

Melt-Compounded Butadiene Rubber Nanocomposites with Improved Mechanical Properties and Abrasion Resistance

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ABSTRACT: Hydrophobic polymers such as polyethylene and polypropylene are very difficult to use for preparing nanocomposites without a compatibilizer. However, in this study, polybutadiene rubber (BR; a hydrophobic polymer) nanocomposites were produced successfully without a compatibilizer with a melt-compounding method. Transmission electron microscopy showed an intercalated and exfoliated clay morphology in the polymer matrix, which led to increased mechanical properties. The tensile and tear strengths of the BR/Cloisite 20A hybrids were 4.4 times and 2 times larger than that of BR, respectively. The rebound resilience, compression set, and abrasion resistance were

also improved by the addition of organoclay. The abrasion resistance of BR/Cloisite 20A was approximately 2 times larger than that of BR. The cure time (t_{90}), scorch time (t_2), and their difference ($t_{90} - t_2$) of the BR/organoclay hybrids were much reduced than those of BR. Thus, organoclays behaved as good fillers and effective accelerant agents for BR vulcanization. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2062–2066, 2006

Key words: nanocomposites; organoclay; polybutadiene; rubber; vulcanization

INTRODUCTION

In recent years, polymer/organophilic layered silicate (organoclay) nanocomposites have attracted considerable attention from both a fundamental research and an applications point of view because of the remarkable improvement they impart on material properties. Because of the nanometer thickness and the extremely high aspect ratio of silicate layers, these nanocomposites exhibit dramatic improvements in mechanical, thermal, and barrier properties.^{1–4}

Many studies have been done on plastic/organoclay nanocomposites. However, investigations have recently started on rubber/organoclay nanocomposites.^{5–13} Rubbers have been reinforced by various fillers to improve the mechanical properties, and among several fillers, carbon black is the most important filler in this regard. To produce the same mechanical strength as in polymer/3–5% silicate nanocomposites, 30–60% filler has to be incorporated in conventional composites. Therefore, rubber/organoclay nanocomposites can make much lighter rubber parts with im-

proved elastic properties over conventional composites.

Polybutadiene rubber (BR) accounts for approximately 25% of the world's production of synthetic rubber. Seventy percent of total production is used in tire compounds, with another 20% being used for the modification of plastics. Until now, there has been very little information available regarding BR/organoclay nanocomposites. Because hydrophobic polymers, such as polypropylene and polyethylene, are very difficult to use for creating nanocomposites without a compatibilizer, BR, being a hydrophobic polymer, was expected to be difficult in the formation of nanocomposites. On the other hand, it has been reported that the layered structure of organoclay can be broken up and peeled off on high-acting shear forces.^{14,15} Because rubbers are very high-molecular-weight materials showing extremely high viscosities during melt compounding, the preparation of rubber nanocomposites with melt compounding can be a good way for achieving rubber nanocomposites.

To obtain a deeper understanding of the melt intercalation of organoclay with BR, the structures, mechanical properties, and cure characteristics of BR/organoclay hybrids were investigated in this study.

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TABLE I
Important Characteristics of the Materials Used in This Study

	Material	Supplier	Characteristics
Rubber	Butadiene rubber	Kumho Petrochemical, (Yeosu, Korea)	cis-1,4 content = 95%, ML1+4(100°C) = 45, and specific gravity = 0.91
Reinforced filler	Carbon black N330	Korea Carbon Black Co. (Miryang, Korea)	Iodine adsorption = 82 mg/g and nitrogen surface area = 79 m ² /g
Organoclay	Cloisite 15A Cloisite 20A	Southern Clay Southern Clay	Specific gravity = 1.66 Specific gravity = 1.77
Crosslinking agent	Sulfur	Saekwang Chemical (Gyeongju, Korea)	Common grade
Crosslinking coagent	Zinc oxide	Gil-Chun Chemical (Ulsan, Korea)	
Accelerator	Stearic acid MBTS	LG Chemical (Ulsan, Korea) Dong Yang Chemical (Incheon, Korea)	Specific gravity = 0.84 and mp = 70°C Molecular weight = 332 and mp = 160°C
Antioxidant	Pentaerythryl-tetrakis[3-(3,5-di- <i>t</i> -butyl-4-hydroxy phenyl)-propionate] (Songnox 1010)	Songwon (Ulsan, Korea)	Molecular weight = 1178 and mp = 110-125°C

EXPERIMENTAL

Materials and preparation of the BR/organoclay nanocomposites

The important characteristics of the materials used in this study are summarized in Table I. Organically modified montmorillonites (organoclays) were purchased from Southern Clay Products (Gonzales, TX) under the trade names of Cloisite 20A and Cloisite 15A. The organic modifier of Cloisite 20A and 15A was dimethyl dihydrogenated tallow quaternary ammonium. The modifier concentration was 125 mequiv/100 g of clay for Cloisite 15A and 95 mequiv/100 g of clay for Cloisite 20A. The organic modifier of Cloisite 15A and 20A was the same, and the only difference between Cloisite 15A and 20A was the modifier concentration existing between the layers.

BR, organoclay, zinc oxide (ZnO), antioxidant, and stearic acid were mixed in a Haake internal mixer (Karlsruhe, Germany) at 120°C for 15 min. BR was first

allowed to melt; then, organoclay and other additives were added. Then, the obtained BR hybrids were mixed with sulfur and dibenzothiazyl disulfide (MBTS) in a two-roll mill. The recipes of the compounds are described in Table II.

After they were mixed in a two-roll mill, the hybrids were vulcanized at 155°C in an electrically heated hydraulic press to their respective cure times (t_{90} 's). The t_{90} values were derived from an oscillating disk rheometer (Gotech, Taichung, Taiwan) measurements.

Characterization of the nanocomposites

X-ray diffraction (XRD) patterns were taken with a Rigaku D/max 2200H X-ray diffractometer (40 kV, 50 mA, Tokyo, Japan). The scanning rate was 0.5°/min. The basal spacing of the silicate layer (d) was calculated with Bragg's equation: $n\lambda = 2d \sin \theta$ (n : integer, θ : half the angle of diffraction, λ : wavelength of the

TABLE II
Recipes (in phr) of the Rubber Compounds

Material	Sample			
	BR	BR/Cloisite15A	BR/Cloisite 20A	BR/carbon black
Butadiene rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Sulfur	1	1	1	1
MBTS	1	1	1	1
Antioxidant	0.5	0.5	0.5	0.5
Cloisite 15A organoclay		3		
Cloisite 20A organoclay			3	
Carbon black				10

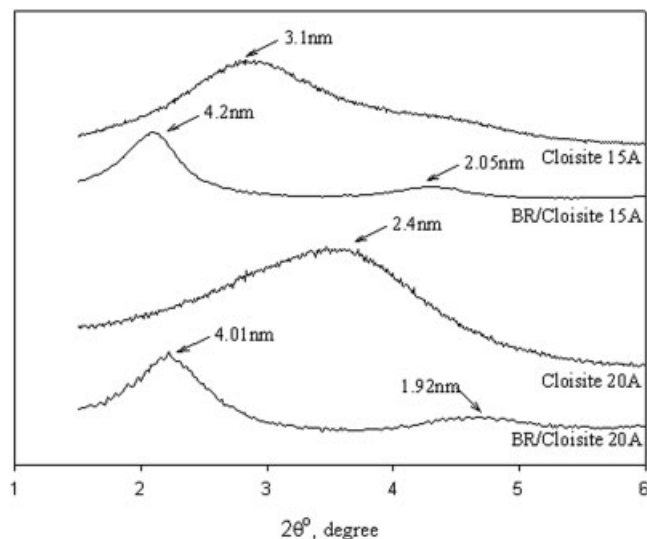


Figure 1 XRD patterns of the BR/organoclay hybrids.

X-ray). Transmission electron microscopy (TEM) images were taken from cryogenically microtomed ultrathin sections with energy filtering transmission electron microscopes (EF-TEM) (EM 912 Omega, Carl Zeiss, Jena, Germany).

Property measurements

A universal testing machine (model UL25, Hounsfield Co., Surrey, England) was used to obtain the tensile properties of the nanocomposites at room temperature. The crosshead speed was 10 mm/min. All measurements were taken for five replicates of dog-bone-shaped specimens and averaged to get the final result. Also, the tear strength was measured with unnicked 90° angle test pieces at a crosshead speed of 500 mm/min in the universal testing machine.

The rebound resilience (elasticity) was measured according to Deutsches Institut für Normung (DIN) 53512. The pendulum was released from a horizontal position and struck the samples at a vertical point. The abrasion test was carried out with the DIN abrader according to DIN 53516. The abrasion was defined as a volumetric loss of a cylindrical sample. The cylindrical sample, 16 mm in diameter, was brought into contact with the abrasive surface of a rotating drum under an added weight of 1 N. The direction of abrasion changed continuously through the rotation of the specimen on its own axis while it underwent abrasion. The degree of abrasion was determined through five measurements with the aid of a standard rubber sample (BAM, Berlin, Germany). Compressions set measurements were performed according to ASTM D 395 for 24 h at 70°C with 25% compression.

Cure characteristics were studied with the oscillating disk rheometer (Gotech) according to ASTM D 2084. The rheometer rotor oscillated through a 1° arc at 1.66 Hz and exerted a shear strain on the sample during curing.

RESULTS AND DISCUSSION

Characterization of the BR/organoclay hybrids

Figure 1 shows the XRD patterns of the BR/organoclay hybrids. For BR/Cloisite 20A hybrids, we observed two peaks at 4.01 nm ($2\theta = 2.2^\circ$) and 1.92 nm ($2\theta = 4.6^\circ$), and for BR/Cloisite 15A hybrids, we observed two peaks at 4.2 nm ($2\theta = 2.1^\circ$) and 2.05 nm ($2\theta = 4.3^\circ$) corresponding to 001 and 002 planes. The peaks at $2\theta = 2.2^\circ$ for the BR/Cloisite 20A hybrid and at $2\theta = 2.1^\circ$ for the BR/Cloisite 15A hybrid indicated the intercalation of BR molecules into the interlayers of Cloisite 20A and Cloisite 15A, respectively, which resulted in the expansion of the interlayer distance. The degree of expansion of the interlayer distance for BR/Cloisite 20A (2.4 → 4.01 nm) was higher than that for BR/Cloisite 15A (3.1 → 4.2 nm).

To confirm further the dispersion states of Cloisite 15A and 20A in the BR matrix, TEM studies were carried out. Figures 2 and 3 presents the TEM photographs of ultrathin sections of the BR/organoclay hybrids exhibiting intercalated (mostly) and exfoliated (scarcely) morphologies. The dark lines are silicate layers. The original interlayer distances of Cloisite 15A and Cloisite 20A were 3.1 and 2.4 nm, respectively. However, Cloisite 15A and Cloisite 20A, as shown in Figures 2 and 3, had an interlayer distance of approximately 4 nm. The larger interlayer distance (4 nm) of organoclays than the original interlayer distance of

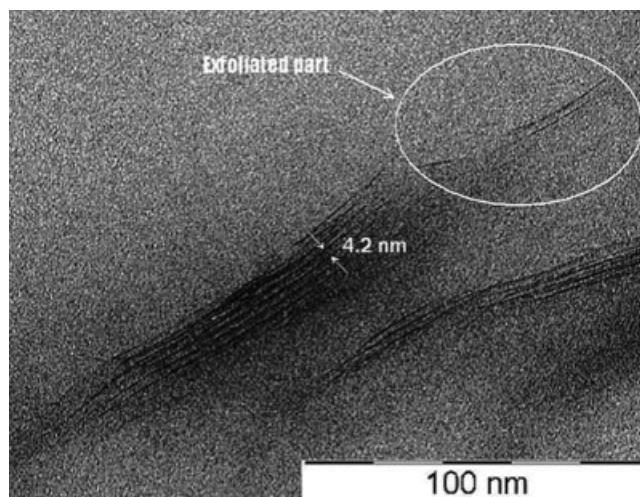


Figure 2 TEM photograph of an ultrathin section of the BR/Cloisite 15A hybrid.

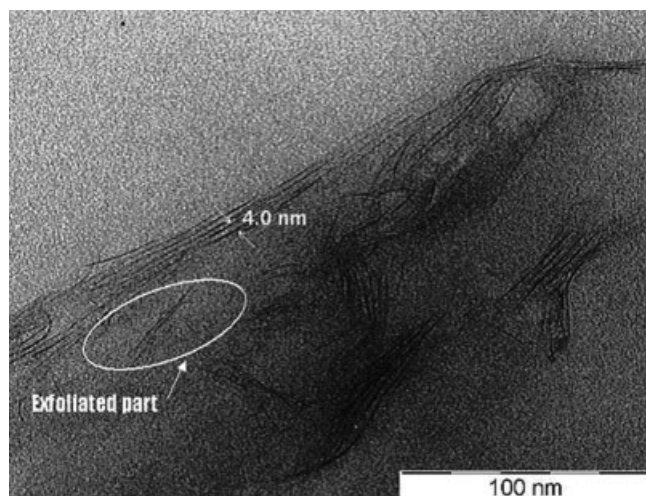


Figure 3 TEM photograph of an ultrathin section of the BR/Cloisite 20A hybrid.

organoclays observed in TEM photograph was due to the intercalation of BR into the organoclay. These TEM results agreed well with the XRD results. The exfoliated silicate layers are also indicated by circles in the figures. Polar interactions between the polymer and organoclay are critical for the production of nanocomposites with the melt-compounding method.^{16–18} Because BR is a hydrophobic polymer and there was no compatibilizer used in this study, the intercalation and exfoliation of the silicate layers observed in the XRD and TEM results were possibly due to the high-acting shear stress on the layers and polar vulcanization curatives. It was recently reported that hydrophobic rubber nanocomposites were prepared successfully without a compatibilizer with a melt-compounding method.^{6,11–13,19,20} Because of the extremely high viscosities of rubbers during melt compounding, high shear stress acts on the clay layers and results in the peeling off of the layers.¹² Also, because curatives, such as ZnO, MBTS, stearic acid, and sulfur, are polar low-molecular-mass compounds, they may penetrate

between organoclay layers, which results in rubber crosslinking inside the layer galleries.²⁰ The detailed mechanism of the intercalation and exfoliation for the BR/organoclay hybrids will be studied further in our laboratory.

Mechanical properties

The mechanical properties of the BR/organoclay hybrids are shown in Table III. A remarkable increase in the mechanical properties was observed for the BR/organoclay hybrids. The tensile and tear strengths of the BR/Cloisite 20A hybrids were 4.4 and 2 times greater than those of BR, respectively. There were 228 and 312% improvements observed in the 100 and 300% modulus, respectively, over those of BR. The rebound resilience, compression set, and abrasion resistance were also improved by the addition of organoclay. In addition to the reinforcing effect, the addition of organoclay in the BR nanocomposites led to improved elastic characteristics in the BR, as deduced from the rebound resilience and compression set measurements. The abrasion resistance of BR/Cloisite 20A was approximately 2 times higher than that of BR. The abrasion resistance is a very important property for the application of tire and velt. BR/Cloisite 20A (3 phr) hybrids displayed better mechanical properties, except compression set, than BR/carbon black (10 phr).

Cure characteristics

The curing characteristics are summarized in Table IV. Both the maximum torque (MH) and the difference between the maximum and minimum torque (ML) increased with the addition of organoclay into BR. The nanocomposite with 3 phr organoclay (15A and 20A both) showed higher torque and torque difference than BR. Interestingly, the BR/Cloisite 15A (3 phr) hybrid exhibited a larger increase in torque difference and MH than the BR/Cloisite 20A hybrid.

TABLE III
Physical Properties of the BR/Organoclay Nanocomposites

Sample	Density	Tensile strength (MPa)	100% modulus (MPa)	300% modulus (MPa)	Elongation at break (%)	Tear strength (N/mm)	Rebound resilience (%)	DIN abrasion (mm ³)	Compression set (%)
BR	0.953 ± 0.099	1.31 ± 0.06	0.32 ± 0.01	0.41 ± 0.03	955 ± 30	11.94 ± 0.10	45	62	27
BR/Cloisite 15A (3 phr)	0.958 ± 0.095	5.68 ± 0.14	0.55 ± 0.03	0.95 ± 0.06	997 ± 21	29.35 ± 0.49	59	39	18
BR/Cloisite 20A (3 phr)	0.962 ± 0.079	5.73 ± 0.16	0.73 ± 0.03	1.28 ± 0.05	783 ± 29	24.01 ± 0.22	58	38	23
BR/carbon black (10 phr)	1.007 ± 0.002	3.84 ± 0.26	0.56 ± 0.01	1.04 ± 0.01	695 ± 28	19.80 ± 1.10	46	61	15

TABLE IV
Crosslinking Characteristics of BR/Organoclay Nanocomposites

Sample	MH (N m)	ML (N m)	t_2 (min)	t_{90} (min)	Torque difference (N m)	$t_{90} - t_2$ (min)
BR	0.720	0.199	38.18	53.44	0.521	15.26
BR/Cloisite 15A (3 phr)	0.955	0.278	2.11	3.55	0.677	1.44
BR/Cloisite 20A (3 phr)	0.868	0.304	4.08	7.50	0.564	3.42
BR/carbon black (10 phr)	0.816	0.287	16.33	23.87	0.529	7.54

t_{90} (the cure time) (time required to reach 90% crosslinking), scorch time (t_2), and their difference ($t_{90} - t_2$) in BR/organoclay were much lower than in BR, which led us to conclude that the organoclays behaved as effective accelerant agents for BR vulcanization. Such an accelerating effect has already been reported for some other rubber nanocomposites.^{21,22} The possible formation of a Zn complex, in which sulfur and amine intercalant participate, may facilitate the development of elemental sulfur. The existence of a Zn-sulfur-amine complex has been suggested in the previous literature.²³⁻²⁵

The reduction t_{90} , t_2 , and their difference ($t_{90} - t_2$) for the BR/Cloisite 15A hybrid were more than those of the BR/Cloisite 20A hybrid. This may have been due to the larger concentration of the amine intercalant in Cloisite 15A than in Cloisite 20A.

CONCLUSIONS

BR nanocomposites were produced successfully with a melt-compounding method without a compatibilizer, unlike with other hydrophilic polymers, such as polypropylene and polyethylene. The intercalation of BR into the organoclay was evident from XRD and was confirmed by TEM study.

Interestingly, as a result of the good dispersion of clays, a significant improvement in the mechanical properties was observed. The tensile and tear strengths of the BR/Cloisite 20A hybrids were 4.4 times and 2 times larger than those of BR, respectively. There were 228 and 312% improvements in the 100 and 300% modulus, respectively, over BR. Again, the rebound resilience, compression set, and abrasion resistance were also improved by the addition of organoclay. The abrasion resistance of BR/Cloisite 20A was approximately 2 times larger than that of BR. The nanocomposite with 3-phr organoclay showed higher torque values and torque difference than BR. Again, t_{90} , t_2 , and their difference ($t_{90} - t_2$) were reduced dramatically when organoclays were incorporated

into BR. The organoclay behaved as a good filler and an effective accelerant agent for BR vulcanization.

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