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Natural rubber / OMMT nanocomposites for reinforcement in tyre ply

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Abstract

Natural rubber/OMMT nanocomposites of varying filler loading were prepared by melt mixing method. Different phr of organically modified montmorilonite (OMMT) nano clay was incorporated into the natural rubber (NR) using lab scale banbury mixer and two roll mixing mill. In this study carbon black - N220 dosage kept constant; 47 phr and the effect of OMMT content on the rheological, mechanical, thermal and morphological properties of NR nanocomposites were investigated. Nanocomposite filled with 7 phr OMMT has the best thermal and mechanical stability. Compared to the control composite, OMMT incorporated nanocomposites showed higher aged physical retention properties. Intercalated structure in NR-OMMT nanocomposites was confirmed by small angle XRD analysis and scanning electron microscopy (SEM) analysis. Improvement in storage modulus with the addition of OMMT in NR nanocomposites was observed by DMA analysis. The results obtained for diverse properties (rheological, mechanical, and thermal) in conjunction with tyre ply compound applications indicate that NR-OMMT nanocomposites can be used as a suitable candidate for tyre and conveyor belt applications

Keywords: natural rubber; OMMT; nano clay; nanocomposites

1. INTRODUCTION

The development of rubber nanocomposites is an emerging area in advanced research due to their excellent mechanical and thermal properties. The reduced size and hence increased surface area and enhanced interfacial adhesion between nano particles and the matrix distinguish it from conventional composites, where filler particles are in micron size. Such improved properties make nanocomposites attractive in various applications such as automotive, construction, medical, packaging, agricultural and space industries.

Over the past decades, nanoclay has been used as a potential reinforcing agent for various elastomers. The nanoclay offers a wide array of property improvements at very low filler loadings, owing to the dispersion of a few nanometer thick clay platelets of high aspect ratio [1-5]. On the other hand, much effort has not been focused to understand the effect of nanoclays on the adhesion behaviour of elastomers. There are only few reports in the literature that examine the effect of OMMT based nano clay on the adhesion behaviour of acrylic elastomer [6-7]. Very recently, Want et.al have studied the effect of laponite nano clay on the tack of acrylic based pressure sensitive adhesive [8]. Most of the early efforts have been focused to understand the influence of these nano clays on mechanical, thermal and physical properties of various polymers [9-12].

From the studies conducted, it is clear that nano fillers exhibit excellent improvement in the mechanical and thermal stability of the polymer nanocomposites [8-14]. In order to achieve desired dispersion of nano fillers, there are various methods for obtaining elastomer nanocomposites such as, solution mixing, melt mixing [13-15] and latex compounding [16-19]. Out of these, melt mixing is the most widely used due to its simplicity and industrial acceptability.

The main objective of the present work is to study the effect of OMMT on the mechanical, thermal and rheological properties of carbon black (CB) incorporated natural rubber (NR) nanocomposites (NC) and its application in calendaring reinforcement process in tyre industry to enhance functional properties of calendered fabric. During the extended period of time, that is the tyre service life, the physical properties like elongation, tensile strength etc of the rubber undergoes significant changes due ozone, temperature, humidity and other environmental factors. Hence better aged retention properties are necessary for a good tyre compound. With regard to this, the effect of OMMT on retention properties of the natural rubber – OMMT nanocomposites were also studied.

2. EXPERIMENTAL PROCEDURES

Materials

All the ingredients used for the preparation of NR-OMMT nanocomposites are commercially available and were used as such without further treatment. Natural rubber (RSS IV) was purchased from Rubber board, Kerala. OMMT (Cloisite® 20A) was obtained from BYK additives and instruments. Carbon black (N – 220, ISAF) was purchased from Hi -tech carbon Gumidipundi, Chennai. DCBS (N,N-Dicyclohexyl-2-

Benzothiazole sulfenamide) was obtained from Lanxess. TMQ (2,2,4-trimethyl-1,2-dihydroquinoline) and 6PPD (N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine) were purchased from Nocil Limited Mumbai. Zinc oxide (ZnO) was purchased from the Standard chemical Co. Pvt ltd, Chennai. Cobalt stearate purchased from Sigma-Aldrich was used as adhesion promoter and insoluble sulphur purchased from OCCL, India as curative.

Preparation of nanocomposites

The OMMT was mixed with natural rubber under controlled condition in a lab scale Banbury mixer [11] with rotor speed of 50 rpm and a laboratory two roll mill. Fill factor of the mixer was 0.800. The calculated maximum volume was found to be 2200 cc and optimum volume for a good dispersed mixing was 1760 cc. The nanocomposites were prepared with 0, 5, 7 & 10 phr OMMT. . The composition of NR-OMMT nanocomposites are tabulated in Table 1.

Table 1 Composition of NR-OMMT nanocomposites

Composition	Formulation			
	OMMT-0	OMMT-5	OMMT-7	OMMT-10
RSS – IV(Dirt free)	100.00	100.00	100.00	100.00
N220 ISAF CB	47.00	47.00	47.00	47.00
OMMT-NANOCLAY	0.00	5.00	7.00	10.00
DCBS accelerator	1.00	1.00	1.00	1.00
TMQ	2.00	2.00	2.00	2.00
Zinc oxide	8.00	8.00	8.00	8.00
6PPD	1.00	1.00	1.00	1.00
Cobalt stearate	2.00	2.00	2.00	2.00
Sulphur	4.40	4.40	4.40	4.40

The mixing was conducted in two stages and 8 h maturation time was given in between the first and second stages for getting good homogenisation. NR and the other required chemicals were weighed as per the formulation and added in the following sequence in first stage; NR, ZnO, OMMT, TMQ, 6PPD and carbon black N220. The dump temperature was set as 140°C. In the second stage, sulphur and accelerator were added in to the master batch prepared in the first stage and the dump temperature of final compound was kept 110 C.

The mixed compound was again masticated in two roll mill for getting a good dispersion of fillers in the mix. The mixed compound rolled through a laboratory two roll mill to achieve 7.2 mm thickness and stored for 24 h at room temperature. The optimum cure times for the composites were determined by Moving Die Rheometer (MDR 2000 Alpha Technologies USA). The vulcanization of the rubber compound was carried out in a hydraulically operated press at 150°C for 15 minutes (Moor press UK). The vulcanized samples were kept in an air-circulating oven at 100°C for 48 h for the aging test.

Characterisation
Rubber properties such as compound mooney viscosity as per ASTM D 1646 and cure characteristics as per ASTM D7271 were studied for the green compound to determine the cure indices. Mechanical properties of the prepared NR-OMMT nanocomposites such as hardness as per ASTM D 2240, tear strength as per ASTM D624, tensile strength and percentage elongation at break as per ASTM D-412 were investigated. The dynamic mechanical analysis was conducted using parallelepiped samples with dimensions 20 x 6 x 2 mm in a DMA machine, METRAVIB, France, model VA 4000. Thermo gravimetric analysis (TGA) was conducted to study the thermal stability of the NR-OMMT nanocomposites. X-ray diffraction patterns of nanocomposites were obtained by using a PANalytical XPET PRO diffractometer system equipped with a Goniometer PW3050/60 θ-θ. A high resolution scanning electron microscope (HRSEM – FEI Quanta FEG 200) was used to examine the morphology of the fractured surface of the nanocomposite.

3. RESULT AND DISCUSSIONS

Rheological Properties
The effect of OMMT content on the prevulcanizate properties such as mooney viscosity and the vulcanisation characteristics such as torque, T_{s2} and T_{90} are illustrated in Figure 1 – 4 respectively..
Mooney viscosity was found to be increased with respect to the increasing content of OMMT. This provides good green strength to the compound and hence reducing the distortion of the calendaring fabrics. Maximum torque observed in the nanocomposites was increased with increasing OMMT content. The increase in maximum torque indicates the better dispersion of nano clay and hence reinforcement in the natural rubber composites. The high torque values in the NR-OMMT nanocomposites are directly related to the optimum cure time of the compound.

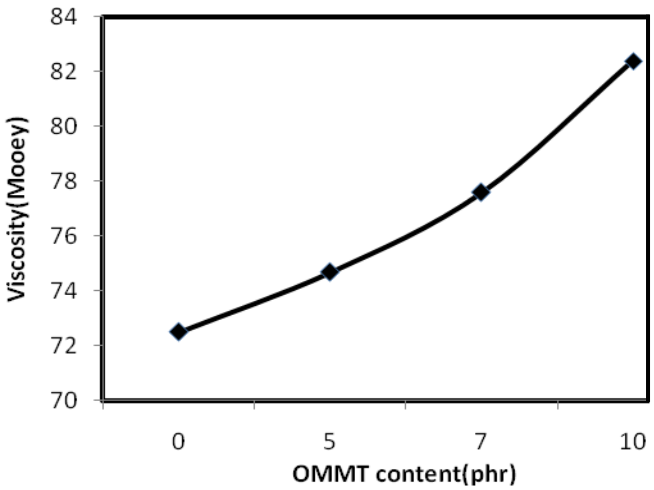

Figure 1 Effect of OMMT content on mooney viscosity

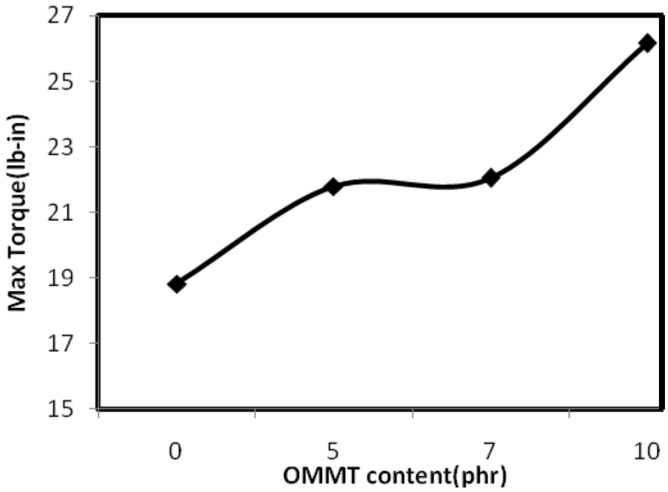

Figure 2 Effect of OMMT content on maximum torque

As shown in Figure 3, the time required for the premature vulcanisation (Ts2) is very less in higher phr OMMT filled compounds. The reduction in scorch time and increase in cure rate with increasing amount of OMMT are significant because of the presence of quaternary alkyl ammonium ion present in OMMT. Benzothiasolaccelerator which combines with amine produce benzothiazyl anions, which accelerates cleavage rate of cyclic sulphur [20] ultimately results in faster curing of rubber. The nanocomposite with 5 phr OMMT shows increasing trend in torque indicating the better dispersion of OMMT in rubber matrix. The presence of OMMT in the nanocompistes act as a cure promoting agent. On contrary, with very high doses of OMMT the maximum torque shows lower value because of the formation of some inter filler networks, including “Nano-units” and “haloing effect”[8]. Optimum cure was found to be stable and not very much affected with increase in the OMMT content in NR.

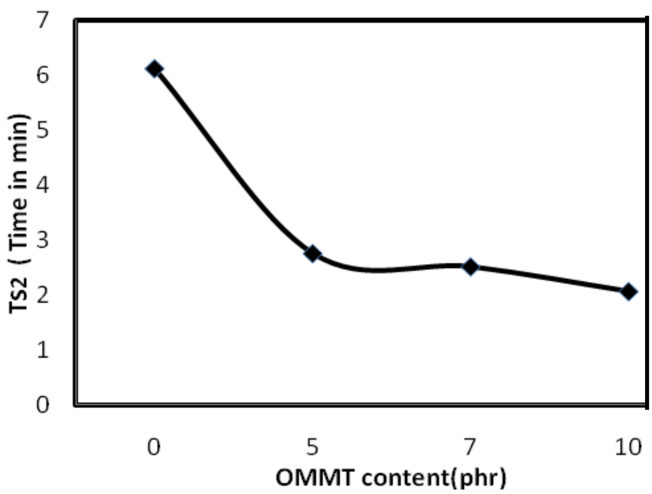

Figure 3 Effect of OMMT content on scorch time (T_{s2})

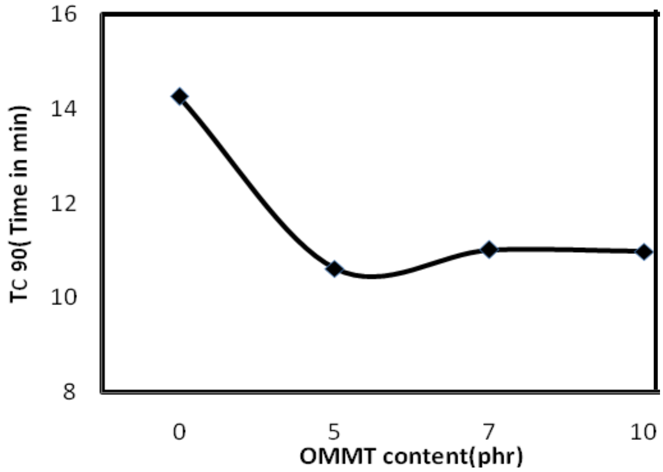

Figure 4 Effect of OMMT loading on Optimum Cure time (T_{c90})

Small angle X-ray diffraction

The X-ray diffraction analysis is often used to identify the degree of the polymer and partial exfoliation of the clay layers leads to an increase of the interlayer spacing and decrease in the degree of ordering of silicate layers. XRD pattern of OMMT and the nanocomposites in the range of 1.5-12° are shown in Figure 5. The broad peak of OMMT between 2 and 4 degree has been disappeared in the case of 5, 7 and 10 phr OMMT filled nanocomposites, which confirms the penetration of rubber chains in between the silicate layers.

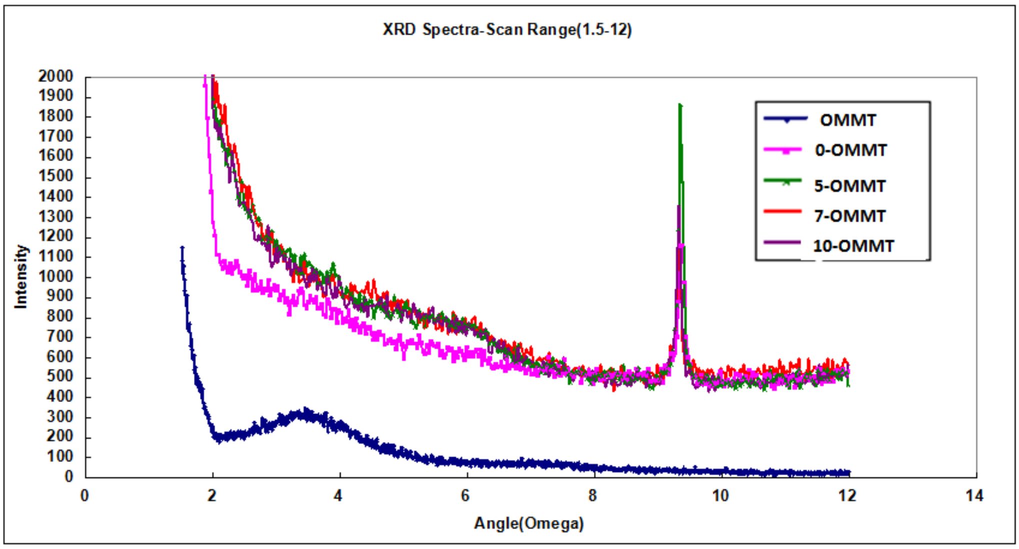

Figure 5 X-ray diffraction patterns of OMMT and NR- OMMT nanocomposites

Mechanical Properties

The effect of OMMT content on the mechanical properties such as tensile strength and elongation at break of natural rubber based nanocomposites was analysed and the results are presented in Figure 6 and 7 respectively. Carbon black is well known reinforcing filler for NR due to the presence of strong filler rubber interactions. Tensile strength of NR-OMMT nanocomposites was found to be increased to 81% by the addition of 7 phr of OMMT. Percentage elongation at break was found to be increased up to 69% at loading of 7 phr OMMT. The values for tensile strength and percentage elongation were decreased as the level of OMMT content increased beyond 7 phr. This may be because of the more filler - filler interaction and "Haloing effect" [8, 13, 14, 20]. The effect of OMMT content on hardness of NR-nanocomposites is shown in Figure 8. With increasing OMMT content, the usual trend of increasing hardness has been noticed.

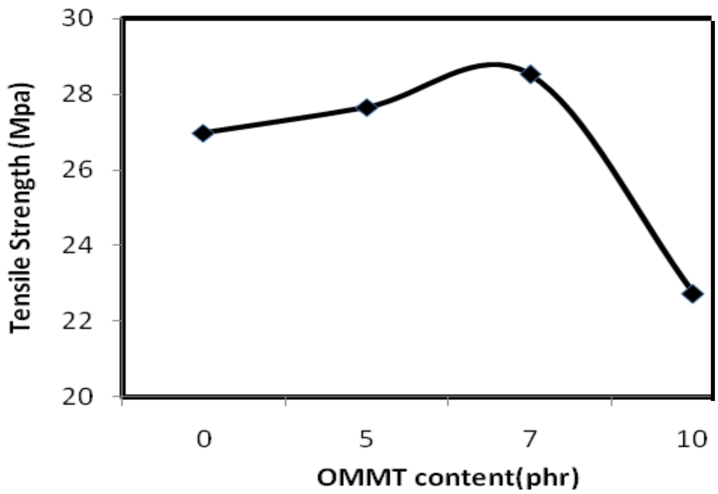

Figure 6 Effect of OMMT content on tensile strength of NR nanocomposites.

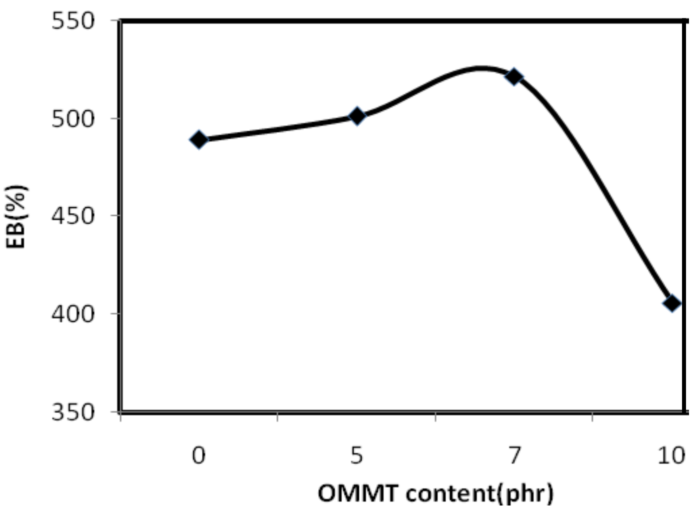

Figure 7 Effect of OMMT content on % elongation at break of NR nanocomposite

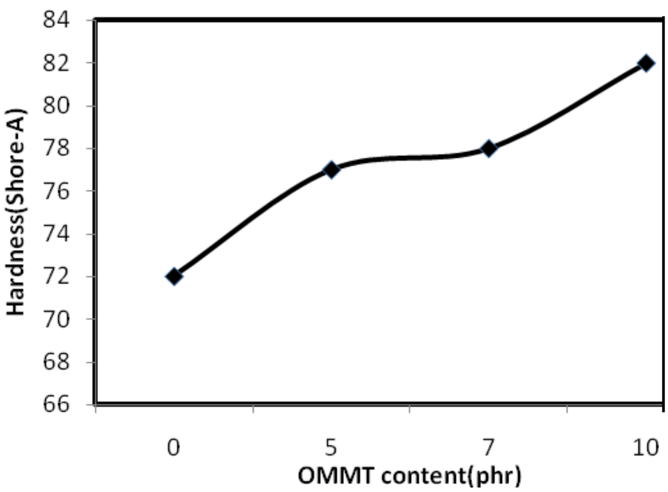

Figure 8 Effect of OMMT content on hardness of NR-nanocomposites.

Aged retention properties

Retention properties are very important for tyres, especially in radial tyres. Compared to bias tyres, life cycle of radial tyres are high and they need to with stand more flex cycles. Aged retention properties of the control compound and the prepared nano composites were studied for evaluating the performance as ply and the results are shown in Figure 9. Compared to the control sample, up to 76% aged retention properties were observed in NR-OMMT nanocomposites.

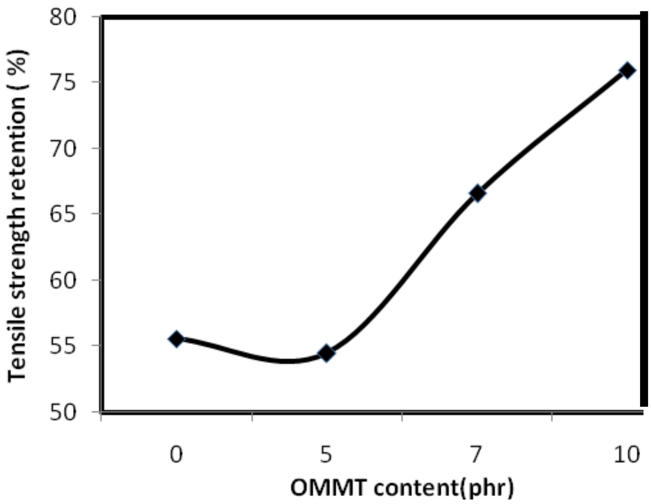

Figure 9 Effect of OMMT content on aged retention properties of nanocomposites.

Dynamic Mechanical Analysis

The dynamic mechanical analysis of the prepared NR – OMMT nanocomposites was conducted in tension mode and temperature sweep at laboratory atmosphere 23°C ±2°C. In temperature sweep, temperature varying from -100°C to 90°C at measuring frequency 10 Hz. The change in storage modulus (E') and loss modulus (E'') observed are presented in Figure 10 and 11 respectively. These results are clearly indicating the dispersion on OMMT in the rubber matrix. Temperature sweep results denote the reinforcing capability of OMMT and it is linear to the addition of OMMT. The results observed are given in Table 2.

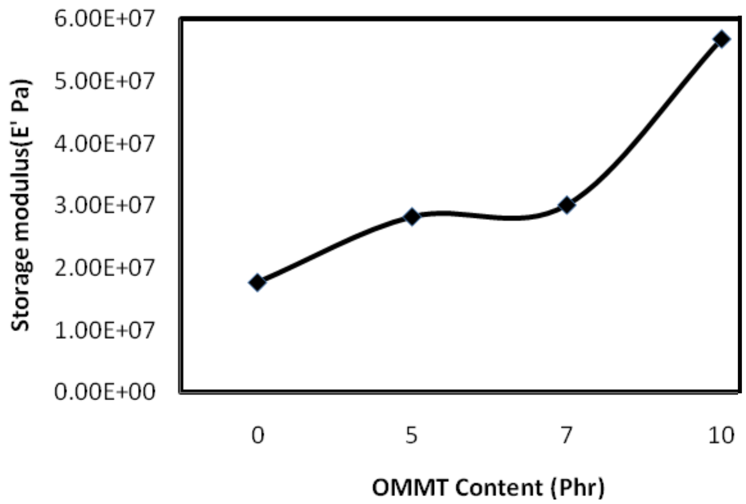

Figure 10 Effect of OMMT content on storage modulus (E') of NR nanocomposites

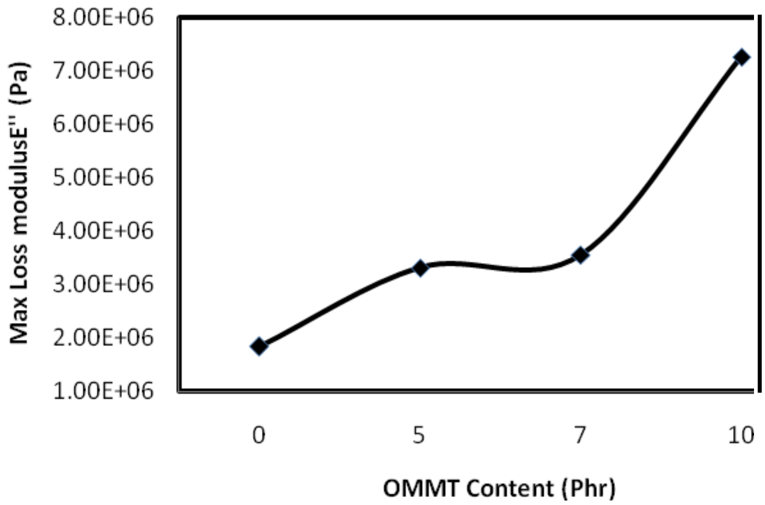

Figure 11 Effect of OMMT content on loss modulus (E'') of NR nanocomposites

The storage modulus of the nanocomposites was found to be increased with increase in OMMT content. OMMT clay induces a strong and more developed filler network, which sustains under repeated dynamic strain [14].

Table 2 Temperature sweep results of NR-OMMT nanocomposite

Sample ID	Tg	Tan δ from Tg curve	Tan δ at 0°C	Tan δ at 60°C
OMMT-0	-46.8 °C	0.748	0.1537	0.1076
OMMT-5	-42.35°C	0.612	0.1974	0.1135
OMMT-7	-45.3°C	0.599	0.1411	0.1214
OMMT-10	-45.45°C	0.506	0.1427	0.1441

At zero degree, higher tan δ is better for the tyre application and the nanocomposite with 5 phr OMMT showed better result. In 60°C, lower tan δ value is better for tyre tread components. Since the modulus of steel is higher than the rubber and for matching with the stiffness of both skim and steel, slightly higher tan δ value is better for steel ply skim.

Scanning electron microscopy

Scanning electron microscopy (SEM) analysis was done for ensuring the quality of dispersion of OMMT nano filler in the matrix. Rheological, mechanical and thermal studies showed 7 phr based NR nanocomposite is the best candidate. Hence NR-OMMT – 7 phr nanocomposite was subjected to SEM analysis and the respective micrographs observed are shown in Figure 12 and Figure 13. The SEM micrographs clearly showed an intercalated structure, homogeneously dispersed into the rubber matrix.

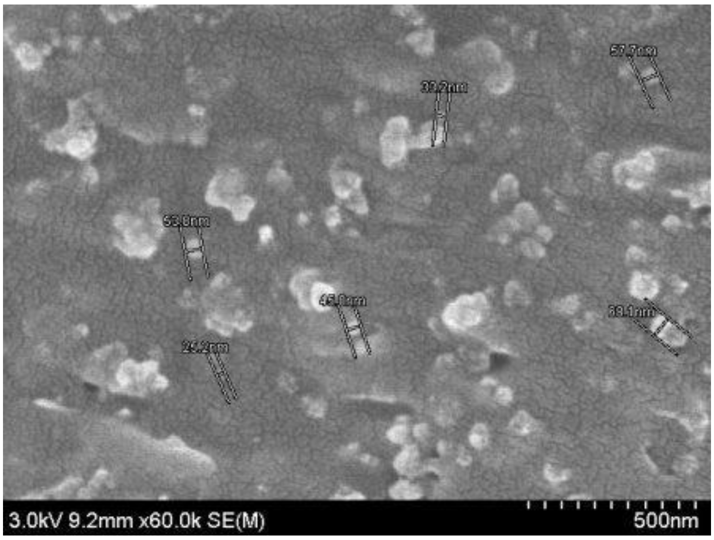

Figure 12 SEM micrograph of 7phr OMMT –NR NC

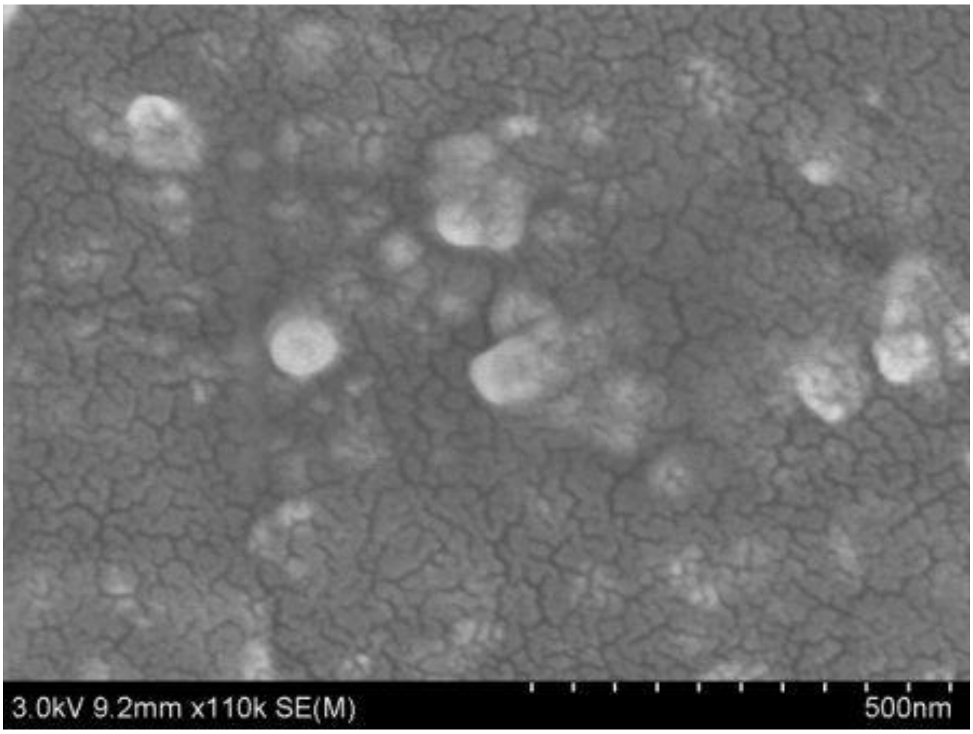

Figure 13 SEM micrograph of NR - OMMT-7 phr nanocomposite

Thermal analysis (TGA)

In this study, TGA analysis was carried out in an effort to investigate the thermal stability of NR - OMMT nanocomposites. The addition of OMMT in NR shows insignificant difference in the decomposition temperatures up to the temperatures at which 50% of mass loss occurs. TGA curves in Figure 14 showed that thermal stability of nanocomposites increased with increase in filler loading. This trend was valid up to 7 phr OMMT [16]. The temperature corresponding to 50% weight loss was shifted towards a higher level with increase in the filler content up to 7 phr as shown in Table 3. It indicates that, the thermal degradation of NR-OMMT nanocomposites occurred at higher temperatures with the incorporation of these nanoparticles. Compared to 7 phr OMMT filled compound, the decomposition temperature of 10 phr OMMT was found to be lower, may be because of the filler agglomeration formed; but the its higher value than that of compound with 0 phr OMMT confirmed its improved thermal stability .

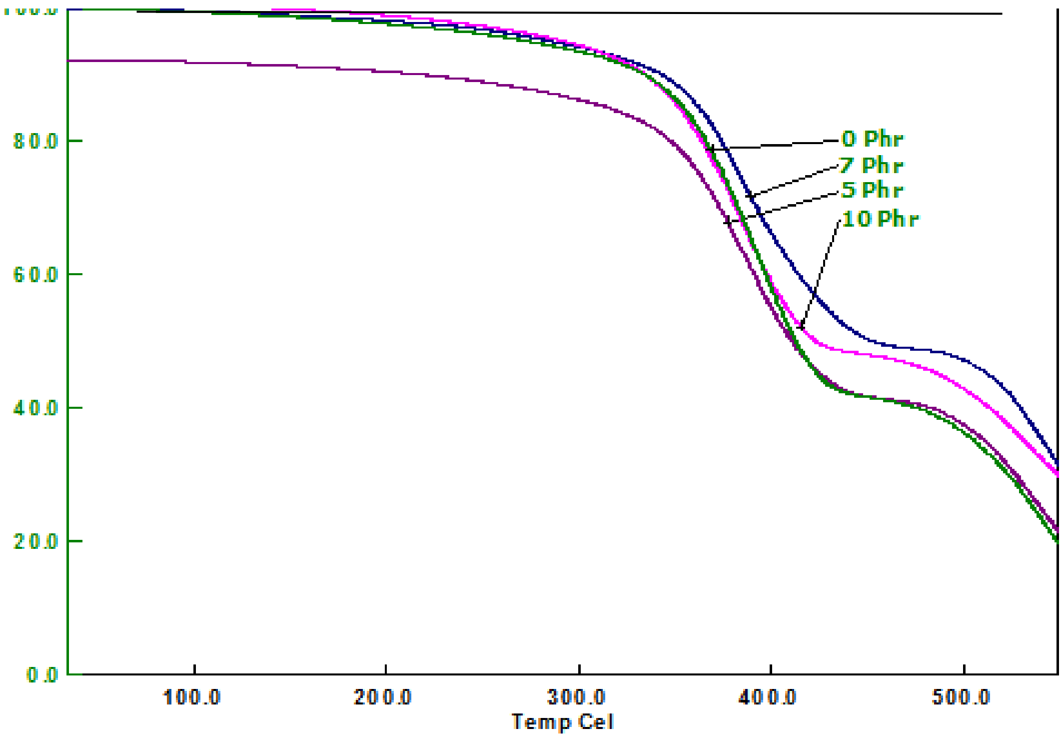

Figure 13 TGA curves of NR- OMMT nanocomposites

Table 3 50% decomposition temperature of NR-CB-OMMT nanocomposite

Composition	OMMT-0	OMMT-5	OMMT-7	OMMT-10
50% decomposition temperature (°C)	413.4	411.5	454.1	423.6

CONCLUSION

The mechanical properties of the NR-OMMT nanocomposites showed significant improvement in tensile strength and elongation at break up to 7 phr loading of the filler. Improvement in thermal stability with the addition of OMMT reveals that, OMMT is a good competitor for silica to improve the properties of the calendared skim compounds for making tyres. DMA results of NR-OMMT nanocomposites showed increase in the storage and loss modulus. SEM image of OMMT-7 showed the homogeneous dispersion of the filler in NR matrix.

The experimental results showed that, NR-OMMT nanocomposite could be a better candidate for tyre and conveyor belt applications due its enhanced rheological, mechanical and thermal characteristics. Better aged retention properties proving the suitability of OMMT in tyre industry.

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