Oxide					3			
10	Stearic Acid					1			
11	BHT					1			
12	TBBS					1			
13	Sulfur					1.75			
The optimal vulcanization time (t_{90} ; min:sec)		19 : 44	25 : 05	19 : 33	22 : 04	21 : 59	17 : 37	16 : 19	19 : 21

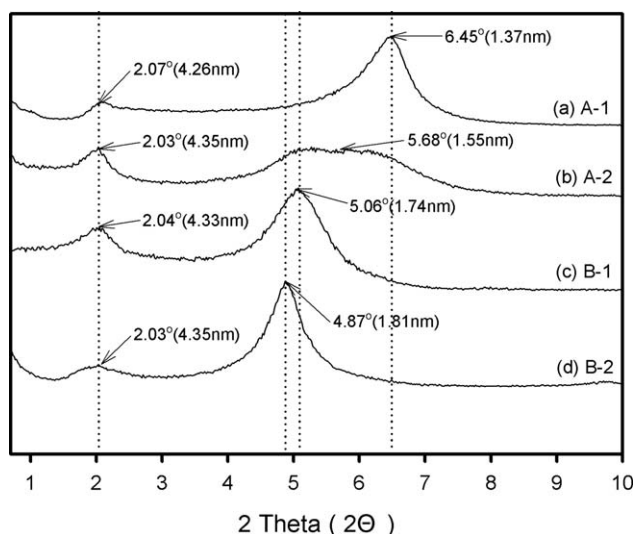


Figure 1 X-ray diffraction (XRD) patterns of SBR/organo-clay vulcanizates: A-1 and A-2; without PEG, B-1 and B-2; with PEG.

(Japan) X-ray diffractometer and a Cu-K α radiator. The X-ray diffraction data were obtained in the reflection mode from 1° to 10° (2 θ) at a rate of 1°/min.

Measurement of swelling ratio

Swelling ratio of the vulcanized rubber compounds was determined. The weight of the 30 × 5 × 2 mm³ specimens was measured after they were impregnated in a toluene solution for 1, 2, 3, 6, 9, 12, and 24 h at 30°C according to ASTM D 471-79. Then the swelling ratio (%) was determined using the following expression with respect to the measured weight of the specimens.

$$Q(\%) = \frac{(W_1 - W_0)/d_2}{W_0/d_1} \times 100$$

Q: Swelling ratio (%)

W₀: Weight of the specimen before swelling

W₁: Weight of the specimen after swelling

d₁: Density of SBR (0.94 g/mL)

d₂: Density of toluene (0.87 g/mL)

Measurement of bound rubber

Toluene was used for the bound rubber determination. In this experiment, 0.2 g of the uncured compound was placed into a wire mesh cage. The cage and the uncured rubber compound were immersed in 200 mL of the solvent for 7 days at room temperature, and the solvent was renewed after 3 days. After extraction, the rubber and the cage were immersed in 200 mL of acetone for one day. The bound rubber was dried for one day at room temperature and then for 24 h in an oven at 105°C. The

percentage of bound rubber in the uncured compound was calculated using the following equation.

$$R_B(\%) = \frac{[W_{fg} - W_t[m_f/(m_f + m_r)]]}{W_t[m_r/(m_f + m_r)]} \times 100$$

R_B(%): The bound rubber content

W_{fg}: The weight of the filler and gel

W_t: The weight of the sample

m_f: The fraction of the filler in the compound

m_r: The fraction of rubber in the compound

Analysis of the dynamic viscoelastic behavior

The storage modulus (*E'*) and tan δ of the cured SBR nanocomposites were measured using the tensile film mode of DMA (TA Instruments, USA, Model; DMA Q800 V7.1 Build 116) with an amplitude of 10 μ m and a frequency of 10 Hz at a temperature sweep of 5°C/min from -60 to 80°C.

Mechanical properties

Dumbbell-shaped specimens (100 × 25 × 2 mm³; gauge length 20 mm and gauge width 5 mm) were cut from a flat sheet using a single stroke to ensure that the substance was smooth. The mechanical properties, such as the moduli at 100 and 300% elongation, the tensile strength and the elongation at break, were examined at an applied extension speed of 500 mm/min using a 5000N load cell with a Universal Testing Machine (UTM, KSU Co., Korea, Model; KSU-05M-C) according to the ASTM D412.

RESULTS AND DISCUSSION

Layer-to-layer structure analysis of the SBR nanocomposites depending on existence of PEG

SBR/organo-clay master batches were prepared using APTES and DDA as the modifiers for the clay to prepare the SBR nanocomposites using dual (organo-clay/silica) and ternary filler systems (carbon black (CB)/silica/organo-clay). The formulation of the SBR compounds depended on the existence of PEG is shown in Tables I and II. The activating agent, accelerator and sulfur contents were determined from the nonoil type SBR standard formulation of ASTM D3185. For the layer-to-layer analysis of the silicate depending on the existence of PEG, the XRD patterns of the SBR/organo-clay compounds are shown after vulcanization in Figure 1. The SBR/DDA-MMT compound (A-1) without PEG exhibited a sharp peak at 6.45° (1.37 nm), while the SBR/APTES-MMT compound (A-2) had a broad peak in the range of 4.5°–7.0°. In previous studies, the layer-to-layer distance of Na⁺-MMT was 1.24 nm. When

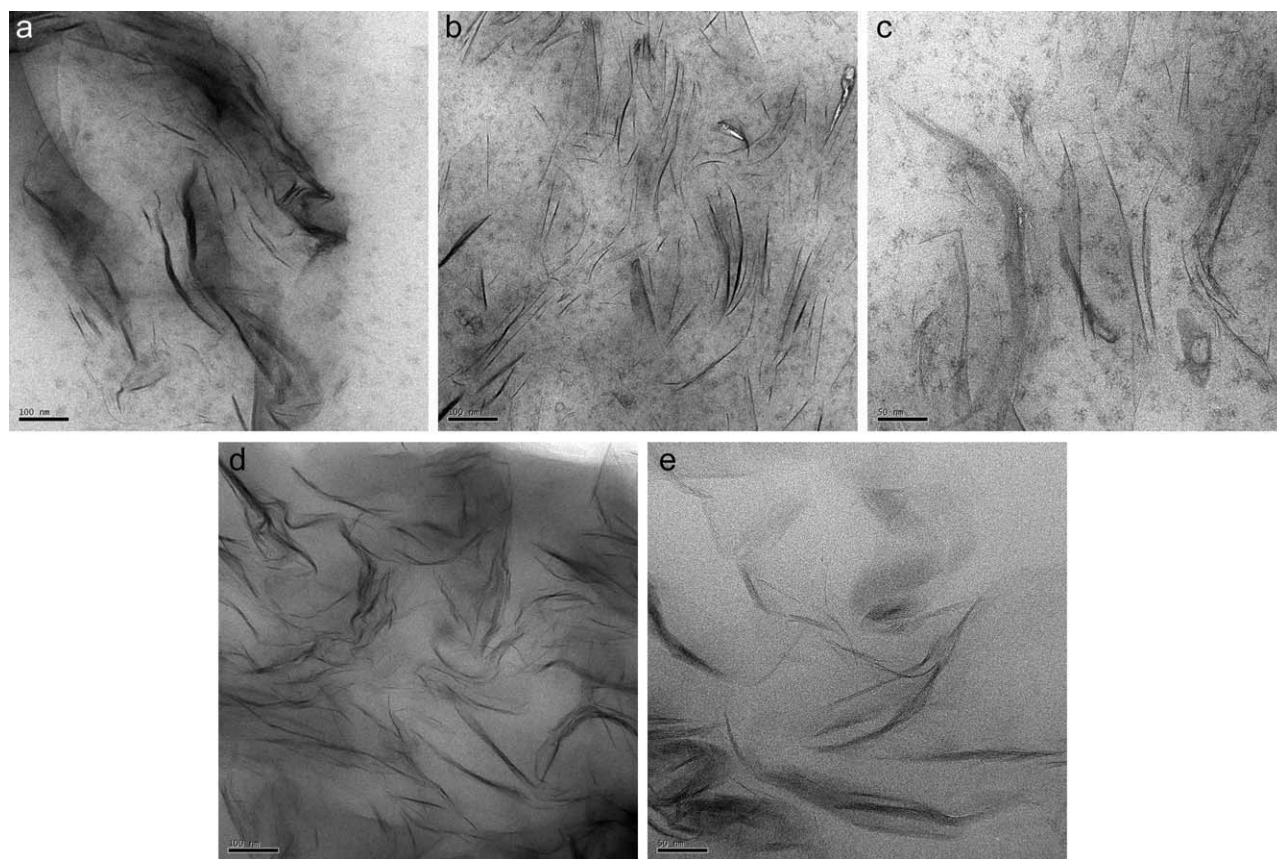


Figure 2 TEM images of the (a) SBR/Na-MMT, (b) and (c) SBR/DDA-MMT (A-1), and (d) and (e) SBR/APTES-MMT (A-2) compounds after vulcanization.

the SBR/clay (unmodified clay) compound was manufactured using the latex method, the layer-to-layer distance of the silicate was 6.45° (1.37 nm).⁴ The layer-to-layer structure formed through the flocculation of ions (H^+ and SO_4^{2-}) that were supplied when coagulation (coagulant; sulfuric acid) occurred after the MMT-suspension solution and the SBR latex were mixed.^{4,10} As a result, the XRD analysis of the A-1 compound did not confirm that DDA was intercalated between the silicate layers. For this reason as shown in Figure 2, transmission electron microscopy (TEM) images were used to observe the morphology of the silicate in the rubber matrix. At a scale bar size of 50 nm, the image showed that the SBR/DDA-MMT compound had 2–4 silicate layers. At a scale bar size of 100 nm, the silicates were exfoliated in all of the rubber matrix areas, and any areas that appeared to have a layer-to-layer structure that formed from flocculating ions were sporadic. The XRD analysis was used to analyze only the intercalated structure, however, a gallery distance of 8 nm or longer could not be observed in the 2 θ range of the XRD.⁹ Therefore, when the hydrophobic DDA was applied, the DDA molecules grafted onto the silicate surface and silicates were exfoliated within the rubber matrix. Additionally, a layer-to-

layer structure was formed because of some flocculating ions. When the latex method was used, the SBR/APTES-MMT compounds did not exhibit a strong peak at 6.45° . However, since the cation exchange reaction between the amino group of APTES and the Na^+ ions of the silicate occurred simultaneously with the coagulation of the SBR latex during the latex method, APTES and the flocculating ions coexisted between the silicate layers. The intercalated structure with flocculating ions was relatively less prevalent because of the ion-dipole interactions between APTES and the silicate, leading to the broad peak that was observed. In previous studies, the TEM analysis of the SBR/APTES-MMT compound showed a silicate structure with two to eight layers.⁴ When the hydrophobic DDA was applied, the dispersion of the silicates was superior than when APTES was applied.

The SBR/DDA-MMT compound (B-1) with PEG had a layer-to-layer distance of 1.74 nm (5.06°), while the SBR/APTES-MMT compound (B-2) had a distance of 1.81 nm (4.87°). A previous report showed that when PEG was added to the NR/clay compound, the layer-to-layer distance of the clay differed according to the PEG content, and the *d*-spacing size increased up to 1.80 nm.⁸ Therefore, these

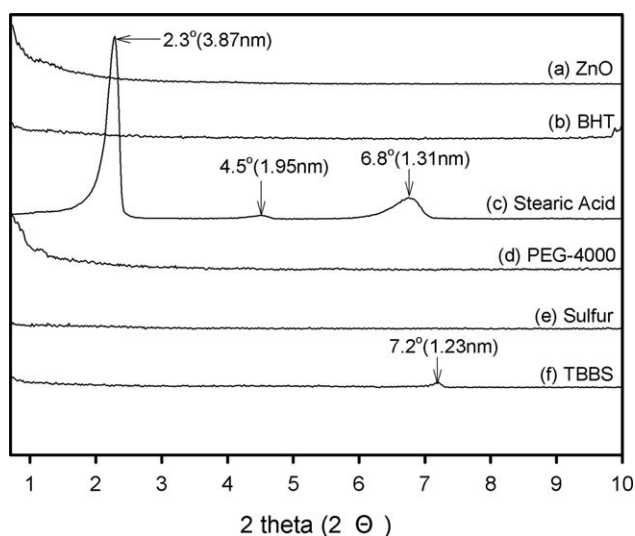


Figure 3 X-ray diffraction (XRD) patterns according to the additives for SBR compounds.

results were attributed to the intercalation of PEG between the silicate layers. Additionally, after PEG was added, the layer-to-layer distance of the SBR/APTES-MMT compound differed by 0.07 nm compared to the SBR/DDA-MMT compound because the PEG chain was intercalated between the silicate layers and APTES for APTES-MMT, while the PEG chain was intercalated between the silicate layers where the flocculation ions existed in DDA-MMT.

The XRD analysis was conducted on the additives to verify that the peaks that appeared in the vicinity of 2.0° were due to the modifier or additives that were intercalated between the silicate layers of silicate. According to the results in Figure 3, the stearic acid exhibited two weak peaks (4.5° and 6.8°) and one strong peak (2.3°). The other additives did not

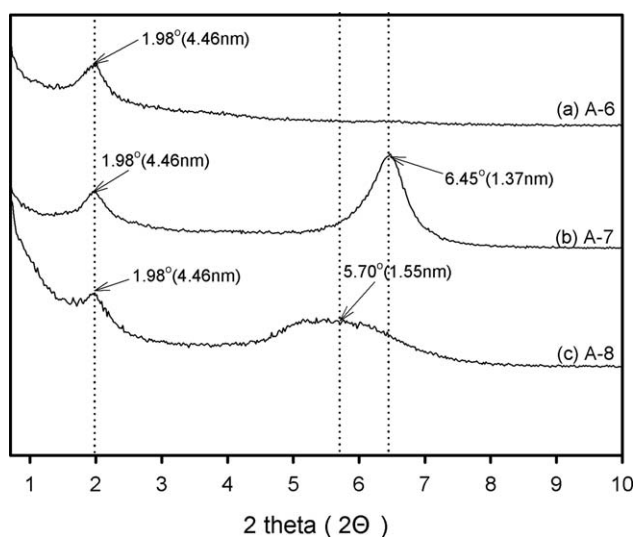


Figure 4 X-ray diffraction (XRD) patterns of SBR and SBR/organoclay vulcanizates filled with silica and carbon black; without PEG.

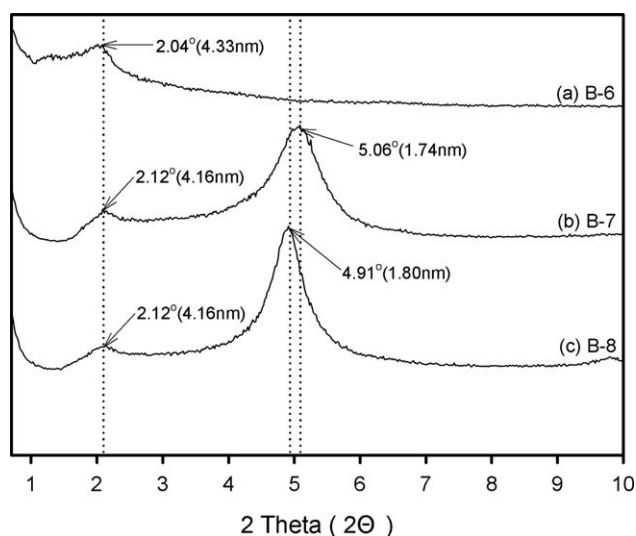


Figure 5 X-ray diffraction (XRD) patterns of SBR and SBR/organoclay vulcanizates filled with silica and carbon black; with PEG.

exhibit a strong peak at the low angles (1°–10°) of the XRD. Therefore, for the SBR/organoclay vulcanizates, the peak in the 2° region was attributed to the unique characteristics peak of the stearic acid crystals.

The effects that silica and CB had on the layer-to-layer structure of the silicate were examined for the SBR nanocomposites with the dual and ternary filler systems. The XRD analysis is shown in Figures 4 and 5. The A-6 and B-6 compounds without the organoclay were only exhibited a peak in the 2° region that was characteristic of the stearic acid crystals. After the organoclay was added, the compounds possessed an intercalated structure in the region of 4.5°–7.0°. The XRD results for the SBR nanocomposites in the ternary filler system with PEG were the same as the XRD analysis of the SBR/DDA-MMT compound and the SBR/APTES-MMT compound, and the layer-to-layer structure of the silicate did not change because of the presence of silica and CB. PEG was intercalated between the organoclay layers.

Effects on the swelling ratio of the SBR nanocomposites depending on the existence of PEG

The swelling ratios were evaluated for the rubber compound to examine the effects of PEG on the crosslinking for the SBR compounds with the dual and ternary filler systems. After immersion for 9 h, the swelling ratios of all of the compounds became constant. Figure 6 shows the swelling ratios of the SBR nanocomposites after immersion for 24 h. For the B-1 and B-2 compounds, 7 phr of clay was added as the filler. When 2 phr of PEG was added

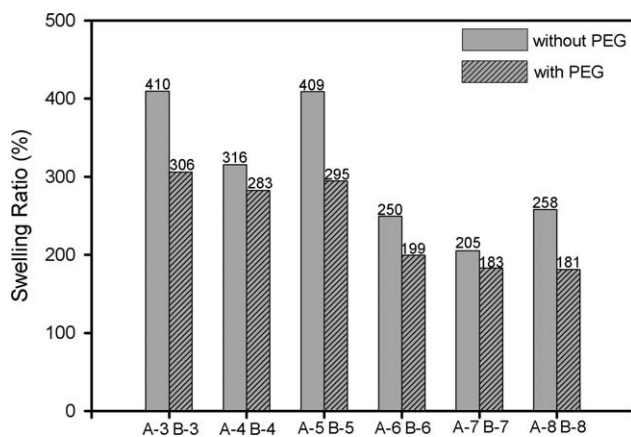


Figure 6 Effect of PEG on the swelling ratio of the various compounds.

in the internal mixer, the viscosity of the rubber compound decreased and the rubber compound stuck to the blade, which prevented the compound from being uniform. The swelling ratio and mechanical properties were excluded from the comparison because of the experimental variations. Without the addition of PEG, the swelling ratios of the A-1 and A-2 compounds were 370 and 417%, respectively. The relatively low swelling ratio of A-1 compound is due to the promoted vulcanization reaction because the amino group of the modifier was more effective for the hydrophobic DDA than the less hydrophobic APTES.⁴

The ternary filler system exhibited a lower swelling ratio than the dual filler system because of the low volume fraction of SBR in the specimen as the filler content increased from 25 phr to 60 phr.

The SBR/silica/DDA-MMT compound (A-4), which was filled with an additional 18 phr of silica compared to the A-1 compound, had the swelling ratio of 316%, decreasing 54% compared to the A-1 compound. On the other hand, the SBR/silica/APTES-MMT compound (A-5) exhibited a swelling ratio of 409%, which was similar to the A-2 compound. Theoretically, when the total content of the filler increased from 7 phr (A-1 and A-2 compounds) to 25 phr (A-3, A-4, and A-5 compounds), the swelling ratio should have decreased. However, the swelling ratios of the A-3 and the A-5 compounds were similar to the A-2 compound because the polar accelerators were adsorbed onto the surface of the silica, which reduced the amount of accelerators that could participate in the vulcanization reaction. In general, the degree of crosslinking of the rubber compound decreased because of the physical adsorption between the hydroxyl group in the silica and the polar accelerator for the SBR/silica compound, reducing the efficiency of the promoted crosslinking in the vulcanization reaction of SBR.^{20,21} Additionally, in the SBR/APTES-MMT compound, a

large quantity of hydroxyl groups formed on the silicate surface through the hydrolysis of APTES. When the SBR/APTES-MMT compound was manufactured using the latex method, the ethoxy group of APTES in an aqueous solution was replaced by a hydroxyl group during the hydrolysis reaction, and a large quantity of hydroxyl groups form on the silicate surface.^{4,10,11} The SBR/silica/DDA-MMT compound (A-4) with the lowest swelling ratio of 316% had a low silica content of 18 phr, and the accelerator loss was low when the hydrophobic DDA was used as a modifier.

The swelling ratios of the SBR compounds reduced by 104% (A-3 versus B-3), 33% (A-4 versus B-4), 114% (A-5 versus B-5), 51% (A-6 versus B-6), 22% (A-7 versus B-7), and 77% (A-8 versus B-8) after the addition of PEG because PEG hydrogen bonded to the silica and clay, reducing the polarity of the silica surface and preventing the adsorption of the accelerators and ingredients. As a result, the vulcanization reaction was facilitated. The cure rate, scorch time, viscosity, hardness, compression set, and abrasion index improved when PEG was added to the NR/silica compound.^{19,20} Additionally, when PEG was applied to diene rubber that was filled with silica, the accelerator and the ingredients could not adsorb to the hydroxyl groups on the silica surface, which improved the vulcanization reaction efficiency and enhanced the degree of crosslinking.^{20,21}

For the compounds with PEG, the SBR/silica/organoclay compound (B-4 and B-5) and the SBR/silica/organoclay/CB compound (B-7 and B-8) had a little lower swelling ratios than the SBR/silica compound (B-3) and the SBR/silica/CB compound (B-6). The vulcanization reaction was somewhat promoted because of the reduced silica content and the presence of the amino group of the modifier. For alkyl ammonium modifiers, the vulcanization reaction of the compound is promoted because of the amino groups of the modifier.^{2-4,6,11}

Consequently, PEG reduced the hydrophilic properties of the filler, which prevented the loss of the polar accelerators and ingredients and increased the vulcanization reaction, improving the crosslinking of the rubber compounds.

Bound rubber of the SBR compound in the ternary filler system

When natural rubber or synthetic rubber is compounded with CB by using a kneader or a two-roll mill, rubber molecule radicals can be generated by the chain scission. Chemical bonding occurs between the reactive sites in CB and the rubber molecule radicals, creating bound rubber on the CB surface.²⁴⁻²⁷ This bound rubber does not dissolve in solvents such as benzene. This compound is called CB gel to

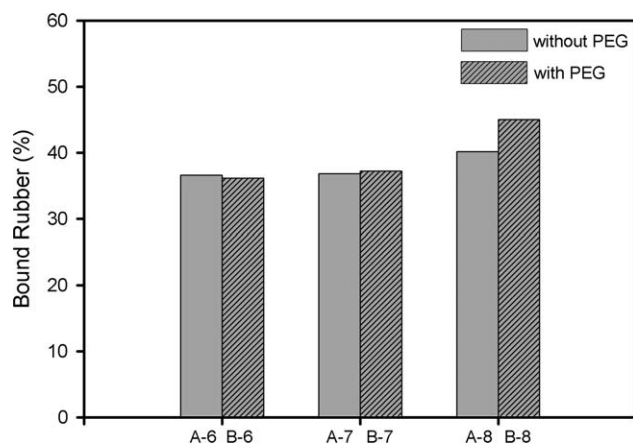


Figure 7 Effect of PEG on the bound rubber content of the un-vulcanized SBR compounds.

distinguish it from the polymer gel, and it is recognized as one of the reinforcing factors of rubber. In other words, the CB gel is a carbon-rubber complex that is insoluble in solutions such as benzene. The CB gel generally exists in unvulcanized compounds and reinforces rubber, while greatly affecting various physical properties of the rubber.^{24–27}

In Figure 7, the bound rubber content was measured by extracting the polymer and additives with a toluene solution to determine the degree of bound rubber formation for the unvulcanized SBR compounds with PEG. Bound rubber did not form for the SBR compound without the CB filler because the filler amount (silica and organoclay) was only 25 phr. Additionally, the compound mixing conditions (the mixing time and temperature of the internal mixer and the milling conditions) that were used in this study did not promote the bound rubber formation.²⁵

The bound rubber depended on factors such as the surface area, the degree of structural development and the surface activity which were influenced by the mixing conditions of the compound.^{25,27}

The SBR/silica/CB (A-6 versus B-6) compounds with or without PEG had similar bound rubber values (~ 37%) to the SBR/silica/DDA-MMT/CB (A-7 versus B-7) compounds, and thus PEG did not affect the degree of bound rubber formation. The bound rubber content of the A-8 and B-8 compounds, with APTES as a modifier, increased around 3% (A-8) and 8% (B-8), respectively, compared with the SBR/silica/CB (A-6 and B-6) compounds and the SBR/silica/DDA-MMT/CB (A-7 and B-7) compounds. When the SBR/APTES-MMT compound was made using the latex method, two types of reactions occurred between APTES and the clay.^{28,29} The first reaction was a cation exchange reaction between the Na⁺ ions in the silicate and the amino groups of APTES. The second reaction was a condensation reaction between the ethoxy groups of APTES and

the silanol groups on the edge of the silicates.³⁰ When APTES was added to improve the rubber-filler interactions for the XNBR/CB compound, the bound rubber content increased with increasing APTES content. The amino groups and the ethoxy groups of APTES acted as bridges between the COOH groups of XNBR and the OH groups of CB.³¹

Consequently, the increased bound rubber content seemed to be due to increase in the interactions between the amino groups of APTES that was grafted to the silicate edge and the CB gel. The ether groups and the OH groups of PEG increased the interaction more in the APTES-MMT/SBR/CB compounds, which revitalized the CB gel formation.

Dynamic viscoelastic properties of the SBR compounds depending on the existence of PEG

Figures 8 and 9 show the dynamic viscoelastic properties as a function of the temperature of the SBR compounds with or without PEG. In Figures 8(a) and 9(a), the storage modulus curves increased in the upper-right direction as the total filler content increased from 25 to 60 phr in the temperature range of -60°C – 80°C . Therefore, the storage modulus increased because of the strain amplification of the rubber molecules that were attached to the surface of the filler. For polymer with CB or an organic pigment that is added as filler, the filler effect caused the entire modulus curve to move in the upper-right direction when the storage modulus is measured at a fixed frequency with increasing temperature, and the filler induced modulus differences become greater at high temperatures.³²

In Figures 8(a) and 9(a), the storage modulus of the SBR/silica/CB compound (A-6) without PEG started to decrease at a slightly lower temperature than the SBR/silica/CB/organoclay compounds (A-7 and A-8). After PEG was added, the starting temperature for this decrease was slightly higher because of the increased crosslinking and the improved filler dispersion after the PEG addition. PEG can reduce the loss of the accelerators and ingredients for the silica, and the surface of the hydrophilic filler becomes less hydrophilic after the PEG addition, which improves the silica dispersion in the rubber matrix.^{19–21} Additionally, the storage modulus curves of the B-7 and the B-8 compounds increased to the right compared to the B-6 compound. Therefore, the filler effect was more remarkable because of the unique plate-like structure of the organoclay.

Figures 8(b) and 9(b) show the loss factors ($\tan \delta$) with respect to temperature from the glassy region to the rubbery region. According to these results, the maximum $\tan \delta$ value decreased in the glass transition temperature region as the total filler content

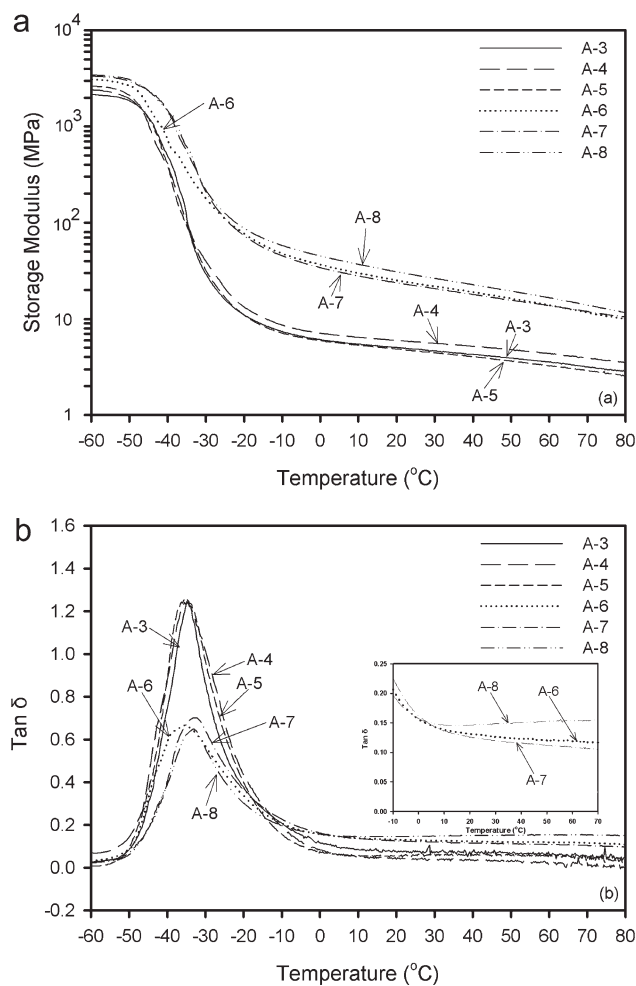


Figure 8 Temperature dependence of (a) the storage modulus (E') and (b) the loss tangent for various SBR compounds; without PEG, after vulcanization.

increased from 25 to 60 phr. The polymer matrix is the major factor that affects the energy dissipation in the glass transition temperature region, while the filler–filler interactions are the main factors that influence the energy dissipation in the rubbery region.^{7,33–35} Therefore, at higher filler contents in the glass transition region, the decreased maximum $\tan \delta$ value for the SBR compounds were attributed to the relatively low energy dissipation that was due to the decreased effective volume of the polymer. In the glass transition region, $\tan \delta$ was measured by increasing the CB content to 70 phr for the SBR compounds.^{33,34} The measurements showed that the maximum $\tan \delta$ value decreased as the CB content increased because of the decreased effective volume of the polymer. Furthermore, in the rubbery region, the $\tan \delta$ value slightly increased as the total filler content increased. The increased filler content led to increased interactions between the fillers, which also increased the energy dissipation.

For the SBR compounds without PEG in the dual filler system, the T_g values based on the $\tan \delta$ values

increased in the order of A-5 (-35.5°C) < A-4 (-34.7°C) = A-3 (-34.7°C). When PEG was added, the values increased in the order of B-3 (-35.0°C) \approx B-4 (-34.9°C) < B-5 (-33.3°C). The SBR/silica compound and the SBR/silica/DDA-MMT compound had similar T_g values. The T_g value of the SBR/silica/APTES-MMT compound increased by 2.2°C after PEG was added. Additionally, for the SBR compounds without PEG in the ternary filler system, the T_g values increased in the order of A-6 (-35.5°C) < A-8 (-33.2°C) < A-7 (-32.9°C). When PEG was added, the T_g values increased in the order of B-6 (-34.0°C) < B-7 (-32.4°C) = B-8 (-32.4°C). For the SBR/silica/APTES-MMT and SBR/silica/APTES-MMT/CB compounds, the T_g values increased after PEG was added. The XRD analysis showed that PEG was intercalated between the APTES-MMT layers, the ether linkages of the intercalated PEG were hydrogen bonded to the hydroxyl groups of APTES, which restricted the mobility of the SBR molecular chain.

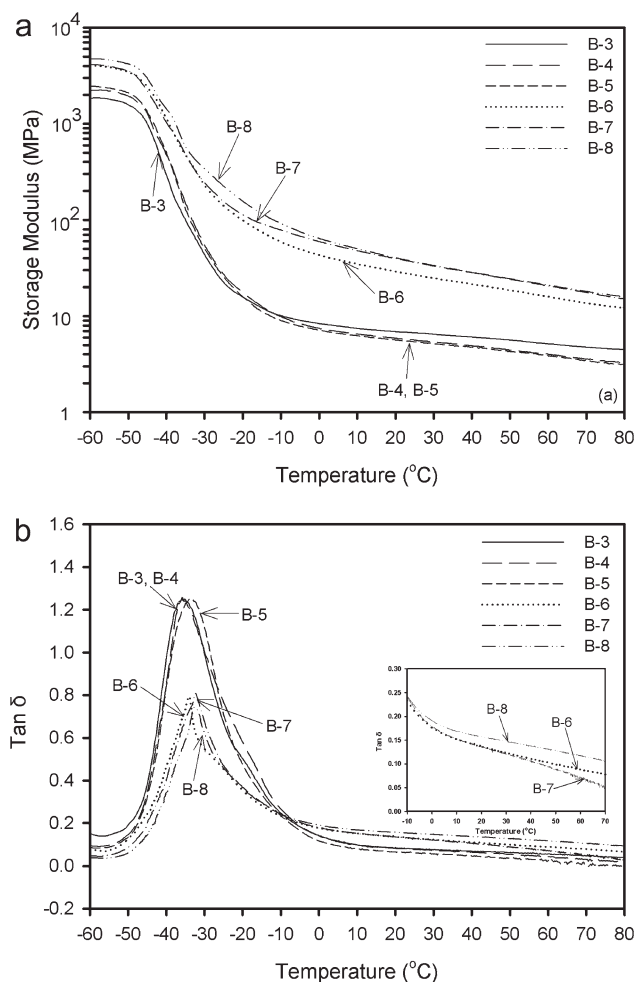


Figure 9 Temperature dependence of (a) the storage modulus (E') and (b) the loss tangent for various SBR compounds; with PEG, after vulcanization.

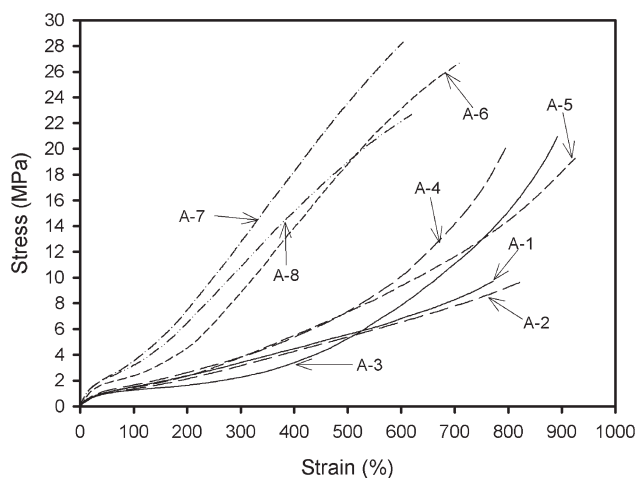


Figure 10 Tensile properties of various SBR compounds; without PEG.

When PEG was added to the SBR compounds in the ternary filler system, the maximum $\tan \delta$ value was relatively higher in the glass transition region than the compounds without PEG. Thus, PEG facilitated the dispersion of filler, and the amount of trapped polymers decreased in the aggregate or agglomerate structure of the silica and CB, increasing in effective volume of the polymers, which affected the energy dissipation. In the dual filler system, the maximum $\tan \delta$ values were similar whether PEG was added or not. Therefore, the reduced energy dissipation due to trapped polymer was low since the total filler content was low with a value of 25 phr.

The inserts in Figures 8(b) and 9(b) are the expanded images of the changes in the $\tan \delta$ values in the temperature range from -10 to 70°C . The $\tan \delta$ value at -10°C indicated the wet skid resistance and increased in the order of A-8 (0.1974) < A-6 (0.2071) < A-7 (0.2269) < B-6 (0.2338) < B-7 (0.2421) < B-8 (0.2433). In the meantime, the $\tan \delta$ value at 60°C , which indicated the rolling resistance, decreased in the order of A-8 (0.1541) > A-6 (0.1186) > B-8 (0.1175) > A-7 (0.1088) > B-6 (0.0889) > B-7 (0.0708). When PEG was added, the $\tan \delta$ value increased at -10°C but decreased at 60°C . The $\tan \delta$ value increased at -10°C because PEG improved the filler dispersion within the rubber matrix, which reduced the amount of trapped polymer, maximizing $\tan \delta$. On the other hand, the $\tan \delta$ value at 60°C decreased because the ether linkages of PEG reduced the filler–filler interactions, thus decreasing the energy dissipation.

For the B-8 compound that was manufactured by adding PEG to the A-8 compound, the $\tan \delta$ value increased more than the other compounds with the PEG addition at -10°C . The T_g value increased because of the hydrogen bonding between the ether linkages of PEG and the hydroxyl groups of APTES, which caused the entire $\tan \delta$ curve to shift to the

right. For the A-8 and B-8 compounds with APTES-MMT, the $\tan \delta$ value increased more than the other compounds at 60°C because of the relative increase in the bound rubber content. The SBR/CB compound had a higher $\tan \delta$ than the SBR/silica compound at 60°C because of the CB network with the bound rubber.³³ When PEG was added, the SBR/silica/DDA-MMT/CB compound (B-7) had a higher $\tan \delta$ value than the SBR/silica/CB compound (B-6) at -10°C , along with the lowest $\tan \delta$ value at 60°C . These results demonstrated the excellent wet skid resistance and rolling resistance properties of the compound.

Mechanical properties of the SBR compounds depending on the existence of PEG

The stress–strain curves in Figures 10–12 show the mechanical properties of the SBR compounds with and without PEG. Tables III and IV show the corresponding data for these evaluation results. The SBR/DDA-MMT compound (A-1) had a higher 100% modulus and 300% modulus than the SBR/APTES-MMT compound (A-2). According to previous studies, DDA-MMT exhibited higher 100% modulus and 300% modulus values than APTES-MMT because DDA-MMT had a superior silicate dispersion to APTES-MMT within the SBR matrix, and the degree of crosslinking was improved.⁴

The SBR/silica compound (A-3), with 25 phr of silica, had a lower 100% modulus and 300% modulus than the SBR/organoclay compounds (A-1 and A-2). A hydrodynamic reinforcement effect was observed because of the unique layered structure of the clay that was distributed in the rubber matrix using the latex method. The hydrodynamic reinforcement can be expressed as a function of the filler volume fraction and the shape factor, but it is also

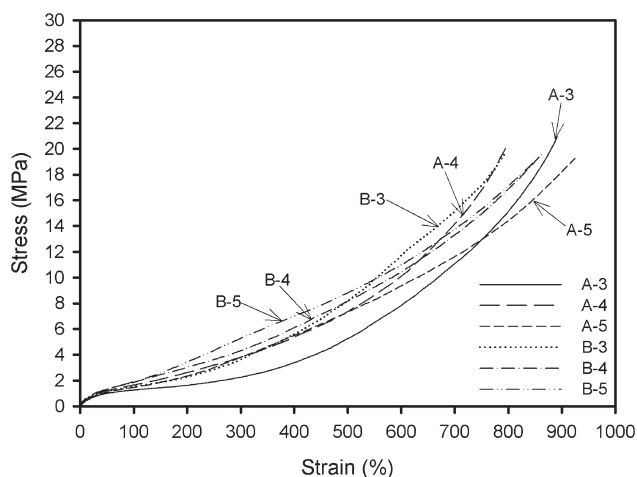


Figure 11 Tensile properties of various SBR/organoclay compounds filled with silica.

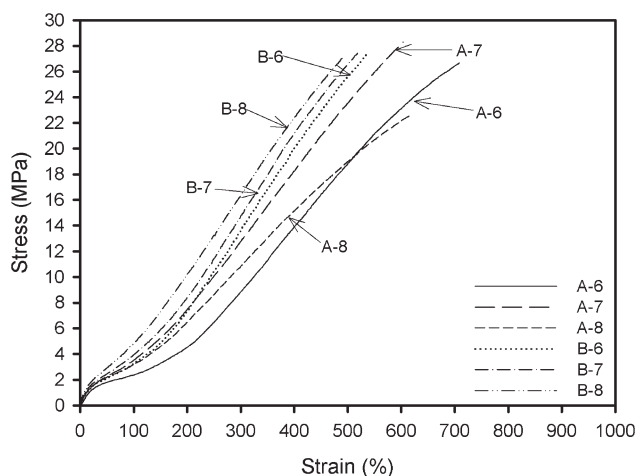


Figure 12 Tensile properties of various SBR/organoclay compounds filled with silica and carbon black.

influenced by the surface area, the surface energy and the aggregate structure of the filler.³⁶ However, the SBR/silica compound had a higher tensile strength at the breaking point because of the higher total content of the filler that was added during the rubber compounding and the improved filler-rubber interactions due to the chemical bonding between the hydroxyl groups on the surface of the silica and the ethoxy groups of TESPT.

The SBR/organoclay compounds, with the dual and ternary filler systems, had higher 100 and 300% modulus values than the SBR/silica compounds (A-3 and B-3) and the SBR/silica/CB compounds (A-6 and B-6). A synergistic effect was observed because of the unique plate-like structure of the silicate with a high aspect ratio.

In Figures 11 and 12, the moduli of the SBR compounds in the dual and ternary filler systems were compared with and without PEG. When PEG was added, the 100% modulus and the 300% modulus increased, which was in accordance with the increased degree of crosslinking for the rubber compound. However, from the compound comparisons, the degree of crosslinking that was predicted based on the swelling ratio was not proportional to the modulus that was measured in the stress-strain curves because the modulus values of the SBR/organoclay nanocomposites that were filled with silica

TABLE III
Tensile Properties of the Various SBR Compounds;
Without PEG

Items	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8
M_{100} (MPa)	1.52	1.36	1.26	1.64	1.47	2.37	3.52	3.17
M_{300} (MPa)	3.40	3.16	2.25	3.82	3.82	8.82	12.8	10.8
Tensile Strength (MPa)	9.74	9.76	20.9	20.3	19.3	26.6	28.3	22.6
Elongation (%)	772	829	892	799	925	708	604	620

TABLE IV
Tensile Properties of the Various SBR Compounds; with PEG

Items	B-3	B-4	B-5	B-6	B-7	B-8
M_{100} (MPa)	1.52	1.86	1.90	3.26	3.94	4.85
M_{300} (MPa)	3.65	4.33	5.27	13.6	14.7	16.3
Tensile Strength (MPa)	19.7	19.6	19.2	27.3	27.4	27.0
Elongation (%)	794	863	854	535	518	490

and CB were more greatly influenced by the shape of the filler, rather than the degree of crosslinking. The moduli of rubbery materials with fillers depend on the filler geometry, orientation, loading amounts, and crosslinking density.²²

For the SBR/silica/DDA-MMT compound (B-4) with PEG, the modulus decreased at an elongation of approximately 650% or higher, while the elongation at break increased compared to the A-4 compound without the addition of PEG. The XRD analysis results indicated that PEG was intercalated between the silicate layers during compounding after PEG was added to the SBR/organoclay compounds. Therefore, for the B-4 compound, the silicate surface was grafted with alkyl chains that had 11–13 carbons, causing DDA to act as a lubricant for the friction with the PEG molecular. This lubricating effect caused the slippage phenomenon in the large deformation. On the contrary, the modulus increased for the SBR/silica/APTES-MMT compound (B-5) with PEG, whereas the elongation decreased compared to the A-5 compound without PEG because PEG intercalated between the APTES-MMT layers and the interactions between the silicates and the rubber increased through the formation of hydrogen bonds between the hydroxyl groups of APTES and the ether linkages of PEG. The slippage phenomenon did not occur between APTES-MMT and PEG.

In Figure 12, the compounds with PEG in the ternary filler system had higher modulus values than the compounds in the dual filler system. The total content of the filler increased with a synergistic effect between the filler (silica and CB) and the organoclay. The A-8 compound exhibited higher 100 and 300% modulus values than the A-6 compound, whereas the tensile strength decreased by $\sim 15\%$. The modulus increased because of the increased bound rubber content, while the decreased elongation at break of the compound led to the relative decrease in the tensile strength.

In the ternary filler system, the 100% modulus and the 300% modulus of the SBR compounds increased in the order of B-6 < B-7 < B-8 compounds. The SBR/silica/CB/APTES-MMT compound exhibited the highest modulus values along with the highest T_g and amount of bound rubber.

Consequently, the change in the modulus for the SBR/organoclay compounds that were filled with the silica and CB had no proportional relationship with the degree of crosslinking and was influenced by the shape and orientation of the filler. Furthermore, in the dual filler system, the slippage phenomenon was observed between the silicate and PEG for the compounds with DDA-MMT and PEG. For APTES-MMT, the modulus improved because of the interactions between the ether linkages of PEG and the silicate. The SBR/silica/APTES-MMT/CB compound (with PEG) exhibited the highest modulus values along with the highest T_g and amount of bound rubber.

CONCLUSIONS

The XRD analysis results showed that PEG was intercalated between the silicate layers DDA-MMT and APTES-MMT. After vulcanization, the peak in the vicinity of 2° was attributed to stearic acid, which was used as an additive for the SBR/organoclay compound. After PEG was added, the swelling ratio of the compound decreased because of the vulcanization reaction that occurred as PEG reduced the hydrophilic nature of the filler and prevented the adsorption of the accelerators and the ingredients. In the dual filler system, the increased elongation at break in the SBR/silica/DDA-MMT compound (B-4) with PEG caused a slippage phenomenon to occur between DDA and PEG. Slippage was not observed for APTES-MMT when PEG was added. Additionally, for the SBR/silica/APTES-MMT compound, the T_g value increased with the addition of PEG because of the formation of hydrogen bonds between the hydroxyl groups that were created on the surface of silicate during the hydrolysis of APTES and the ether linkages of PEG. In the ternary filler system, the SBR/silica/APTES-MMT/CB compound (with the PEG added) had the highest T_g value and the highest bound rubber content along with the highest values for the 100% modulus and the 300% modulus. When PEG was added in the ternary filler system, the $\tan \delta$ value increased at -10°C and decreased at 60°C , so the SBR/silica/DDA-MMT/CB compound exhibited the best wet skid resistance and rolling resistance properties. The rolling resistance value of the SBR/silica/APTES-MMT/CB compound increased because of the formation of the CB network, with increasing amounts of bound rubber.

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