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EPOXIDISED NATURAL RUBBER LAYERED SILICATES NANOCOMPOSITES

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Polymer/layered silicate nanocomposites exhibit remarkable improvement in mechanical and barrier properties compared to their virgin polymers or microcomposites. Nanoclay being organophilic are more compatible with polar polymers. Epoxidised natural rubber (ENR), a polar form of natural rubber is expected to show high affinity and better performance with layered silicates. Epoxidised natural rubber nanocomposites were prepared by melt compounding of ENR having an epoxy content of 50 mole per cent at ambient temperature. Two grades of organically modified montmorillonite (MMT) having layer distances of 2.1 and 1.85nm were used in this study. Accelerated sulphur curing system was used for the vulcanization of the composites. For comparison, commercial clay was included in this study and the filler loading was kept at 10 phr in all mixes. The cure characteristics and mechanical properties were evaluated. The dispersion of the silicate in the matrix was studied by transmission electron microscopy (TEM). The addition of modified MMT to the ENR reduced its cure time and scorch time. The maximum torque was higher for these composites. The montmorillonite filled composites showed better mechanical properties when compared to the reference material.The enhancement in properties was believed to be due to the partial exfoliation/ intercalation of the layered silicates in ENR. Among the two types of nanoclays, the one having higher inter-layer distance showed better mechanical properties.

Keywords: Epoxidised natural rubber, Exfoliation, Intercalation, Layered silicate, Montmorillonite, Nanocomposites

INTRODUCTION

Nanocomposites are a new class of materials, which exhibit excellent barrier, mechanical, thermal, optical and physicochemical properties, compared to the corresponding microcomposites. 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 such as silica nanoparticles, they are called isodiamentional nanoparticles (Mark, 1996; Reynaud *et al.*, 1999; Von Werne *et al.*, 1999). Nanotubes or whiskers (Calvert *et al.*, 1996; Favier *et al.*, 1997; Chauzeau *et al.*, 1999) are included in the second category where two dimensions are in the nanometer scale. The third type, having only one dimension in the nanometer range is layered silicates nanocomposites. These materials are obtained by the intercalation of the polymers inside the galleries of layered silicates.

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Several reports are available regarding the processing and properties of natural rubber/ organically modified layered silicate nanocomposites (Lopez Menchado *et al.*, 2004; Varghese *et al.*, 2004). However, NR being a non-polar rubber is less compatible with polar organo-silicates. The effect of ENR as a compatibilizer in natural rubber organoclay nonocopmposites have studied extensively (Teh *et al.*, 2006; Hakim *et al.*, 2009). ENR, a polar form of rubber is expected to have high affinity and better performance with nanomaterials. The objective of the present work is to evaluate the properties of ENR nanocomposites based on organically modified silicates.

MATERIALS AND METHODS

Epoxidised natural rubber (ENR) used for the study was ENR50 having an epoxidation level of 50 mol per cent was supplied by Rubber Research Institute of Malaysia. The organoclays used were octadecylammine modified (MMT-ODA) and methyl tallow *bis*-2-hydroxyethyl quarternary ammonium (MMT-TMDA) modified monmorillonites. The layer distance of MMT-ODA and MMT-TMDA are 2.10 and 1.85 nm respectively. Commercial clay was used as the reference material. The basic properties of the silicates used are given in Table 1. All the other ingredients were supplied by Bayer (India) Ltd.

The rubber compounds were prepared on a laboratory model two-roll mixing mill (David Bridge, England) of roll size 15 x 30 cm and having a friction ratio 1:1.25, as per the formulation given in Table 2. The mixes were cured at 150 °C in an electrically heated hydraulic press to their respective cure time (t$_{90}$). The cure characteristics were measured using a moving die rheometer, Rheotech MD+ (Alpha Technologies, USA). Tensile and tear properties were determined according to ASTM standards D 412 and D 624 using 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 according to the DIN standards. Ageing studies were carried out at 100 °C for 72 h.

The dispersion of the silicates was studied by transmission electron microscope (TEM). Scanning was conducted using a LEO 912 Omega transmission electron microscope with an acceleration voltage of 120 keV. The specimens were prepared using an Ultracut E ultramicrotone. The sections of about of 100 nm were cut with a diamond knife at -120 °C. X-ray diffractograms (XRD) were obtained from Ni-filtered Cu K

Table 1. **Characteristics of the silicates**

Material	Grade/ Supplier	Characteristics
MMT-ODA	Nanomer 1.30 P, Nanocor Inc., USA	Octadecylamine (ODA) modified montmorillonite, specific gravity 1.9 g cm^{-3}, interlayer distance 2.10 nm
MMT-TMDA	Cloisite 30B, Southern ClayProducts, USA	Methyltallow bis-2-hydroxyethyl quaternary ammonium (TMDA), modified montmorillonite, specific gravity 1.5–1.7 gcm^{-3}, interlayer distance 1.85 nm
English Indian clay (Commercial clay)	English Indian Clays, Trivandrum, India	Amorphous clay

Table 2. **Formulation of the mixes**

Ingredients	phr
ENR50	100
Zinc oxide	5
Stearic acid	2
Sodium carbonate	0.3
Antioxidant HS (2,2,4-trimethyl 1,2-dihydroquinoline)	1
CBS (*N*–cyclohexyl benzothiozole-2 –sulphenamide)	1.5
Sulphur	1.5
*Filler	10

* Commercial clay (CC), MMT-ODA, MMT-TMDA

radiation (λ = 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° per min in the range, 2θ < 12°.

RESULTS AND DISCUSSION

Cure characteristics of the compounds

Table 3 shows the cure characteristics of the compounds. It was observed that addition of modified silicates (MMT-ODA and MMT-TMDA) accelerated the rate of vulcanization. This may be due to the action of modifiers present in the silicates (Mousa *et al.*, 2001; Varghese *et al.*, 2003; 2004). Consequently the scorch time and cure time are low for modified silicate incorporated compounds. The M_H-M_L value which is a measure of the modulus is comparatively high for the modified silicates filled composites.

Dispersion of the silicates

Fig. 1 shows the XRD diffractograms of the NR composites containing MMT-ODA and MMT-TMDA. MMT-ODA and MMT-TMDA filled composites showed a shoulder at lower diffraction values. This might be due to the intercalation of NR chains into 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 towards lower 2θ values

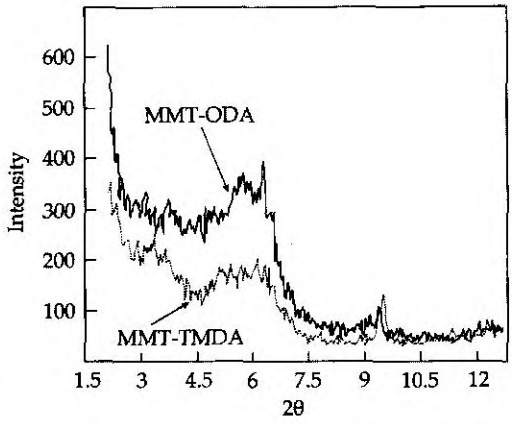
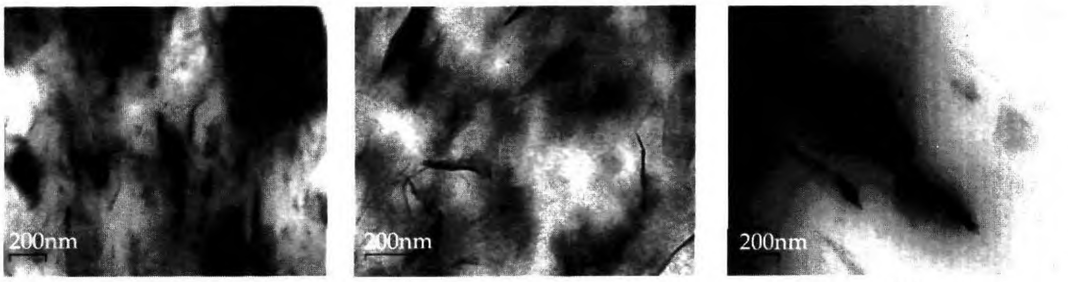


Fig. 1. XRD spectra of MMT-ODA and MMT-TMDA

Table 3. **Cure characteristics of the compounds**

Parameters	Gum	CC	MMT-TMDA	MMT-ODA
Maximum torque, M_H (dNm)	7.0	7.9	8.30	8.52
Minimum torque, M_L (dNm)	0.33	0.30	0.47	0.41
Optimum cure time, t_{90} (min)	8.01	6.7	3.37	3.01
Scorch time, t_{s2} (min)	3.42	3.44	2.23	2.11
M_H - M_L dNm	6.67	7.6	7.83	8.11



MMT-TMDA MMT-ODA CC

Fig. 2. TEM pictures of the composites

in the XRD spectrum. Fig. 2 shows the TEM micrographs obtained for the ENR composites containing MMT-ODA and MMT-TMDA and commercial clay. The TEM photographs of MMT-ODA showed an exfoliated structure compared to the MMT-TMDA incorporated vulcanizates.

Mechanical properties

Mechanical properties of the different silicate filled composites are given in Table 4. Tensile strength follows the order MMT-ODA > MMT-TMDA > commercial clay > gum. Due to the initial high interlayer distance intercalation process is fast and the degree of exfoliation is high in MMT-ODA compared to MMT-TMDA. Exfoliation causes significant increase in surface area. MMT-ODA incorporated composites also recorded high tensile strength and modulus for 100 and 300 per cent elongation.

The hardness values of the MMT-ODA incorporated composites showed higher values because of exfoliated silicate layers.

Table 4. **Mechanical properties of the composites**

Parameters	Gum	CC	MMT-TMDA	MMT-ODA
Tensile strength, MPa	20.6	20.8	22.3	24.7
100% Modulus, MPa	0.9	1.2	1.6	1.8
300% Modulus, MPa	1.7	2	3.8	4.5
Elongation at break, %	658	656	656	646
Tear strength, N/mm	29.8	31.0	35.2	38.9
Hardness, Shore A	42	46	54	56
DIN abrasion loss, mm^3	162	160	110	103
Compression set, %	21	26	22	22
Resilience, %	78.3	75.7	68.8	67.3
Heat build up, "T °C	6	12	16	16

Table 5. **Retension (%) of mechanical properties after ageing at 100 °C for 72 h.**

Parameters	Gum	CC	MMT-TMDA	MMT-ODA
Tensile strength	20	10	30	41
100 % Modulus, MPa	-	31.4	40.0	46.2
300 % Modulus, MPa	-	-	-	45.1
Elongation at break, %	37	37	41	52

Hardness and modulus of the commercial clay filled composite showed lower values than the modified silicate. This may be due to the larger particle size and low level of dispersion of commercial clay in ENR.

MMT-ODA filled composites showed the lowest elongation at break whereas the gum sample, commercial clay and MMT-TMDA composites showed comparatively high elongation at break. The values of tear strength, a useful tool for characterizing nanocomposites, were highest for MMT-ODA and MMT-TMDA filled composites. It can be seen that commercial clay has little effect on tear strength properties. DIN abrasion loss is less in the case of MMT-ODA and MMT-TMDA filled composites than the control and commercial clay. This improved abrasion resistance in the modified silicate filled composites is due to the improved rubber-filler interaction generated *via* intercalation/exfoliation. The intercalation and exfoliation of the modified silicate increased the surface area of the filler leading to more interaction between the filler and the rubber matrix.

Compression set values of the MMT-ODA and MMT-TMDA filled composites are lower compared to commercial clay filled composite. The higher compression set values of commercial clay filled composites may be due to the less elastic nature of the matrix. Rebound resilience also showed the same trend as in the case of elongation. The resilience values are in the order gum > commercial clay > MMT-TMDA > MMT-ODA. Heat generation under dynamic condition is higher in MMT-ODA and MMT-TMDA filled composites compared to gum and commercial clay filled composites. This may be due the increased polymer filler interaction. Ageing properties of the composites are given in Table 5. The MMT-ODA filled composites showed superior ageing resistance compared to the MMT-TMDA and commercial clay filled composites.

CONCLUSIONS

The addition of MMT-ODA and MMT-TMDA to ENR decreased the cure time and scorch time of the compounds. Mechanical properties such as tensile strength, modulus, hardness, abrasion resistance, tear strength etc. of ENR were improved by the addition of modified layered silicate. The improvement in the mechanical properties of the modified silicates incorporated ENR is due to the exfoliation of the silicates which causes several fold increase in surface area of the filler. The TEM studies showed that modified layered silicates are partially exfoliated and partially intercalated in the composites. The ageing resistance of ENR is also found to be improved by the addition of MMT-ODA.

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