

Morphology and Dynamic Mechanical Properties of Styrene-Butadiene Rubber/Silica/Organoclay Nanocomposites Manufactured by a Latex Method

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ABSTRACT: In this study, the styrene-butadiene rubber (SBR)/*N*, *N*-dimethyldodecylamine-montmorillonite nanocomposite was prepared with a latex method by applying DDA to Na⁺-MMT as a modifier. The dispersion of silica and the dynamic viscoelastic properties of the SBR/silica (60 phr) compound were studied by replacing 7 phr of the silica with organoclay. By the analysis of transmission electron microscopy images and the Payne effect, the dispersion of silica in the SBR/silica (53 phr)/DDA-MMT (7 phr) compound was further improved as compared to the SBR/silica (60 phr) compound that used only silica as a filler. The Payne effect curve of the SBR/silica/DDA-MMT compound was close to the curve of the SBR/silica (53 phr) compound. This indicates that organically modified silicate did not form filler-filler networks with silica. Also, the SBR/DDA-MMT compound filled with silica showed the highest values of T_g and $\tan \delta$ at 0°C. This result was attributed to the shift of the $\tan \delta$ curve to the right because of the relatively higher degree of crosslink. Consequently, the SBR/silica/organoclay nanocomposite showed the best skid resistance due to the increase of T_g , and the best rolling resistance due to the reduced filler-filler networks. High 100% and 300% modulus values were also achieved. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: SBR latex; organoclay; silica; dual filler system; dynamic viscoelastic properties

Received 17 April 2012; accepted 17 June 2012; published online

DOI: 10.1002/app.38253

INTRODUCTION

Much research is actively being conducted to improve the effect on fuel efficiency of tires, owing to the recent European Union (EU) labeling enforcement and the onset of high oil prices. It is known that 1–2% of fuel consumption can be saved if the rolling resistance of tires is reduced about 10%.^{1,2} Tires consist of tread, side wall, bead, inner liner, and carcass, and it is known that about 50% of the rolling resistance of a tire is affected by the tread.³

The $\tan \delta$ values obtained from dynamic mechanical analyzers (DMA) are widely used to evaluate the wet traction and fuel economy of a tire.^{4,5} The wet traction of a tire can be improved by increasing $\tan \delta$ at 0°C, and the rolling resistance can be improved by decreasing $\tan \delta$ at 60°C.^{4,5} The energy dissipation in the tread is due to repetitive breaks and reformations of filler networks when the tire is deformed repeatedly by rotation.^{4,5} This energy loss can be reduced by increasing the distance between filler particles or by reducing the specific surface area of fillers.^{4,5}

Silica has been used as a filler instead of carbon black (CB) to improve the hysteresis performance of tread compound at 60°C, and there is some research in progress to increase the silica content of styrene-butadiene rubber (SBR) compound with dual filler systems (CB/silica).^{6–8} During compounding, silane coupling agents such as bis(triethoxysilylpropyl)tetrasulfide (TESPT) introduce chemical bonding between the hydroxyl group of silica and the ethoxy group of TESPT, and also between the sulfide group of TESPT and the double bond of the diene rubber molecules. These chemical bonds improve the dispersion of silica and the filler-rubber interaction leading to the reduction of energy dissipation at 60°C.^{9,10}

A recent study regarding SBR nanocomposites using organoclay reported that application of silica (18 phr) and CB (35 phr) to SBR/organoclay (7 phr) compound prepared with *N*, *N*-dimethyldodecylamine (DDA) as a modifier of clay showed better wet grip and rolling resistance than SBR/silica (25 phr)/CB (35 phr) compound.¹¹ This result implies that the hysteresis performance of SBR compound can be improved by replacing some parts of silica with organoclay.

In this study, a portion of the silica content in the SBR/silica compound is replaced with organoclay to examine the reasons for the improved hysteresis performances of $\tan \delta$ at 0°C and 60°C. The changes of the dispersion, degree of crosslink, and mechanical properties of the SBR compound filled with 60 phr of silica are examined by replacing 7 phr of silica with organoclay, and the possibility to improve wet grip and rolling resistance performance is examined.

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, Korea) was used for the SBR latex, and KUNIPIA-F (cation exchange capacity; 115 mequiv./100g; Kunimine, Japan) was used for the sodium montmorillonite (Na^+ -MMT). DDA (97%, Aldrich) was used as a modifier, and TESPT was used as the coupling agent. Zeosil-175 (particle size; 20–35 μm , specific surface area; 50–180 m^2/g , Rhodia-Korea, Korea) was used as the filler. Additionally, zinc oxide (ZnO), stearic acid, antioxidant (BHT; 2, 6-di-tert-butyl-4-methyl-phenol), treated distillate aromatic extract (TDAE) oil, sulfur, and accelerator (TBBS; *N*-tert-butyl-2-benzothiazol sulfonamide, DPG; diphenylguanidine) 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 of DDA was added to the MMT-suspension solution and stirred at 500 rpm using a hot plate stirrer for 15 h at 65°C.

Co-Coagulation of SBR Latex/Modifier-MMT

The modifier-MMT suspension and 420 g of SBR latex were intensively stirred at 1,500 rpm using a high speed stirrer for 30 min at room temperature to 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.

Preparation of SBR/Clay/Silica Nanocomposites

The SBR/organoclay compound was mixed in an 8-inch two-roll mill (rotor speed ratio; 1 : 1.4) for 3 min at 50°C. Additionally, this compound was mixed in a Banbury type kneader for 3 min at 110°C. After that silica, TESPT and TDAE oil were added, and mixed in the kneader for 5 min. The primary additives, including ZnO, stearic acid, and BHT, were added and mixed for 3 min. At this time, the dump temperature ranged from 130–140°C. Additionally, the secondary additives, including sulfur as the crosslinker and TBBS and DPG as the accelerators, were added, and the compound was mixed for 3 min at 40°C using a two-roll mill in order 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 (Japan) X-ray diffractometer and a $\text{Cu-K}\alpha$ radiation. The X-ray diffraction data were obtained in the reflection mode from 1° to 10° (2 θ) at a rate of 1°/min.

Morphology

The specimens were cut up to a thickness of 70 nm in a liquid nitrogen atmosphere by using a microtome, and then TEM (transmission electron microscopy; JEOL, Japan, Model; JEM2100F) images were obtained at an acceleration voltage of 200 kV to examine the dispersion and exfoliation states of the organoclay in the matrix.

Analysis of the Dynamic Viscoelastic Behavior

After vulcanization, for the SBR/silica compounds and the SBR/organoclay compound filled with silica, the storage modulus (E') was measured with respect to the strain sweep at a frequency of 100 Hz and a temperature of 60°C in the tension film mode using a DMA (MetraviB, France, Model; R.D.S. VISCOANAYSEUR) in order to determine the Payne effect. These measurements were performed with an increasing strain amplitude from 0.1 to 20%.

After vulcanization, $\tan \delta$ of the SBR/silica compounds and the SBR nanocomposite filled with silica were measured using the tensile film mode of a DMA (TA Instruments, USA, Model; DMA Q800 V7.1 Build 116) with an amplitude of 30 μm and a frequency of 10 Hz at a temperature sweep of 5°C/min from –70 to 120°C.

Measurement of Swelling Ratio

The swelling ratio of the vulcanized rubber compounds was determined to predict the degree of crosslink. The weight of $30 \times 5 \times 2$ mm 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 the ASTM D 471-79 standard. 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 (%); W_0 , weight of the specimen before swelling; W_1 , weight of the specimen after swelling; d_1 , density of SBR (0.94 g/mL); d_2 , density of toluene (0.87 g/mL).

Mechanical Properties

Dumbbell-shaped specimens (100 \times 25 \times 2 mm; gage length 20 mm and gage 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 5000 N load cell with a Universal Testing Machine

Table I. Experimental Formulations of the SBR/Silica Compounds and SBR/DDA-MMT Nanocomposite Filled with Silica (Amounts; weight parts per 100 weight parts of rubber [phr])

Materials	A-1	A-2	A-3
SBR 1502		100	
Silica (zeosil-175)	53	60	53
DDA-MMT	-	-	7
TDAE oil		25	
TESPT		4.8	
Zinc oxide		3	
Stearic acid		1	
BHT		1	
Sulfur		2.2	
TBBS		1.5	
DPG		0.2	

(UTM, KSU, Korea, Model; KSU-05 M-C) according to the ASTM D412.

RESULTS AND DISCUSSION

The mixing formulation was prepared as shown in Table I to compare the characteristics of the compound with a dual (organoclay/silica) filler system to which silica had been added after preparing an SBR/organoclay master batch using DDA as a modifier of clay. It is known that the optimum TESPT content in SBR/silica compound is 8 wt % of silica content,¹² and the TESPT content was maintained at the same level as that of the A-2 compound.

XRD test was performed for the SBR/DDA-MMT master batch to confirm the layer-to-layer structure between silicates, and the result is shown in Figure 1. The Na⁺-MMT layer-to-layer distance was 1.24 nm, and the layer-to-layer distance between silicates in the SBR/clay (unmodified clay) compound was 1.37 nm. This was due to the layer-to-layer structure created by flocculating ions (H⁺ and SO₄²⁻) supplied during the coagulation (coagulant; sulfuric acid) after mixing the MMT-suspension solution and the SBR latex.^{13,14} There was a broad peak in the range of 4.0°–6.5° in the SBR/DDA-MMT compound prepared with DDA as a modifier, and the position of the maximum peak was 4.84° (1.82 nm). It was thought that this broad peak was shown because DDA created layer-to-layer structure with silicate layers, and flocculating ions also created layer-to-layer structure. As shown in Figure 2, TEM images were examined to evaluate the exfoliation state of silicates, which was not confirmed in the XRD diffraction peak. In the SBR/clay (unmodified) compound, silicates formed aggregate structures and were insufficiently dispersed in the nonpolar rubber matrix due to the hydrophilic nature of silicates. In the SBR/DDA-MMT compound, silicates were exfoliated all over the rubber matrix, and some aggregate structures were observed, as shown in Figure 2(b). Moreover, 1–3 layers were confirmed when exfoliated silicates were examined in enlarged images, as shown in Figure 2(c), and they showed layer-to-layer distances of 1.57, 1.61, and

1.87 nm, which are similar to the periodicity of the layer-to-layer structure of silicates observed in the XRD test.

Figure 3 shows the TEM images (scale bar; 200 nm) used to examine the dispersion of filler in the dual filler system when 7 phr of silica in the SBR/silica (60 phr) compound is replaced with DDA-MMT. The result showed that the dispersion of silica in the SBR/silica/DDA-MMT compound was relatively superior to that in the SBR/silica compound. This was due to the low silica content in the SBR/silica/DDA-MMT compound. In Figure 3(b), it was also shown that the silicates maintained exfoliated structure within the rubber matrix, and the organically modified silicate and silica failed to form the silicate-silica network. In order to examine the dispersion state of filler in the compound, the Payne effect at small strain was measured, and the result is shown in Figure 4. Typical nonlinear Payne effect behavior was shown, in which the storage modulus (E') is reduced as the strain amplitude is increased by the reduction of filler–filler network.^{4,15} The storage modulus in the small strain (0.1–1.0%) region was reduced in the order of A-2 > A-3 > A-1. In the SBR/silica compounds, a low value for the storage modulus was measured as the silica content was reduced from 60 phr (A-2 compound) to 53 phr (A-1 compound), and this was due to the relatively superior dispersion of silica in the A-1 compound with 7 phr less silica content. In the rubbery state, the storage modulus at small strain was higher as the filler content was increased, and the increase was dependent on the effective volume fraction of the filler. In other words, the increase of trapped polymer content in the agglomerates of the filler, which occurred by the reduction of the dispersion of the filler within the rubber matrix, leads to the increase of the effective volume fraction of the filler. As a result, the high storage modulus can be obtained.^{4,15–17} Though the total filler content was the same as for the A-2 compound, the A-3 compound showed low storage modulus at small strain compared to the A-2 compound with the silica content of 60 phr. It is thought that the silicate surface prepared with a modifier was less hydrophilic than the

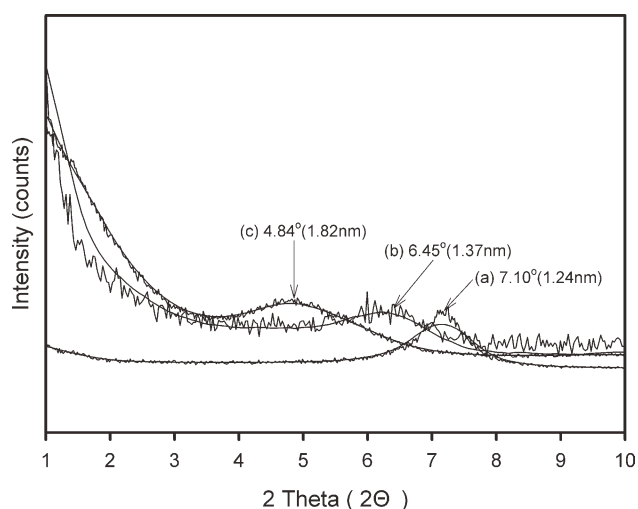


Figure 1. XRD patterns of (a) the pure sodium montmorillonite, (b) the SBR/Na-MMT (unmodified) compound, and (c) the SBR/DDA-MMT nanocomposite after coagulation (dry sample).

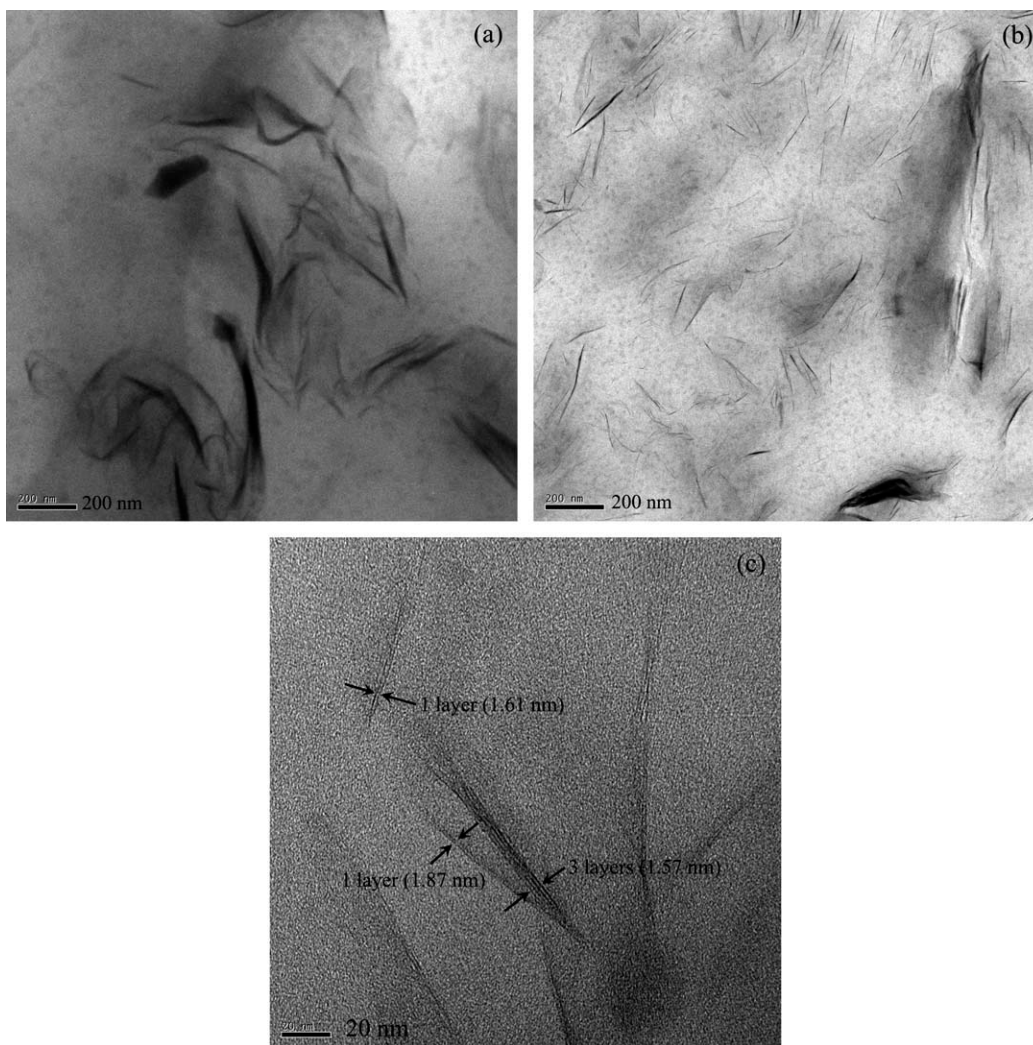


Figure 2. TEM images of (a) the SBR/Na-MMT and (b) and (c) the SBR/DDA-MMT nanocomposite after coagulation (dry sample).

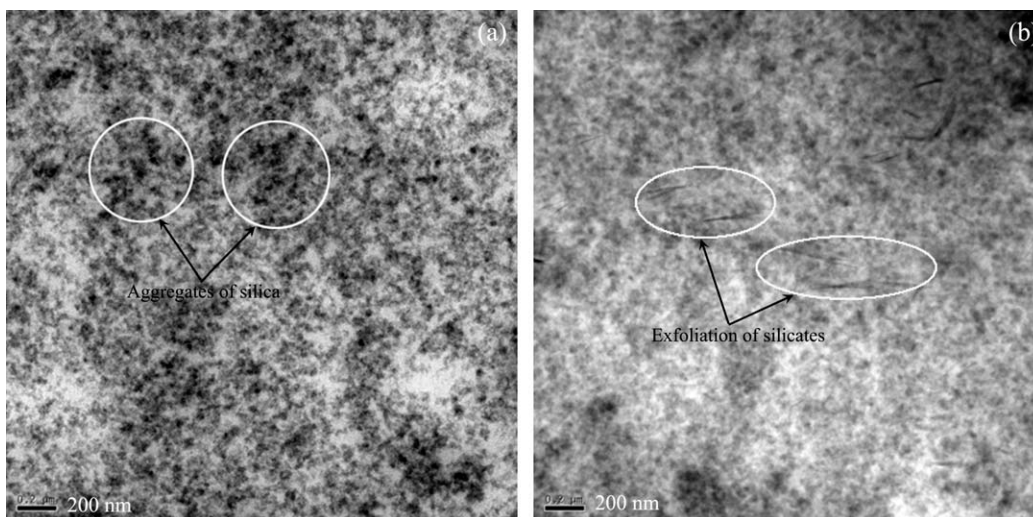


Figure 3. TEM images of (a) the SBR/silica compound and (b) the SBR/DDA-MMT nanocomposite filled with silica after vulcanization.

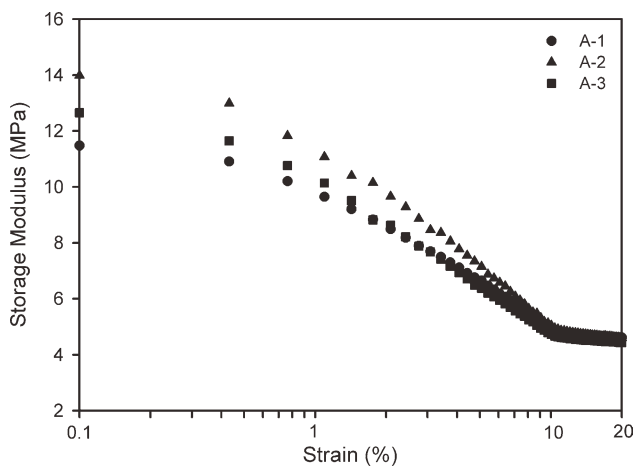


Figure 4. Strain dependence of the storage modulus for the SBR/silica compounds and the SBR/DDA-MMT nanocomposite filled with silica.

silica surface, which resulted in the improved dispersion of the filler within the rubber matrix. Furthermore, the distributed layered structure of DDA-MMT within the rubber matrix did not form the silicate–silica network.

Figure 5 shows the results of swelling ratios measured in order to predict the degree of crosslink of the SBR/silica and the SBR/silica/organoclay compounds, and they were reduced in the order of A-1 > A-2 > A-3. In the SBR/silica compounds, the swelling ratio of the A-2 compound was slightly reduced as the silica content was increased by 7 phr, and this was caused by the reduction of the volume fraction of rubber in the A-2 compound. The swelling ratio of the A-3 compound was the lowest, and therefore, the degree of crosslink was expected to be the highest. This was because the crosslink promotion during the vulcanization reaction was relatively better than the SBR/silica compound due to the presence of amino group in DDA. This resembled the result in which the cure rate was accelerated and the degree of crosslink improved when the vulcanization characteristics of the SBR compound and the SBR/DDA-MMT

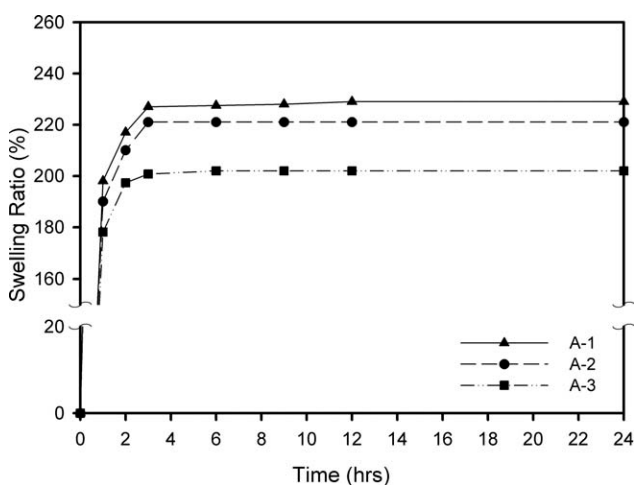


Figure 5. Swelling ratio of the SBR/silica compounds and the SBR/DDA-MMT nanocomposite filled with silica.

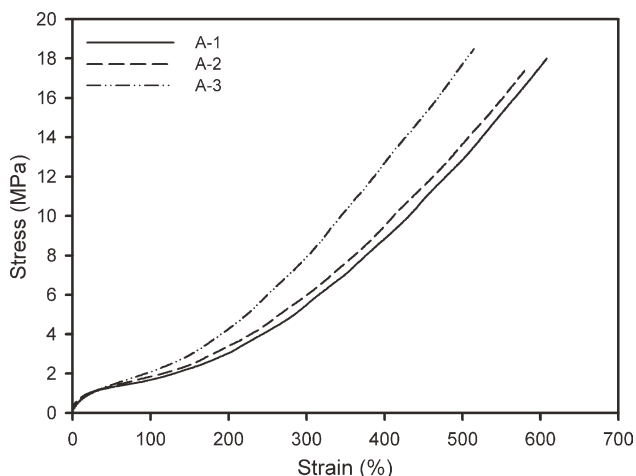


Figure 6. Tensile properties of the SBR/silica compounds and the SBR/DDA-MMT nanocomposite filled with silica.

compound were compared.¹³ In addition, it is widely known that amino group promotes the vulcanization reaction of SBR and natural rubber (NR) compound.¹⁸

The stress-strain curves are shown in Figure 6, which were used to evaluate the mechanical properties of the SBR/organoclay compound. The result showed that the 300% moduli were increased in the order of A-1 (5.49 MPa) < A-2 (5.98 MPa) < A-3 (7.92 MPa). There was also a tendency for the modulus to increase in proportion to the degree of crosslink predicted in the swelling ratios. The 300% modulus in the A-3 compound in which 7 phr of silica was replaced with organoclay showed 32% improvement compared to that of the A-2 compound, whereas the 300% modulus in the A-2 compound was increased by 9% compared to the A-1 compound as the silica content was increased by 7 phr. It is thought that this was because the degree of crosslink was improved by the amine modifier, and the reinforcing effect occurred because of the unique layered structure of silicates when the dual filler system (silica/DDA-MMT) was applied rather than only silica. The tensile strength of all compounds were similar with the figures of the A-1 (18.4 MPa), A-2 (18.0 MPa), and A-3 (18.5 MPa) compounds.

As shown in Figure 7, the values of $\tan \delta$ were measured in the temperature range of -10 – 70°C in order to predict the wet grip and the rolling resistance of the SBR/silica and the SBR/silica/DDA-MMT compounds. The values of T_g measured from the peak $\tan \delta$ values of DMA were increased in the order of A-1 (-37.2°C) \approx A-2 (-37.4°C) < A-3 (-34.5°C). The A-3 compound showed the highest T_g value, and this was due to the relatively higher degree of crosslink compared to the SBR/silica compounds. $\tan \delta$ at 0°C is increased when the T_g of the compound is increased or the volume fraction of the rubber is increased.^{15–17} Accordingly, the $\tan \delta$ values measured at 0°C were increased in the order of A-2 \approx A-1 < A-3. It was thought that the highest $\tan \delta$ value in the A-3 compound at 0°C was due to the $\tan \delta$ curve, which was slightly shifted to the right side as the T_g was relatively higher than the SBR/silica compounds (A-1 & A-2). The $\tan \delta$ values at 60°C are reduced as the distances between filler particles within the compounds are

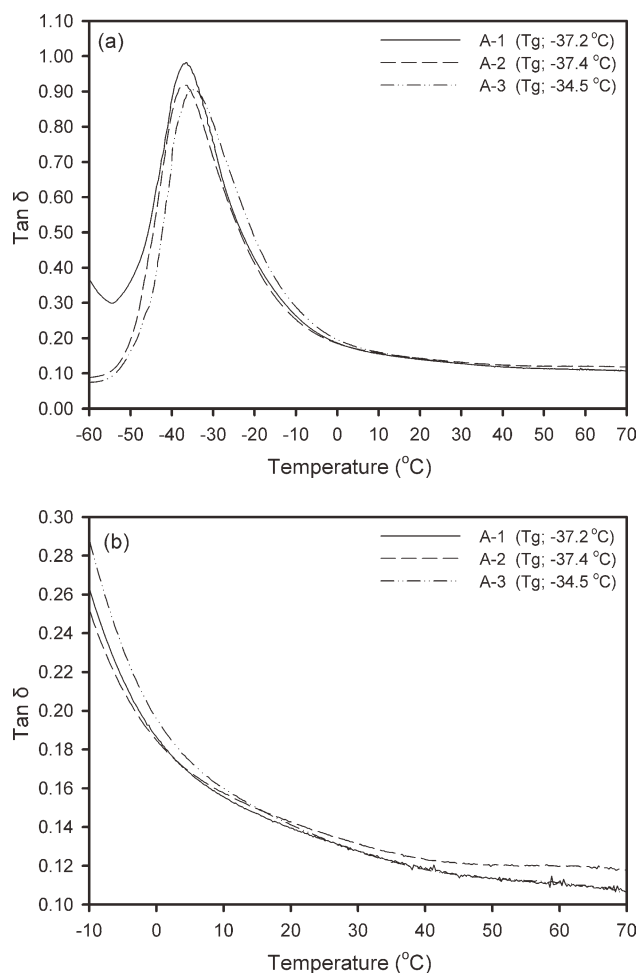


Figure 7. Temperature dependence of the loss tangent for the SBR compounds and the SBR/DDA-MMT nanocomposite filled with silica after vulcanization.

increased. For this reason, the $\tan \delta$ values measured at 60°C were reduced in the order of A-2 > A-1 \approx A-3. The SBR/silica compound (A-1) with 53 phr of filler content and the SBR/silica/organoclay compound (A-3) with 60 phr of filler content showed similar levels of dynamic characteristics at 60°C, and it was thought that this was because the organically modified silicate did not form filler–filler networks with the silica.

CONCLUSIONS

In the SBR/DDA-MMT nanocomposite prepared by the latex method, it was confirmed that MMT was well dispersed within the rubber matrix. The Payne effect curve of the SBR/silica (53 phr)/DDA-MMT (7 phr) compound was close to the curve of the SBR/silica (53 phr) compound. This indicates that organically modified silicates do not form filler–filler networks with silica. The silica (53 phr)/DDA-MMT (7 phr) dual filler system showed a high 300% modulus and high glass transition temperature, owing to the high degree of crosslink caused by amine modifier and the reinforcing effect of silicate. Moreover, the SBR/silica (53 phr)/DDA-MMT (7 phr) compound showed $\tan \delta$ values at 60°C similar to those for the SBR/silica (53 phr)

compound, as the organically modified silicate did not form a silicate–silica network. In conclusion, superior tensile properties and $\tan \delta$ values at 0°C and 60°C as laboratory indices for wet traction and rolling resistance can be obtained when a silica/DDA-MMT dual filler system is used in tread compound compared to when 100% silica is used.

ACKNOWLEDGMENTS

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, and by the Brain Korea 21 Project, Republic of Korea.

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