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SBR/Organoclay Nanocomposites for the Application on Tire Tread Compounds

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Abstract: *N*,*N*-dimethyldodecylamine (tertiary amine)-modified MMT (DDA-MMT) was prepared as an organically modified layered silicate (OLS), after which styrene-butadiene rubber (SBR) nanocomposites reinforced with the OLS were manufactured via the latex method. The layer distance of the OLS and the morphology of the nanocomposites were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). By increasing the amount of *N*,*N*-dimethyldodecylamine (DDA) up to 2.5 g, the maximum values of torque, tensile strength and wear resistance of the SBR nanocomposites were increased due to the increased dispersion of the silicate layers in the rubber matrix and the increased crosslinking of the SBR nanocomposites by DDA itself. When SBR nanocomposites were manufactured by using the ternary filler system (carbon black/silica/OLS) to improve their dynamic properties as a tire tread compound, the tan δ (at 0 °C and 60 °C) property of the compounds was improved by using metal stearates instead of stearic acid. The mechanical properties and wear resistance were increased by direct substitution of calcium stearate for stearic acid because the filler-rubber interaction was increased by the strong ionic effect between the calcium cation and silicates with anionic surface. However, as the amount of calcium stearate was further increased above 0.5 phr, the mechanical properties and wear resistance were degraded due to the lubrication effect of the excessive amount of calcium stearate. Consequently, the SBR/organoclay nanocomposites that used carbon black, silica, and organoclay as their ternary filler system showed excellent dynamic properties, mechanical properties and wear resistance as a tire tread compound for passenger cars when 0.5 phr of calcium stearate was substituted for the conventionally used stearic acid.

Keywords: styrene butadiene rubber, organically modified layered silicates, latex method, morphology, cure characteristics, tan δ, wear resistance, calcium stearate.

Introduction

Active development of nanotechnology began in the 1990s in all fields of science and engineering. Since organoclay was introduced to polyamide by the Toyota group,[1,2] many researchers have studied a variety of polymer nanocomposites using organoclay. Clay such as montmorillonite (MMT) is composed of silicate layers. When MMT is mixed with polymer showing hydrophobic nature, it forms agglomerates because MMT has a hydrophilic nature. To alleviate this problem, sodium ions existing between the MMT layers are ion-exchanged by appropriate long chain alkyl ammonium ions, as a result, the gallery distance between the layers can be increased and the modified MMT shows less hydrophilic nature. When these OLS (organically modified layered silicates) are used, the compatibility between the OLS and polymer matrix will be improved, as a result, the dispersion of OLS can be improved.

Preparations for rubber matrix MMT nanocomposites can be classified as follows: the solution methods,[3~7] the compounding methods,[8~16] and the latex methods.[17~26] Dispersion and exfoliation of the layered silicates in the SBR nanocomposite prepared by the latex method is much better than those prepared by the compounding method. This is due to the presence of long chain alkyl ammonium ions on the surface of silicates and their hindrance of reaggregation of the swelled silicates during coagulation of rubber particles.[25] This is a big benefit of the latex method because rubber molecules which show very high molecular weight do not need to penetrate into the galleries of silicates.[26] Another benefit of the latex method is that the rubber latex can be readily used and the dispersion effect can be maximized because swelled MMT can be evenly dispersed in the latex solution.

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In rubber compounds, stearic acid is used as an activator for sulfur curing, and also as a lubricant during the compounding process. Metal stearates which have cations on its chemical structure can replace stearic acid. These cations also can interact with the surface of silicates which show anionic characters, so the dynamic properties of silicate filled SBR compounds can be affected.

It is generally accepted that the values of tan δ of carbon black filled SBR vulcanizates at 60 °C and those of tan δ at 0 °C are suitable for laboratory indices to evaluate rolling resistance and wet traction of tire tread compounds for passenger cars, respectively.[27~29]

In this study, SBR/clay nanocomposites are prepared by a latex method. After evaluating the physical properties of SBR/clay nanocomposites according to the content of *N*,*N*-dimethyldodecylamine (DDA) compared to that of the clay, the appropriate DDA content was established, and the study on the effect of metal stearate has been carried out to improve the wet traction and rolling resistance of tire tread, and a comparative evaluation was made on the curing characteristic, dynamic viscoelasticity, wear resistance and mechanical properties of the SBR/organoclay nanocomposites applied with metal stearates.

Experimental

DDA-MMT Suspension Solutions. Five grams of Na-MMT (Na^+-montmorillonite) was agitated for 1 h in 500 mL of distilled water at 65 °C after that *N*,*N*-dimethyldodecylamine(DDA: 0.0, 0.5, 1.0, 1.5, and 2.5 g, respectively) was mixed with the prepared 500 mL of swollen Na-MMT suspension. Then, the mixture was agitated strongly for 1.5 h. 425 g of SBR-1502 latex (bound styrene content: 23.5% in styrene-butadiene rubber; 25 wt% of solid contents in the latex; Kumho Petrochemical Co., Korea) was poured into this suspension solution and then the mixture was agitated with 400 rpm at 30 °C for 2 h.

Co-Coagulation of SBR Latex/DDA-MMT. A solution of 400 mL of distilled water and 20 mL of conc. HCl solution (35 wt%) poured into the above mixture for co-coagulation. The co-coagulated SBR latex/organically modified layered silicates (OLS) is washed until the pH becomes about 7, after that dried in an oven at 80 °C for 15 h.

Manufacturing of SBR Nanocomposites. With a two-roll mill (roll speed ratio; 1:1.4), the co-coagulated nanocompound was premixed for 3 min at 50 °C. Silica and carbon black were mixed by introducing a step compounding method as follows.[30] After that compounded in a Banbury type mixer for 2 min at 110 °C, silica (Zeosil-175), PEG-4000 and a coupling agent (bis-(3-triethoxysilylpropyl)-tetrasulfide (TESPT, trade name; Si-69)) were added to the mixed compound and compounded by using the same mixer for 5 min at 110 °C. Then carbon black (N 220) was added in this compound and mixed during 5 min. This compound was added with ZnO as an activator, stearic acid or metal stearates as a lubricant, and 2,2,4-trimethyl-1,2-dihydroquinoline (TMDQ) as an antioxidant after that mixed for 5 min. Then the dumped compound was added with sulfur as a curing agent and *N*-tert-butyl-2-benzothiazoyl sulfonamide (TBBS) as an accelerator in the two-roll mill at 50 °C. The mixed compounds were pressed using a hydraulic press at 160 °C for appropriate vulcanization time (t_{90}) for the manufacturing of SBR nanocomposites.

Characterization. To measure the change of gallery distance of OLS, X-ray diffraction (XRD) test was performed at room temperature using a Rigaku D/MAX 2200 (Japan) X-ray diffractometer. X-ray diffraction data were obtained from 2.5° to 10° (2θ) at a rate of 1°/min. To examine the dispersion and exfoliation states of the clay in the matrix, the sample was microtomed up to thickness 70 nm at a liquid nitrogen atmosphere and then TEM (transmission electron microscope; Philips; Model CM 200) images were obtained with 120 kV of acceleration voltage.

Cure characteristics were measured using a cure-meter (MYUNG-JI Tech, Model; ODR 2000, KOREA) under the following conditions: oscillation angle; +/–1°, temperature; 160 °C, and running time; 30 min.

Stress-strain curves were obtained by using a UTM (universal testing machine; Instron 4485, USA) with an extension rate of 500 mm/min.

The dynamic mechanical properties were measured using a rheometric scientific DMA analyzer (model DMA Q800, TA Company, USA) under the following conditions: frequency; 10 Hz, amplitude; 30 μm, heating rate; 2 °C/min., tension mode, and temperature range; 60~80 °C.

Abrasion experiments were performed in an air atmosphere at room temperature using a blade abrader.[31,32] The rotation speed of the rubber disk was controlled to 10 rpm to prevent heat generation due to the frictional sliding. The applied normal load was 2 kg (19.6 N).

Results and Discussion

As shown in Figure 1, detailed observations for the manufacture of modified clay that follows the SBR nanocomposites manufacturing process and latex coagulation process have been made by using X-ray diffraction pattern to find 2θ=7.1° with 1.24 nm of d-space for Na-MMT, and the result after swelling in distilled water came up with 2θ=5.7° with 1.55 nm by showing the widening of d-space. As it can be found in Figure 1(b), the stirring of Na-MMT at distilled water for 1 h showed a presence of a peak at the range of 2θ, which suggests incomplete exfoliation. As shown in the Figure 1(c), the swelling of Na-MMT for 1.5 h resulted 2θ= 4.2° by increasing the d-space to 2.10 nm, and the strength of the peak was weaker than the result that was measured after stirring for 1 h by showing the gradual exfoliation of Na-MMT.

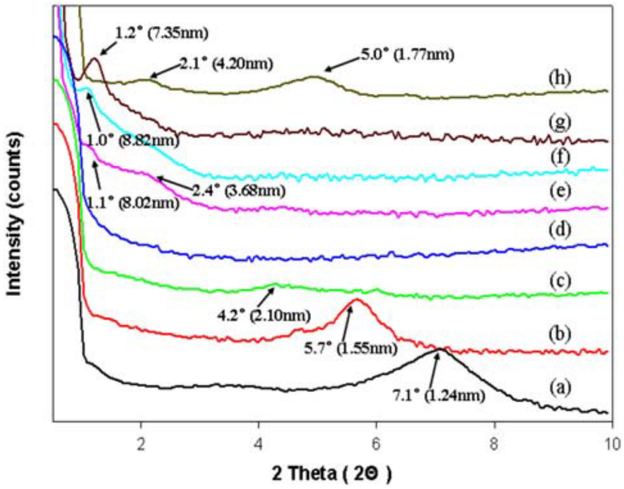

Figure 1. X-ray diffraction (XRD) patterns at various stages of the preparation process: (a) Na-MMT; (b) Na-MMT + water (swelling, after 1 h); (c) Na-MMT + modifier + water (after 1.5 h); (d) OLS + SBR latex (after 2 h); (e) after co-coagulation with HCl; (f) after co-coagulation (dried); (g) after compounding; (h) after vulcanization.

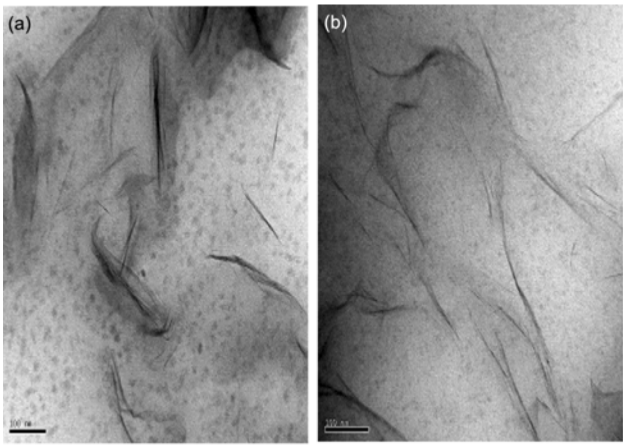

Figure 2. TEM images of (a) SBR/Na-MMT and (b) SBR/DDA-MMT nanocomposites.

By seeing the disappearance of X-ray diffraction peak at the Figure 1(d), a complete exfoliation of Na-MMT was made in distilled water and the stirring time 2 h is considered to be enough. At the Figure 1(e), broad peaks were found from 3° to lower angle, which are considered to be the result of reaggregation of exfoliated silicates in various d-spaces by the simultaneous progression of latex coagulation. In addition, through the Na^+ ion exchange by dimethyldodecylammonium ion, a 3-fold increase of d-space of silicates was found compared to that of Na-MMT. As the Figure 1(f) and (g) show, the d-space of silicates after drying resulted to show more distinctive peaks at 1.0° (8.82 nm) and 1.2° (7.35 nm), respectively, which are considered to be the result of removing water through a drying process. At the Figure 1(h), two separated peaks were observed at 2.1° (4.20 nm) and 5.0° (1.77 nm). These peaks were not detected in the range of 2θ before vulcanization because of the long layer-to-layer distance of silicates. It is considered to be the result of narrowing of d-space by DDA modifier molecules that were presented in between the silicate layers as the molecules obtained thermodynamically stable conformation after the high pressure and heat for the time of curing.

Figure 2 shows TEM image that could be used to observe the dispersion of clay in the SBR/clay nanocomposites that were manufactured by using Na-MMT and DDA-MMT. The SBR/Na-MMT nanocomposite photographed in Figure 2(a) showed unsatisfactory dispersion caused by the aggregation of silicates. The result is thought to be the phenomenon caused by the reaggregation between polar silicates at the time of coagulation even if clay was exfoliated during swelling.[33] Contrary to the result it was possible to observe 4~8 layers of silicate in the SBR/DDA-MMT nanocomposite. It is considered to be the result of using dimethyldodecyl ammonium that induced the cation exchange reaction with the Na^+ ions presented in silicate layers and less polar surface of silicates as the result of the reaction, which led to the lowering of silicate-silicate interaction and improved the dispersion of silicates. Such pattern was well correspond to the result of increased d-spacing of silicates by DDA, which was observed at the XRD diffraction peak of the Figure 1(g).

When the amounts of filler content were restricted to 60 phr, the optimum ratio of dual phase fillers were 25/35 phr of silica/carbon black as the tire tread compounds.[30,34] It was found that these system gives overall good properties in tear strength, crack resistance, cutting resistance and dynamic viscoelastic properties. Based on this, at first, by removing carbon black and replacing 5 phr of silica with the same amounts of MMT, silica/MMT filled SBR compounds were evaluated. It is important to analyze the effect of the amounts of DDA modifier on the properties of SBR/DDA-MMT nanocomposites. Test formulations by the content of *N*,*N*-dimethyldodecylamine (DDA) and the cure characteristics were listed in Table I, and the curves of cure characteristic were represented in Figure 3. Scorch time is the spent time just before initiating the curing, which revealed reduction of the time as the content of DDA to SBR was increased from 0 p to 2.5 phr along with the reduction of optimum curing time t_{90}. In addition, the difference of torque values (ΔT; maximum torque (T_{max})-minimum torque (T_{min})) of SBR/clay nanocomposite has been reported to show the degree of crosslink by the chemical reaction between rubber molecules and sulfur,[35] and the increase of DDA content allowed us to confirm the significant increase of ΔT value in the order of A1<A2<A3<A4<A5 compound. The result is attributable to the ammonium salt presented in between the DDA-modified nanosilicate layers, which acted as an accelerator to speed up the ring opening of sulfur (S_8) that is the cross

Table I. Experimental Formulations for Different Amount of *N*,*N*-Dimethyldodecylamine (DDA) (Amount; phr)

	A1	A2	A3	A4	A5
SBR 1502			100		
Na-MMT			5		
Dimethyldodecyl Amine (DDA)	0	0.5	1	1.5	2.5
Silica (Zeosil-175)			20		
PEG 4000			2		
TESPT (Si-69)			2		
Activator (ZnO)			3		
Lubricants (St/A)			2		
Antioxidant (TMDQ)			1		
Accelerator (TBBS)			1.6		
Sulfur			1		
t_{10} (min:sec)	15:40	6:09	5:33	5:15	4:33
t_{90} (min:sec)	26:19	22:01	21:50	21:26	19:50
T_{min} (N-m)	0.47	0.58	0.72	0.75	0.84
T_{max} (N-m)	1.92	2.25	2.62	2.75	3.04
ΔT (N-m)	1.45	1.67	1.90	2.00	2.20

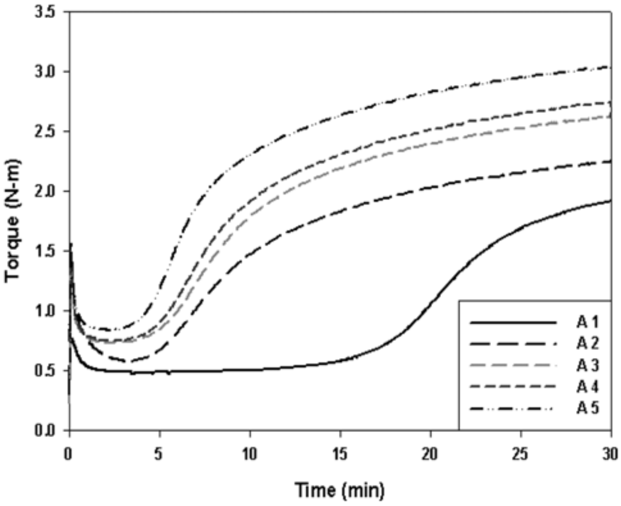

Figure 3. SBR rheometer curves with different amount of *N*,*N*-dimethyldodecylamine (DDA).

linking agent of SBR, and consequently shortened the curing time, and increased the vulcanization rate and the degree of crosslink.[36] In case of SBR and NR compounds, amino group has been reported to accelerate the crosslinking reaction,[37] and the corporate reaction of amino groups in benzothiazyl accelerant and modifiers has been reported to accelerate the rubber curing in case of the NR/organoclay nanocomposite which use octadecylamine as a modifier.[38]

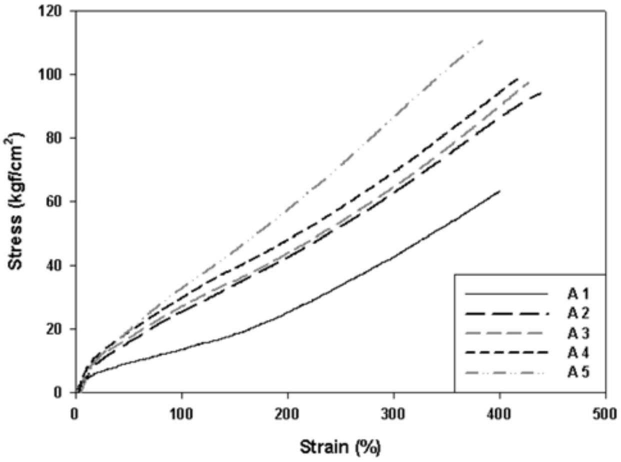

Figure 4. Stress-strain curves with different amount of *N*,*N*-dimethyldodecylamine (DDA).

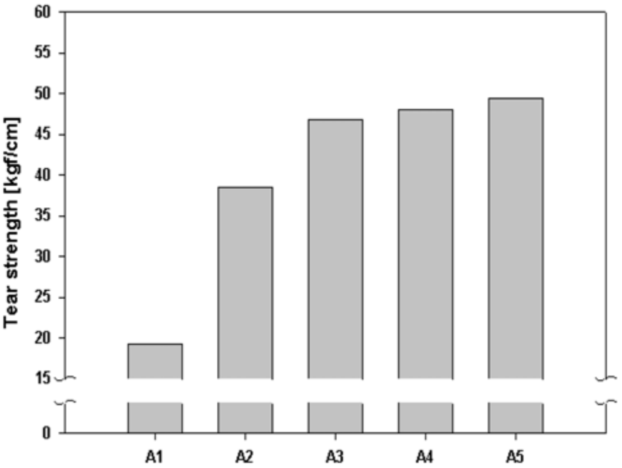

Figure 5. Tear strength with different amount of *N*,*N*-dimethyldodecylamine (DDA).

Figures 4 and 5 represent the results of evaluating mechanical properties by measuring the tensile strength, modulus (100%, 300%) and tear strength of SBR/clay compound that applied up to 50% (2.5 phr) of DDA based on 5 phr of clay. The measured tensile strength and tear strength of SBR/Na-MMT compound (A1 compound) resulted to show 63.48 kgf/cm^2 and 19.56 kgf/cm, respectively. These values were lower than the values of SBR/organoclay nanocomposite manufactured by organo-clay. The result is responsible for the occurrence of silicate aggregation phenomenon within the nonpolar rubber matrix. The clay that was not organically modified is considered to be the cause of lowered physical properties by the reduced dispersion of silicates along with the reduction of the interaction between nonpolar rubber chains and polar silicates. Due to such aggregation phenomenon, it provides internal cracks when the high strain was applied, which resulted to have lower tensile strength and tear strength. Compared to that, the A2~A5 compounds that were organically modified by DDA showed the increase of tensile strength from 93.86 to 110.59 kgf/cm^2

as the DDA content was increased up to 50% (2.5 phr) to 5 phr clay, and the 300% modulus value of each compound was increased by following order of A5 (86.82 kgf/cm^2) >A4 (69.36 kgf/cm^2) > A3 (64.67 kgf/cm^2) > A2 (63.03 kgf/cm^2) > A1 (42.72 kgf/cm^2), which corresponded to the result of maximum torque value that was measured at the cure characteristic curve. In case of 300% modulus, A5 compound revealed more than 2 fold improvement compared to A1 compound. So, these results is thought to be the result of improved dispersion of silicates by the application of DDA, which consequently resulted to have hydrodynamic reinforcement effect, and the effect of amines that increased the degree of crosslink might be the cause to have such result.

The hydrodynamic reinforcement is the function of filler volume fraction and aspect ratio which is affected by surface area of filler, surface energy, and aggregate structure.[39] The aspect ratio is the ratio of the longest length to the shortest length of the filler, and the case of extensively exfoliated clay has very high values of aspect ratio and the arrangement of widely exfoliated clay to tensile direction could be the cause of inducing high tensile strength. For the DDA-MMT that shows the dispersion of 4~8 silicate layers, it could be told as the case of showing excellent reinforcement effect of clay by having anisotropic shape.

For natural rubber and SBR, it is possible to observe the formation of sticky abrasion particles on the surface of abrasion specimens during abrasion test. This phenomenon is called as smearing. The result of forming low molecular weight materials by the chemical degradation of rubber caused by friction, heat, and oxygen could produce the phenomenon of smearing on the abrasion surface.[40~42] This phenomenon is the important evidence for chemical abrasion of rubber, and the occurrence of smearing phenomenon significantly reduce the wear rate, which can often cause an error in the interpretation of the results of rubber abrasion test. The present test was carried out by applying the same amount of aluminum oxide powder in 10 min interval for 3 times on the surface of specimen to prevent the occurrence of smearing phenomenon. By using a blade abrasion tester, 2 kg of normal force was applied, and the speed of motor was fixed at 10 rpm to measure the amounts of abraded rubber debris and the result was represented in Figure 6. As the result indicates, the increase of DDA content up to 50% (2.5 phr) to 5 phr clay reduced the wear rate (W_R) and the wear rate of A5 compound showed 43.9% reduction to that of A1 compound, which is thought to be the result of excellent dispersion of silicates in rubber matrix by DDA modifier and the increased degree of crosslink through the acceleration of cross linkages of rubber by the increased content of ammonium salts.

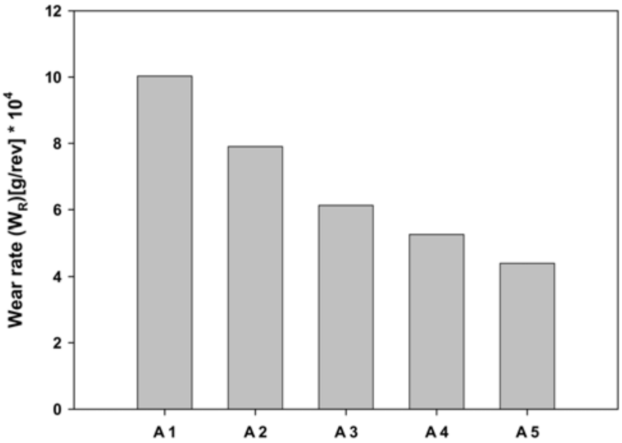

Figure 6. Wear rate at different amount of *N,N*-dimethyldodecylamine (DDA).

As the important physical properties of tire tread compound, the traction at wet road surface and the rolling resistance that indicates the energy loss of viscoelastic material of tread rubber by applying repeated deformation to the rolling tire during driving have been evaluated by using the 50% (2.5 phr) DDA to 5 phr clay applied SBR/organoclay compound that showed excellent mechanical properties and wear resistance while applying different types of metal stearate to evaluate the dynamic viscoelasticity of the compound. As in the low strain DMA test, the behavior change of storage modulus (E'), loss modulus (E''), and tan δ under the repeated dynamic strain with the amplitude of 30 μm has been reported to be attributable to the energy change by the breaking or reunion of filler-filler network.[39] According to the Payne effect, the filler network effect tends to increase as the aggregates become agglomerates and the networks between such small particles are generally easy to be broken down by the application of dynamic strain. In case of silica compound, high filler-filler interaction and low filler-polymer interaction shows the high Payne effect and its high tan δ values have been reported.[34,39,43~45] However, the tan δ values for rubber compounds at the temperature higher than the glass transition temperature (–80~–20 °C) have been reported that the reinforcement by carbon black resulted to show higher tan δ value than the reinforcement was made by silica.[45,46] In other words, the filler-filler interaction of silica is stronger than carbon black, which enables to maintain its filler network under the repeated dynamic strain, but carbon black has a relatively weaker filler-filler interaction and filler network can be easily broken down by repeated dynamic strain to release energy and the tan δ value is also increased. However, the filler-polymer interaction becomes the major function instead of filler-filler interaction as the strain is increased and the behavior of tan δ values of silica and carbon black show contrary phenomenon to the behavior that was observed at low strain. When the correlation between the performance of tire and tan δ value of tread compound was observed, tan δ value at the glass transition temperature range is related to wear resistance characteristic, and the tan δ value at 0 °C has the relationship to the

Table II. Experimental Formulations According to the Metal Stearates (Amount; phr)

	B1	B2	B3	B4
SBR 1502	100			
DDA-MMT	5			
Carbon Black (N-220)	35			
Silica (Zeosil-175)	20			
PEG 4000	2			
TESPT (Si-69)	2			
Activator (ZnO)	3			
Lubricants	St/A (2phr)	K/St (2phr)	Ca/St (2phr)	Zn/St (2phr)
Antioxidant (TMDQ)	1			
Accelerator (TBBS)	1.6			
Sulfur	1			
tan δ (at 0 °C)	0.266	0.301	0.332	0.271
tan δ (at 60 °C)	0.169	0.157	0.151	0.164

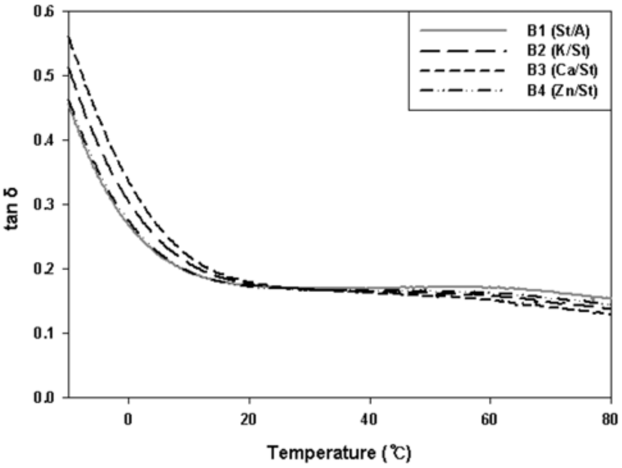

Figure 7. DMA curves of tan δ according to the various kinds of metal stearate applied compounds.

traction at wet road surface. In addition, the tan δ value at 50~60 °C has the relationship to the rolling resistance of tire for passenger cars.[27~29] Namely, higher tan δ value at 0 °C suggests high traction at wet road surface, and the lower tan δ value at 50~60 °C indicates the excellence of rolling resistance.[27] In case of tire tread compounds that are applied with dual phase filler system, the most excellent tan δ value was observed when the carbon black and silica was mixed at the ratio of 35:25.[30, 34] In the test results acquired by the content of DDA, the most excellent wear resistance organoclay manufacturing condition (50% of DDA content to the content of clay) was applied to manufacture DDA-MMT 5 phr, which was used to conduct the test by replacing silica 5 phr with it. Tests have been conducted by applying different types of stearic acid and metal stearates (potassium stearate, calcium stearate, and zinc stearate). The following formulations were provided in Table II. Tan δ value measurement results by the types of metal stearates was represented in Figure 7, which showed higher tan δ values at 0 °C in all metal stearate applied compounds than the B1 compound that was applied with stearic acid. So, the reduction of breaking distance at the wet surface is expected, and the low tan δ values at 50~60 °C could be promising to have fuel cost saving effect by improving the rolling resistance of tire. Before the study of current laboratory, a previous study[46] reported the excellent swelling ratio value for the compound that was applied with metal stearate than the compound that was applied with stearic acid. Especially, the cause of having the most excellent tan δ value at the time of applying calcium stearate is attributable to the ion-effect between the negatively charged surface of silicate layer and divalent ion of Ca^{2+} act more favorably. At the time of applying metal stearate, the mobility of metal stearate may be low at 0 °C and the relatively high energy dissipation is occurred by small strain under the high silicate-silicate layer interaction by showing high tan δ, but the mobility of metal stearate may be increased at the temperature of 50~60 °C to have low silicate-silicate layer interaction and the tan δ value is lowered by showing relatively low energy dissipation by the applied strain.

Samples have been manufactured by using the ternary filler system that applied carbon black, silica, and DDA-MMT based on SBR 100 phr. Because of hydrophobic characteristic of carbon black that is commonly used as the filler of rubber, it shows good dispersion within rubber matrix, but hydrophilic silica has been known to show unsatisfactory dispersion characteristic within rubber matrix. However, it has been reported that the dispersion of silica can be maximized by the use of stepwise mixing method to mix silica and carbon black in the rubber matrix and the use of TESPT that acts as a coupling agent could modify such surface characteristic of silica to be less hydrophilic.[47] So, the current test applied the stepwise mixing and Si-69 to mix silica and carbon black in the rubber matrix. The amount of filler is total 60 phr that is comprised by 35 phr of carbon black, 20 phr of silica, and 5 phr of organoclay to SBR 100 phr. In the measurement result of dynamic viscoelasticity, calcium stearate that showed the most excellent result was used to conduct the test by the content of stearate. Table III listed the formulations by the content of calcium stearate and the curing characteristic curves were represented in Figure 8. As the result indicates, calcium stearate applied C2 (0.5 phr) and C3 (2 phr) compounds showed higher values of 0.50 N-m & 0.47 N-m in the minimum torque values and 0.78 N-m & 0.30 N-m in the maximum torque values, respectively compared to the stearic acid applied C1 compound. The presence of strong ion-effect between negatively

Table III. Experimental Formulations for Different Amount of Calcium Stearate (Amount; phr)

	C1	C2	C3	C4
SBR 1502	100			
DDA-MMT	5			
Carbon Black (N-220)	35			
Silica (Zeosil-175)	20			
PEG 4000	2			
TESPT (Si-69)	2			
Activator (ZnO)	3			
Lubricants	St/A (2phr)	Ca/St (0.5phr)	Ca/St (2phr)	Ca/St (5phr)
Antioxidant (TMDQ)	1			
Accelerator (TBBS)	1.6			
Sulfur	1			
t_{10} (min:sec)	3:19	2:36	3:06	2:37
t_{90} (min:sec)	17:20	17:11	18:37	17:17
T_{min} (N-m)	1.68	2.18	2.15	1.49
T_{max} (N-m)	4.24	5.02	4.55	3.99
ΔT (N-m)	2.56	2.84	2.40	2.50

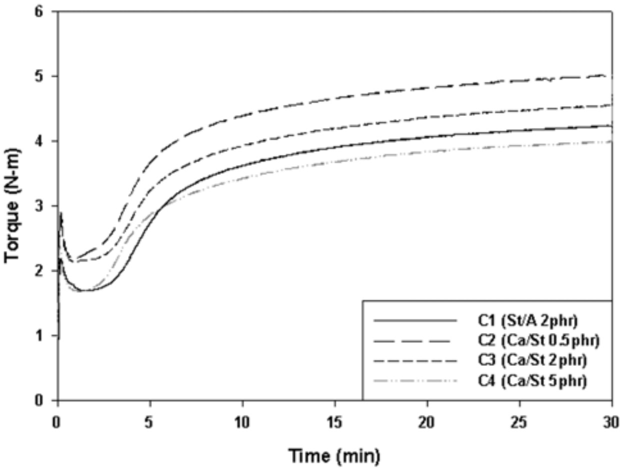

Figure 8. Rheometer curves with different amount of calcium stearate.

charged silicates surface and Ca^{2+} ions is considered to be the responsible reason for the result. In case of C2 compound that applied 0.5 phr of calcium stearate showed the highest maximum torque value of 5.02 N-m. For the result, it is considered to be attributable to calcium stearate that reacted with metallic oxides during curing to form rubber-soluble salt or soap, and these products reacted with accelerants to maximize the effect of the accelerants. If the calcium stearate content to 3 phr of ZnO exceeds more than 0.5 phr, the leftover of calcium stearate after forming soap acts as a lubricant to reduce the tangling of high molecular chains and to reduce the internal friction, which consequently softens the mixing compounds. In addition, the C3 and C4 compounds that were applied with more than 0.5 phr of calcium stearate showed the reduction of torque value difference (ΔT) by indicating the reduction of degree of crosslink compared to C2 compound. The result could be attributable to the inhibition of effective curing reaction by remaining soap, which consequently reduced the degree of crosslink.[35]

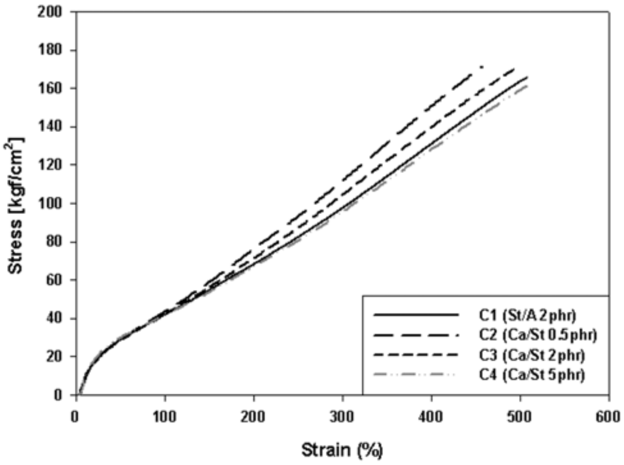

Figure 9. Stress-strain curves with different amount of calcium stearate.

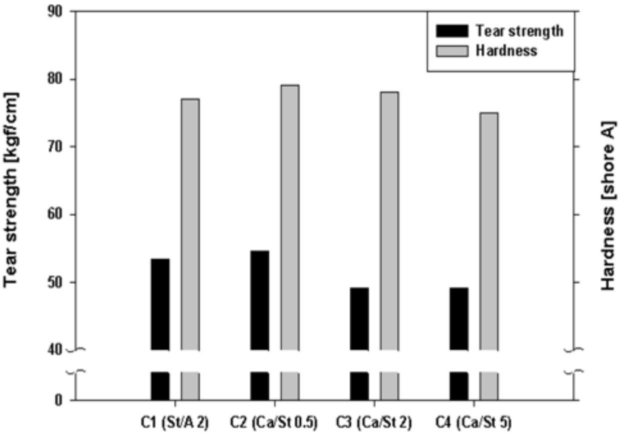

Figure 10. Tear strength and hardness with different amount of calcium stearate.

In Figures 9 and 10, the stress-strain curves, tear strength, and hardness were represented by calcium stearate contents. In case of C3 compound that applied 2 phr of calcium stearate showed higher tensile strength and 300% modulus than C1 compound that was applied with 2 phr of stearic acid.

The result also corresponds to the maximum torque result that was found in the curing characteristic curve. The charged Ca^{2+} ions could be attributable to form strong ion-effect with silicates, which increased the filler-rubber interaction. In the test proceeded by the contents of calcium stearate, the appli-

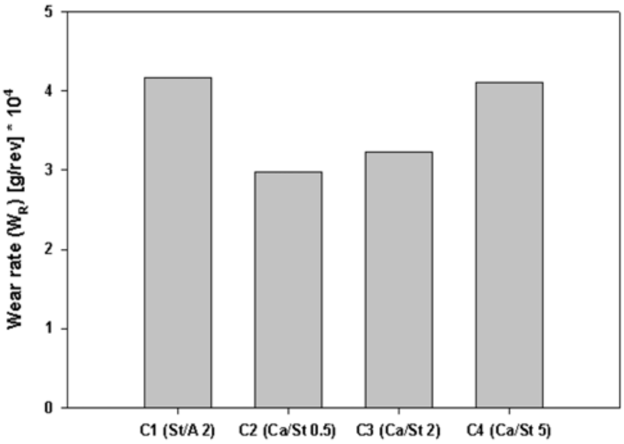

Figure 11. Wear rate with different amount of calcium stearate.

cation more than 0.5 phr of calcium stearate showed declining of tensile strength and 300% modulus, tear strength and hardness. These results well correspond to the maximum torque value result that was observed in the curing characteristic curve, and the remaining calcium stearate after forming rubber-soluble salt or soap with metallic oxides during curing process is considered to act as lubricants to reduce the tangling of high molecule chains and to reduce the internal friction, which consequently lowered the mechanical properties through the reduction of the reinforcement effect between high molecule chains and silicates. In case when carbon black was filled, the mechanical properties have been reported to be lowered when stearic acid was added more than 2% to act as lubricant to reduce the rubber reinforcement effect caused by internal friction.[48]

Figure 11 represented the measurement result of the amount of abrasion for the test compounds by the content of calcium stearate. In case of C3 compound that applied 2 phr of calcium stearate, it revealed 30% reduction of wear rate (W_R) compared to that of C1 compound that applied 2 phr of stearic acid. In case of the rubber compound that contain fillers, the improvement of wear resistance is mainly explained by the interaction between filler and rubber molecules. So, the improvement could be attributable to the Ca^{2+} ions of calcium stearate that formed an ionic interaction with the negatively charged silicate surface, which improved the filler-rubber molecule interaction. The most excellent wear resistance was observed in C2 compound that applied 0.5 phr of calcium stearate, but the C3 and C4 compounds that were applied with 2 and 5 phr, respectively, showed increase of wear rate compared to C2 compound. The result is attributable to the remaining calcium stearate which acted as the lubrication after forming the rubber soluble salt by reacting with ZnO to reduce the rubber-rubber interaction, and it consequently resulted to degrade the mechanical properties and caused the occurrence of tearing phenomenon under low load due to low tear strength, which resulted to increase the wear rate. Based on the previously described dynamic viscoelasticity and wear resistance measurement results, it was possible to know that the SBR/organoclay compounds that used carbon black, silica, and organoclay as its ternary filler system could improve the wet traction, rolling resistance and wear resistance if typically used stearic acid is replaced by calcium stearate.

Conclusions

The present study manufactured the SBR/organoclay compound by applying the latex method by using tertiary ammonium of dimethyldodecyl ammonium and MMT, and the dispersion characteristics of silicates has been evaluated by using XRD and TEM image. The result of analyzing XRD diffraction patterns of SBR/organoclay nanocomposites, the ion exchange reaction with sodium ion (Na^+) by ammonium salt resulted to show approximately 3 fold increase of d-space between silicates compared to that of Na-MMT, and it was possible to confirm that DDA formed a good insertion between silicate layers. In addition, the result of observing the dispersion state of silicates within rubber matrix by using TEM image enabled us to observe the aggregation phenomenon of silicate in case of Na-MMT compound, but the organization of Na-MMT by using DDA resulted the exfoliation of silicate layers into 4~8 layers to have a good dispersion of silicates within rubber matrix. To determine the appropriate content of DDA by the content of clay, the curing characteristics by DDA content, and mechanical properties and wear resistance have been evaluated. As the result of it, the increase of the amount of DDA up to 50% compared to the 5 phr clay showed the improvement of torque value difference (ΔT), maximum torque values, mechanical properties and wear resistance. It might be due to the increased degree of crosslink which is due to the accelerated the ring opening rate of sulfur (S_8) by increasing the content of DDA that act as an accelerator. In addition, the positive ions (Na^+) of Na-MMT in between silicate layers have been substituted with protonated DDA, which improved the dispersion of silicates, and the occurrence of hydrodynamic reinforcement effect of the clay due to its characteristic plate-like structure might has been the cause of such result. When the dynamic viscoelasticity was evaluated for rubber compound that was filled with DDA-MMT by applying stearic acid and metal stearates, the tan δ value measured at 0 ºC by applying metal stearate was high by showing the improvement of wet traction and having low tan δ at 50~60 ºC to allow to have fuel cost saving effect by improving the rolling resistance. The test result carried out by the content of calcium stearate revealed that the application of 0.5 phr to the content of SBR showed the most excellent mechanical properties and wear resistance characteristics. But the application more than 0.5 phr degraded the mechanical properties and wear resistance, and it is attributable to the calcium stearate that acted as lubricants by reducing the tangling of high molecule chains and reducing the internal friction, which reduced the reinforcement effect between high molecule chains and silicates, and consequently reduced the mechanical properties and wear resistance characteristics.

Conclusively, in case of SBR/organoclay compound that used 35 phr of carbon black, 20 phr of silica, and 5 phr of organoclay as its ternary filler system at the current study, the 50% of DDA content to 5 phr clay was used for the manufacture of organoclay, and 0.5 phr of calcium stearate was applied to manufacture the compound that showed the most excellent dynamic viscoelasticity, wear resistance and mechanical properties, which is considered to be the excellent tire tread compound for passenger cars.

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References

(1) A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1174 (1993).

(2) A. Okada, Y. Kojima, M. Kawasumi, Y. Fukushima, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1179 (1993).

(3) Y. T. Vu, J. E. Mark, L. H. Pham, and M. Enhelhardt, *J. Appl. Polym. Sci.*, **82**, 1391 (2001).

(4) S. S. Ray and A. K. Bhowmick, *Rubber Chem. Technol.*, **74**, 835 (2001).

(5) S. Joly, G. Garnaud, R. Ollitrault, L. Bokobza, and J. E. Mark, *Chem. Mater.*, **14**, 4202 (2002).

(6) S. Sadhu and A. K. Bhowmick, *J. Appl. Polym. Sci.*, **92**, 698 (2004).

(7) S. Sadhu and A. K. Bhowmick, *J. Polym. Sci. Part B: Polym. Phys.*, **42**, 1573 (2004).

(8) M. Arroyo, M. A. Lopez-Manchado, and B. Herrero, *Polymer*, **44**, 2447 (2003).

(9) S. Varghese and J. Karger-Kocsis, *J. Appl. Polym. Sci.*, **91**, 813 (2004).

(10) P. L. Teh, Z. A. Mohd Ishak, A. S. Hashim, J. Karger-Kocsis, and U. S. Ishiaku, *J. Appl. Polym. Sci.*, **94**, 2438 (2004).

(11) M. Ganter, W. Gronski, P. Reichert, and R. Mulhaupt, *Rubber Chem. Technol.*, **74**, 221 (2002).

(12) S. H. Wang, Z. L. Peng, Y. Zhang, and Y. X. Zhang, *Symposium of International Rubber Conference 2004*, Beijing, China, Sep. 21-25, **Volume B**, p 257.

(13) C. Nah, H. J. Ryu, W. D. Kim, and Y. W. Chang, *Polym. Int'l.*, **52**, 1359 (2003).

(14) W. H. Kim, S. K. Kim, J. H. Kang, Y. Cheo, and Y. W. Chang, *Macromol. Res.*, **14**, 187 (2006).

(15) N. Hasegawa, H. Okamoto, and A. Usuki, *J. Appl. Polym. Sci.*, **93**, 758 (2004).

(16) H. Zheng, Y. Zhang, Z. Peng, and Y. Zhang, *J. Appl. Polym. Sci.*, **92**, 638 (2004).

(17) J. Ma, P. Xiang, Y. W. Mai, and L. Q. Zhang, *Macromol. Rapid Commun.*, **25**, 1692 (2004).

(18) Y. Q. Wang, H. F. Zhang, Y. P. Wu, J. Wang, and L. Q. Zhang, *Symposium of International Rubber Conference 2004*, Beijing, China, Sep. 21-25, **Volume B**, p 420.

(19) H. F. Zhang, Y. Q. Wang, Y. P. Wu, L. Q. Zhang, J. Yang, and X. F. Wang, *Symposium of International Rubber Conference 2004*, Beijing, China, Sep. 21-25, **Volume B**, p 240.

(20) Y. P. Wu, Q. X. Jia, D. S Yu, and L. Q. Zhang, *J. Appl. Polym. Sci.*, **89**, 3855 (2003).

(21) L. Q. Zhang, Y. Z. Wang, Y. Q. Wang, Y. A. Sui, and D. S. Yu, *J. Appl. Polym. Sci.*, **78**, 1873 (2000).

(22) Y. Z. Wang, L. Q. Zhang, C. H. Tang, and D. S. Yu, *J. Appl. Polym. Sci.*, **78**, 1879 (2000).

(23) Y. Wang, H. Zhang, Y. Wu, J. Yang, and L. Zhang, *Eur. Polym. J.*, **41**, 2776 (2005).

(24) M. J. Wang and W. L. Patterson, *Paper presented at ACS Meeting*, Anaheim, California, May 6 (1997).

(25) W. Kim, B. S. Kang, S. G. Cho, C. S. Ha, and J. W. Bae, *Compos. Interface*, **14**, 409 (2007).

(26) Y. P. Wu, Y. Q. Wang, H. F. Zhang, Y. Z. Wang, D. S Yu, L. Q. Zhang, and J. Yang, *Compos. Sci. Technol.*, **65**, 1195 (2005).

(27) N. Kobayashi, I. Furuta, H. Akrema, and Y. Isono, *Papers American Chemical Society, Division of Rubber Chemistry*, **154**, 697 (1999).

(28) Michael E. Martini, *ACS 122nd*, paper No. 45 (1982).

(29) S. Wolff, *Rubber Chem. Technol.*, **55**, 967 (1982).

(30) W. J. Son, W. Kim, and U. R. Cho, *Elastomer*, **37**, 86 (2002).

(31) C. Nah, Ph.D. Dissertation, The University of Akron (1995).

(32) C. T. R. Pulford, Ph.D. Dissertation, The University of Akron (1979).

(33) Theng, BKG, *The Chemistry of Clays Organic Interactions*, Wiley, New York, 1974.

(34) M. J. Wang, E. H. Tan, and S. Wolff, *Rubber Chem. Technol.*, **66**, 178 (1993).

(35) S. Bandyopadhyay, P. P De, D. K. Tripathy, and S. K. De, *J. Appl. Polym. Sci.*, **63**, 1833 (1997).

(36) T. Lan, P. D. Kaviratna, and T. J. Pinnavaia, *Chem. Mater.*, **6**, 573 (1994).

(37) A. Mousa and J. Karger-Kenny, *J. Macromol. Mater. Eng.*, **286**, 260 (2001).

(38) M. A. Lopez-Manchado, M. Arroyo, B. Herrero, and J. Biagiotti, *J. Polym. Sci.*, **89**, 6 (2003).

(39) A. R. Payne and R. E. Whitaker, *J. Appl. Polym. Sci.*, **16**, 1191 (1972).

(40) A. N. Gent and C. T. R. Pulford, *J. Appl. Polym. Sci.*, **28**, 943 (1983).

(41) Hallamach, *Proc. Phys. Soc.*, **B67**, 883 (1954).

(42) V. A. Garten, K. Eppinger, and D. E. Weiss, *Rubber Chem. Technol.*, **29**, 1434 (1956).

(43) M. J. Wang, *Rubber Chem. Technol.*, **72**, 470 (1999).

(44) J. B. Donnet, *Rubber Chem. Technol.*, **71**, 323 (1998).

(45) M. J. Wang, *Rubber Chem. Technol.*, **71**, 520 (1998).

(46) M. J. Son, Master's Thesis, Pusan National University (2007).

(47) S. S. Park, B. H. Park, K. C. Song, and S. K. Kim, *Polymer (Korea)*, **24**, 220 (2000).

(48) H. Barron, *Reprinted from the India-Rubber Journal*, **90**, 638 (1935).