

Technological and Processing Properties of Natural Rubber Layered Silicate-Nanocomposites by Melt Intercalation Process

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ABSTRACT: Natural rubber nanocomposites were produced by melt-mixing of natural rubber with organically modified silicates. For comparison, a pristine-layered silicate and a nonlayered version [English Indian clay (EIC)] were also included in the study. The layered silicate used was sodium bentonite (BNT) and organoclays used were octadecylamine-modified montmorillonite (MMT-ODA) and methyltallow bis-2-hydroxyethyl ammonium-modified montmorillonite (MMT-TMDA). Accelerated sulfur system was used for the vulcanization of the nanocomposites. The dispersion of these silicates was studied by X-ray diffraction and transmission electron

microscopy. The organoclay-incorporated composites exhibited faster curing and improved mechanical properties. The improvement in the mechanical properties of the composites followed the order MMT-ODA > MMT-TMDA > EIC > BNT. The property improvement was attributed to the intercalation/exfoliation of the organically modified silicates because of their high initial interlayer distance. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2537–2543, 2006

Key words: bentonite; exfoliation; intercalation, layered silicate; nanocomposites; natural rubber

INTRODUCTION

Carbon black represents the predominant class of reinforcing fillers in rubber industry. Silicates, whiting (CaCO_3), and other mineral fillers are also used extensively where high degree of reinforcement is not essential. The degree of reinforcement provided by filler depends on its concentration, particle size, and above all on the degree of polymer–filler interaction. With the introduction of fillers of nano particle size and layered silicates, polymer nanocomposites with markedly improved properties have been developed.

Nanocomposites are a new class of materials, which exhibit excellent barrier, mechanical, thermal, optical, and physicochemical properties, compared to the pure polymers or microcomposites because of their nanometer level dispersion.¹ Nanocomposites can be categorized into three, depending on how many dimensions of the dispersed particles are in the nanometer range. When all the dimensions are in the order of nanometers, as in spherical silica nanoparticles, they are called isodimensional nanoparticles.^{2–4} Nanotubes or whiskers^{5–7} are included in the second category where two dimensions are in the nanometer

scale. The third type of nanocomposites is characterized by only one dimension in the nanometer range. In layered silicate nanocomposites the filler has a layered structure, i.e., the polymer-layered crystal nanocomposites. These materials are obtained by the intercalation of the polymer inside the galleries of layered host crystals.

The four main processes for preparing polymer-layered silicate nanocomposites are exfoliation adsorption, *in situ* intercalation, melt intercalation, and template synthesis.⁸ In exfoliation adsorption technique the layered silicate is exfoliated into single layers using a solvent in which the polymer is soluble. This technique has been widely used for the preparation of nanocomposites based on water soluble polymers.^{9–11} In the case of *in situ* intercalation the silicate is swollen within the liquid monomer and polymerized either by heat or radiation. Extensive studies on polymer-layered thermoplastic nanocomposites have been reported using this technique.^{12,13} They used organically modified Na-montmorillonite to obtain nylon-6-based nanocomposites.^{13,14} This technique has also been used for the preparation of nanocomposites based on thermoset. Burnside and Giannelis have studied the two-step preparation of silicon-based nanocomposites using the melt intercalation technique.¹⁵ Template synthesis is mainly used for the synthesis of double layer hydroxide-based nanocomposites.^{16,17} Here the silicate is formed *in situ* in an aqueous solution containing the polymer and the silicate building-blocks.

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TABLE I
Specifications of NR

Characteristics	Specification
Dirt content (% by mass. max.)	0.05
Volatile matter (% by mass. max.)	0.80
Ash content (% by mass. max.)	0.60
Nitrogen (% by mass. max.)	0.60
Initial plasticity, P_0 (min)	30
Plasticity retention index, PRI (min)	60
Mooney viscosity ML (1 + 4) at 100°C	60 ± 5

Several reports are available on the processing and properties of rubber nanocomposites.^{18,19} However, a complete description of natural rubber nanocomposites, especially about their mechanical properties, is still lacking. Hence, the objective of the present work is to evaluate the properties of natural rubber nanocomposites, based on modified and unmodified layered silicates.

EXPERIMENTAL

Materials, formulation, and curing

Natural rubber used for the study was Indian Standard Natural Rubber (ISNR 5). Table I gives the specifications of this grade of natural rubber. The basic properties of the silicates used are given in Table II. All the other ingredients were supplied by Bayer (India).

The rubber compounds were prepared in a laboratory-model two-roll mixing mill (David Bridge, England) of size 15 × 30 cm², having a friction ratio of 1 : 1.25, as per the formulation given in Table III. The mixes were cured at 150°C in an electrically heated hydraulic press to the respective cure time (t_{90}).

Testing

The t_{90} values and other cure characteristics were derived from a moving die rheometer, Rheotech MD+, Alpha Technologies, USA, having 0.5° to-and-fro motion at a frequency of 1.66 Hz. Mooney viscosity ML (1 + 4) at 100°C was measured using a Mooney

viscometer, model SMV-202 Shimadzu, Japan. Tensile and tear properties were performed respectively, on dumbbell- and crescent-shaped specimens according to ASTM standards D 412 and D 624 on a Zwick 1474 universal testing machine at a crosshead speed of 500 mm/min. Hardness, resilience, and compression set were tested as per the relevant ASTM standards and abrasion resistance was measured as per the DIN standards.

The dispersion of the silicates was studied by transmission electron microscope (TEM) and wide angle X-ray scattering (WAXS). TEM pictures were taken using a LEO 912 omega transmission electron microscope with an acceleration voltage of 120 keV. The specimens were prepared using an Ultracut E ultramicrotome (Leica Microsystems, Wetzlar, Germany). Thin sections of about 100 nm were cut with a diamond knife at 120°C. X-ray diffractograms (XRD) were obtained using Ni-filtered Cu K radiation ($\lambda = 0.1542$ nm) by a D 500 diffractometer (Siemens, Germany) at 40 kV and 35 mA. The samples were scanned in step mode at a scan rate of 1.5°/min in the range, $2\theta < 12^\circ$.

RESULTS AND DISCUSSION

Cure characteristics of the compounds

Table IV shows the cure characteristics of the compounds. Sodium bentonite (BNT) is a natural layered clay (unmodified), whereas octadecylamine (MMT-ODA) and methyltallow bis-2-hydroxyethyl quaternary ammonium (MMT-TMDA)-modified montmorillonite are modified layered silicates. Addition of modified silicates reduced the cure time of the respective compounds compared to that of the reference material (amorphous nonlayered version) filled compound. The reduction in cure time is observed when the loading of MMT-TMDA is increased. In the case of MMT-ODA, the modifier is octadecylamine, whereas for MMT-TMDA methyltallow bis-2-hydroxyethyl quaternary amine is the modifier. These modifiers, being amines, are believed to take part in amine complexation reaction (like an accelerator), which will in effect

TABLE II
Characteristics of the Silicates

Material	Grade/supplier	Characteristics
Sodium bentonite (BNT)	EXM 757, Sud Chemie, Germany	Purified natural layered silicate, CEC: 80 meg/100g, interlayer distance 1.24 nm
MMT-ODA	Nanomer 1.30 P, Nanocov Inc., USA	Octadecylamine (ODA) modified montmorillonite, specific gravity 1.9 g/cm ³ , particle size 16–20 μm, interlayer distance 2.10 nm
MMT-TMDA	Cloisite 30B, Southern Clay Products, USA	Methyltallow bis-2-hydroxyethyl quaternary ammonium (TMDA), modified montmorillonite, specific gravity 1.5–1.7 g/cm ³ , interlayer distance 1.85 nm
English Indian clay (commercial clay)	English Indian Clays, Trivandrum, India	Amorphous clay

TABLE III
Formulations of Mixes

Ingredients	A	B	C	D	E	F	G	H
Natural rubber	100	100	100	100	100	100	100	100
English Indian clay	0	10	30	0	0	0	0	0
Bentonite	0	0	0	10	0	0	0	0
MMT-ODA	0	0	0	0	5	10	0	0
MMT-TMDA	0	0	0	0	0	0	5	10
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
CBS*	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

accelerate the vulcanization reaction^{18–20} and hence there is a reduction in cure time. Consequently, the scorch time is also low for modified silicate-incorporated compounds compared to the others. The M_H – M_L value, which is a measure of the viscosity of the compound, is comparatively high for the modified silicates. Mooney viscosity is also high for the modified silicates. The scorch time obtained from the Mooney viscometer also showed a reduction with the addition of MMT-ODA and MMT-TMDA. The high Mooney viscosity is an indirect indication of intercalation of the polymer into the layered silicate layer. This shows that the rubber molecules underwent intercalation because of the high shear force generated during mixing. Because of this interaction process, the surface area of the layered silicate increased, which might be the reason for the high compound viscosity.

Dispersion of silicates

Two complementary techniques used for the characterization of nanocomposites are XRD and TEM. Figure 1 shows the XRD diffractograms of the NR composites containing MMT-ODA, MMT-TMDA, BNT, and English Indian clay (EIC). MMT-ODA- and MMT-TMDA-filled composites showed a shoulder at lower diffraction values, which corresponds to an interlayer distance of 3 nm (the initial layer distance of MMT-ODA and MMT-TMDA are 2.10 and 1.85 nm, respectively). This might be due to the intercalation of NR chains between the gallery spaces of the silicate. As the

intercalation of the polymer chains increased, the interlayer spacing between the layers increased. This leads to the shifting of diffraction peak toward the lower 2θ values in the XRD spectrum. Apart from the shoulder peak, MMT-ODA showed two diffraction peaks corresponding to 1.30 and 1.63 nm, and MMT-TMDA showed one peak corresponding to 1.30 nm. These values are less than that of the initial interlayer distance of the corresponding layered silicates. This explains the closing of some layers during the preparation process. This confinement of layers may be due to the coordination complexing of accelerated sulfur curing in the presence of zinc. Zinc is prone to coordination complexing, in which amine groups of the intercalants, such as octadecylamine and methyltallow bis-2-hydroxyethyl quarternary ammonium, and sulfur may participate. Thus the intercalant amines may be extracted from the intergallery space and used for sulfur vulcanization and hence the reduced layer distance. Bentonite shows only one peak, which corresponds to its original interlayer distance of 1.24 nm. Since EIC is amorphous, no diffraction peak was observed.

The TEM micrographs obtained for the NR composites containing MMT-ODA, MMT-TMDA, and EIC are given in Figures 2–4, respectively. It can be seen that a portion of the MMT-ODA is exfoliated homogeneously throughout the composites. However, in MMT-TMDA the exfoliation extent is somewhat less than that of the MMT-ODA. Some agglomeration of the silicate particles can be seen in the case of MMT-TMDA composites. As evident from the XRD pattern, exfoliation or intercalation of layers did

TABLE IV
Cure Characteristics of the Compounds

Properties	A	B	C	D	E	F	G	H
Optimum cure time (min)	11.41	13.14	14.52	11.32	8.41	8.34	10.20	9.52
t_{s2} (min)	8.55	8.59	9.16	6.04	2.59	2.34	5.36	4.41
Maximum torque, M_H (dNm)	8.32	9.03	13.84	8.58	11.98	12.45	10.34	11.71
Minimum torque, M_L (dNm)	0.66	0.66	1.02	0.67	0.87	1.32	0.89	1.51
$M_H - M_L$	6.62	8.41	11.05	7.07	11.11	11.13	9.52	10.23
Mooney viscosity ML(1 + 4) at 100°C	37.8	38.0	45.3	37.1	41.7	44.6	46.4	47.4
Mooney scorch time at 120°C (min)	42.42	40.21	32.46	30.40	12.59	11.0	25.47	18.40

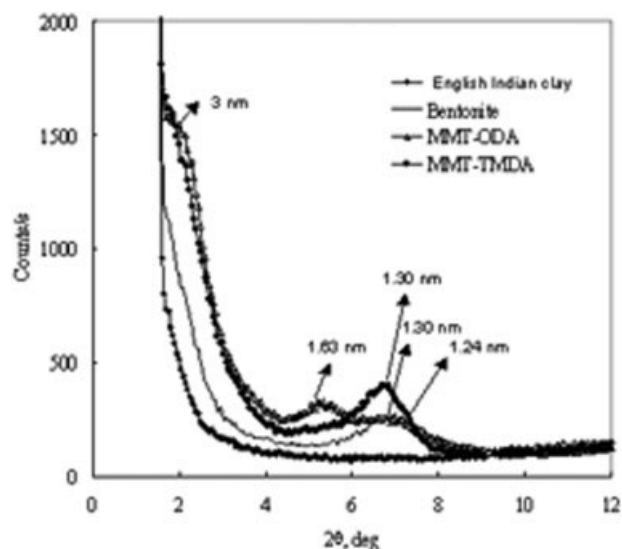


Figure 1 XRD spectra of different silicate-filled natural rubber nanocomposites.

not occur in the case of the EIC-filled NR composite. This can be clearly seen from the TEM picture (Fig. 4). The properties of such composites were in the same range as that of microcomposites.

Physical properties

Tensile strength values of different silicate-filled composites are given in Figure 5. Tensile strength follows the order MMT-ODA > MMT-TMDA > EIC > Bentonite. It is to be noted that the initial inter-layer distance for MMT-ODA and MMT-TMDA are

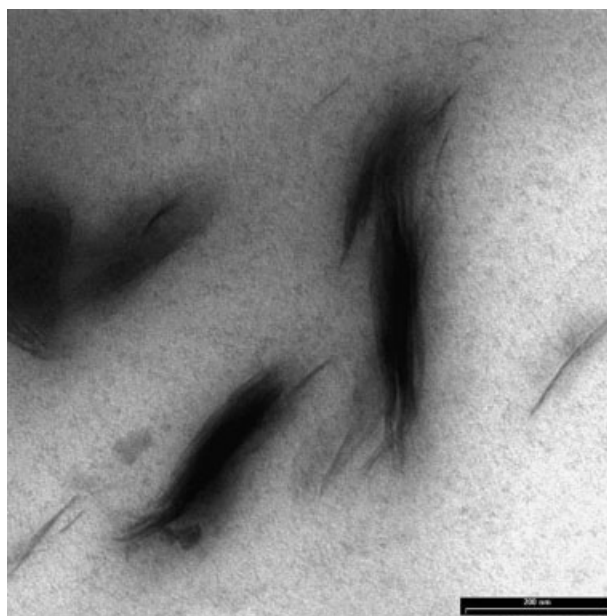


Figure 3 TEM photograph of MMT-TMDA-incorporated natural rubber nanocomposites.

2.10 and 1.85 nm, respectively. Because of the initial high interlayer distance of MMT-ODA, intercalation between the galleries and the degree of exfoliation are high in the case of MMT-ODA than that of MMT-TMDA-filled nanocomposites. This exfoliation causes tremendous increase in surface area. Hence, the MMT-ODA recorded high tensile strength. When the loading of the modified silicate increased from 5 to 10 phr, its tensile strength also increased in both the nanocomposites. Though bentonite is a layered

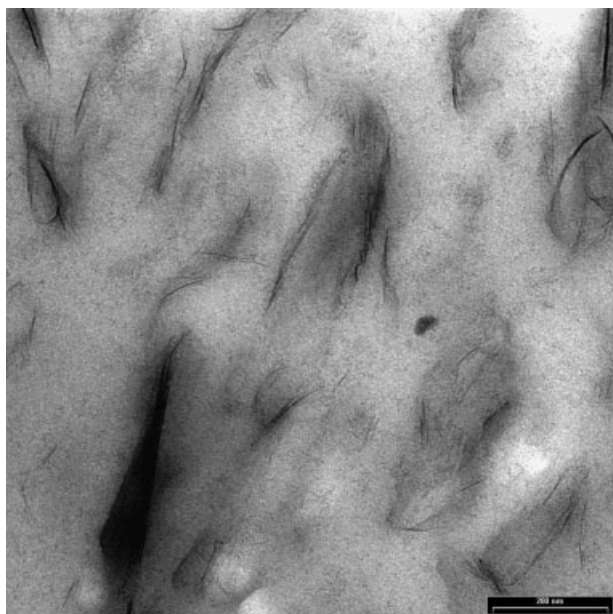


Figure 2 TEM photograph of MMT-ODA-incorporated natural rubber nanocomposites.

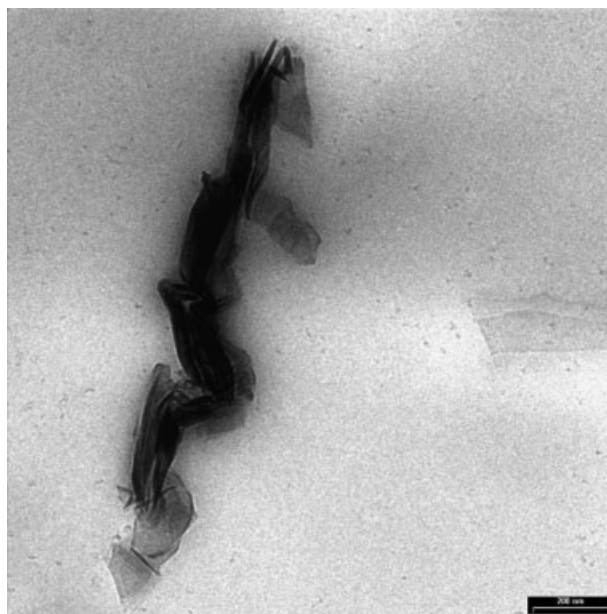


Figure 4 TEM photograph of EIC-incorporated natural rubber nanocomposites.

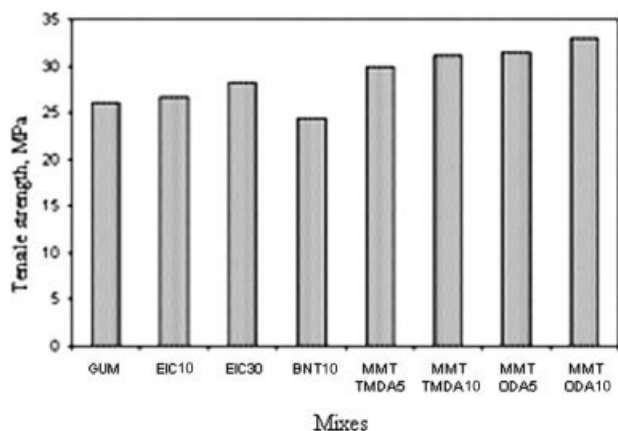


Figure 5 Variation of tensile strength with different silicate-filled natural rubber nanocomposites. EIC 10: English Indian clay 10 phr; EIC 30: English Indian clay 30 phr; BNT 10: Sodium bentonite 10 phr; MMT-ODA 5: Octadecylamine-modified montmorillonite 5 phr; MMT-ODA 10: Octadecylamine-modified montmorillonite 10 phr; MMT-TMDA 5: Methyltallow bis-2-hydroxyethyl quarternary ammonium-modified montmorillonite 5 phr; MMT-TMDA 10: Methyltallow bis-2-hydroxyethyl quarternary ammonium-modified montmorillonite 10 phr.

silicate, its interlayer distance (1.24) is not enough for the penetration of the polymer between the galleries so as to exfoliate the layers. Hence, bentonite recorded the lowest tensile strength. Since EIC is a semi-reinforcing filler, even at 30 phr loading it gives lower tensile strength values compared to the modified layered silicate-filled (10 phr) nanocomposites. Modulus values of the vulcanizates are given in Figure 6. Here also the MMT-ODA-incorporated composite showed maximum values at 300% elongation, which was comparable to that of the 30 phr EIC-incorporated composite. Modulus values at 100% elongation of the composites also followed the same order.

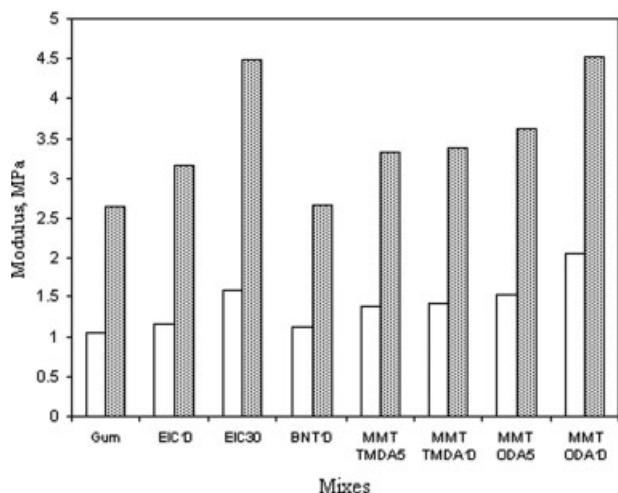


Figure 6 Variation of modulus with different silicate-filled natural rubber nanocomposites.

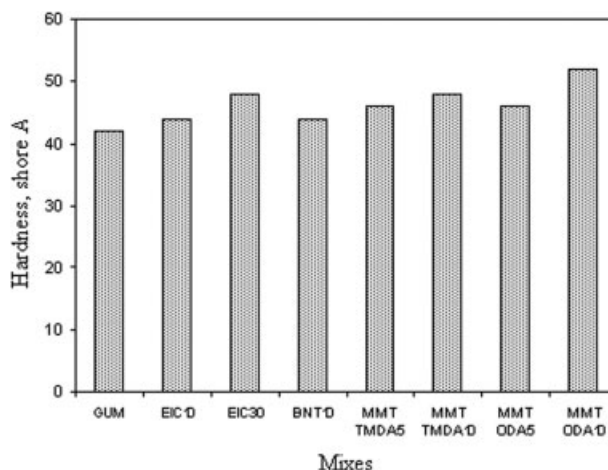


Figure 7 Variation of hardness with different silicate-filled natural rubber nanocomposites.

Figure 7 shows the hardness values of the composites. The MMT-ODA-incorporated composites showed higher hardness values because of the finely exfoliated silicate layers. Hardness and modulus of the EIC-filled composites even at 30 phr loading showed lower values than the modified silicates at 10 phr of loading. This may be due to the larger particle size and low level of dispersion of EIC as seen in the TEM picture. Elongation at break values of the vulcanizates are given in Figure 8. EIC (30 phr) showed the lowest elongation at break, whereas the modified silicate-filled vulcanizates (5–10 phr) showed high elongation at break values. High tensile strength values are usually associated with lower elongation values. However, the nanocomposites showed high tensile strength along with high elongation. This may be possible when the fine reinforcing silicate layers orient along the direction of the stress, which will contribute to increased tensile strength and elongation at break. The values of tear strength, a useful tool

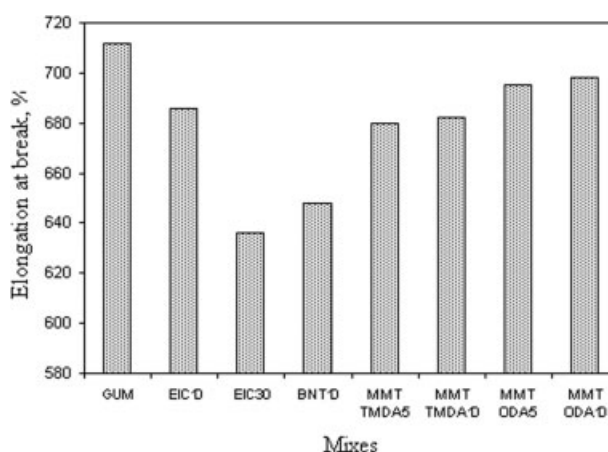


Figure 8 Variation of elongation at break with different silicate-filled natural rubber nanocomposites.

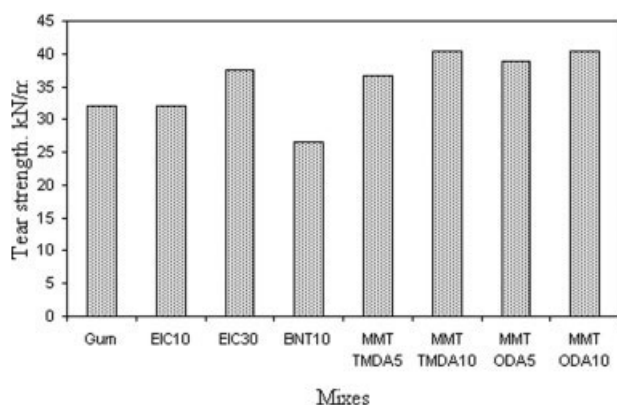


Figure 9 Variation of tear strength with different silicate-filled natural rubber nanocomposites.

for characterizing nanocomposites, are given in Figure 9. This property was highest for MMT-ODA- and MMT-TMDA-filled composites. It can be seen that EIC and bentonite has little effect on this property at 10 phr loading. As the loading increased from 5 to 10 phr, tear strength also increased in the case of the modified clays. EIC-filled vulcanizate at 30 phr recorded lower values than the 10 phr-loaded modified silicates. This effect can be assigned to the extent of dispersion and exfoliation of nanoclay and the high interfacial action between the layers and the rubber. Above all, the finely dispersed silicate layers divert the tear path, which in turn imparts high tear strength to nanocomposites.

Figure 10 shows the DIN abrasion loss of the composites. Abrasion loss is less in the case of MMT-ODA- and MMT-TMDA-filled composites than the case of control, bentonite, and EIC. This improved abrasion resistance in the modified silicate-filled composites is due to the improved rubber-filler interaction. The intercalation and exfoliation of the modified silicate increased the surface area of the filler, leading to more interaction between the filler and the matrix.

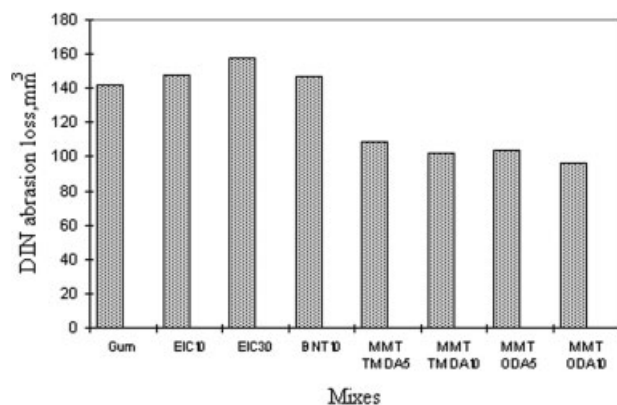


Figure 10 Variation of DIN abrasion loss with different silicate-filled natural rubber nanocomposites.

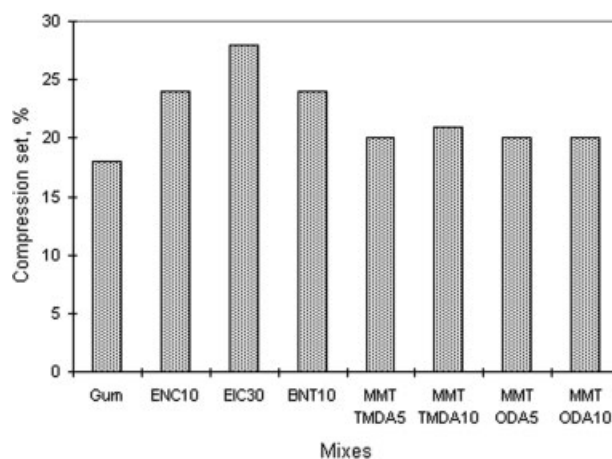


Figure 11 Variation of compression set with different silicate-filled natural rubber nanocomposites.

Figure 11 shows the compression set with silicate loading. Compression set values of the MMT-ODA- and MMT-TMDA-filled composites are found to be lower than those of the EIC- and bentonite-filled composites. The lower compression set values indicate a more restrained matrix. The higher compression set values of bentonite- and English Indian clay-filled composites may be due to the reduced elasticity of the matrix. Rebound resilience (Fig. 12) also showed the same trend as in the case of elongation. The resilience values are in the order Gum > MMT-ODA > MMT-TMDA > EIC > bentonite. It is to be noticed that the modified silicate-incorporated composites have high resilience. There is a decrease in resilience as the EIC loading is increased from 10 to 30 phr. However, in the case of the modified silicates the decrease is marginal as the loading is increased from 5 to 10 phr. Heat build-up values are given in Figure 13. Heat generation under dynamic condition is higher in EIC- and bentonite-filled composites. The modified silicate showed lower heat build up values.

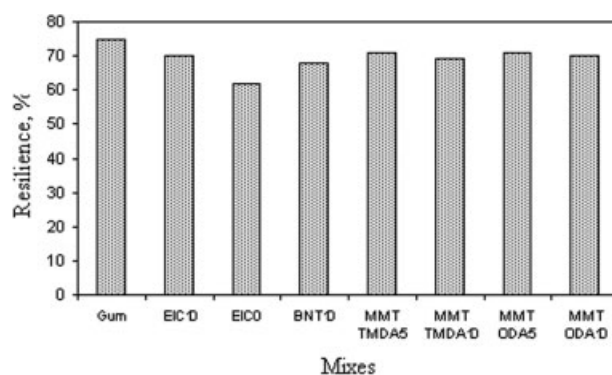


Figure 12 Variation of resilience with different silicate-filled natural rubber nanocomposites.

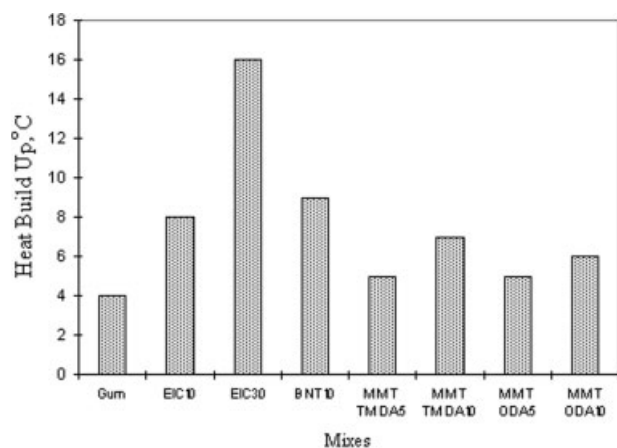


Figure 13 Variation of heat build-up with different silicate-filled natural rubber nanocomposites.

CONCLUSIONS

The addition of MMT-ODA and MMT-TMDA to natural rubber decreased the cure time and scorch time of the compounds, whereas in the case of bentonite and EIC there is not much change compared to the gum compound. High Mooney viscosity values revealed that intercalation occurred during mixing of the silicate into the rubber. Mechanical properties such as tensile strength, modulus, hardness, abrasion resistance, tear strength, etc. of natural rubber improved by the addition of organo clays, even at low loading (5–10 phr). The improvement in the mechanical properties of the organo silicates are due to the exfoliation of the silicates, which causes several fold increase in surface area.

It was also observed that some amount of the modifier in the organoclays was consumed for vulcanization, which in turn resulted in closing a part of the

interlayers. XRD and TEM studies show that organoclays are partially exfoliated, partially intercalated, and partially confined in the composites.

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