International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 03, March-2016

Studies on Halloysite Nanotubes(HNT) Natural Rubber Nanocomposites for Mechanical Thermal and Wear Properties

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***Abstract*—Natural rubber nanocomposites have been prepared by incorporating various content (phr) of Halloysite Nanotubes (HNT), a kind of aluminosilicate clay onto natural rubber using banbury & two roll mill. Effect of addition of HNT content on rheological, mechanical and morphological properties of the NR-HNT nanocomposites was studied. Rheological properties include mooney viscosity, mooney scorch, cure index. Mechanical properties studied are tensile strength, elongation at break and hardness. Thermal stability was checked by TGA for analyzing the effect of nanofiller loading to rubber matrix. Wear characteristics was also studied with the help of Din abrader. XRD & SEM analysis indicate good dispersion of the HNT filler into NR. The results obtained for various properties indicate that the NR-HNT nanocomposites have improved wear, mechanical, thermal and morphological properties.**

Keywords—Natural Rubber; HNT; Nanocomposites

I. INTRODUCTION

Polymer nanocomposites are polymers that have been reinforced with small quantities (less than10%) of nanosized filler particles. Several advantages of these nanocomposites have been identified. These include efficient reinforcement with minimal loss of ductility and impact strength, heat stability, flame retardance, improved abrasion resistance, reduced shrinkage and residual stress and altered electronic and optical properties (1-6). Elastomer nanocomposites have been found to be promising materials for excellent mechanical and wear resistance due to their advantages over traditional materials such as carbon black and silica.

The literature survey indicates that the addition of fillers imparts enhanced performance in polymeric materials.(7) Conventional Fillers such as carbon black , conventional grade silica, were used in the preparation of elastomer based compounds in tyre. It is also noted that the addition of silane coupling agent can improve the performance of elastomer filled with silica(3).

From the studies conducted it is clear that nanofillers exhibit excellent improvement in the mechanical and thermal stability of the polymer nanocomposites.(1) Most of the research work on elastomers based nanocomposites reveal the use of carbon nanotubes and organoclay based nano fillers(8,9). Halloysite ($Al_2Si_2O_5(OH)_4.2H_20$), is a naturally occurring aluminosilicate nanotube. Naturally formed in the Earth over millions of years, halloysite natural tubules are unique and versatile materials that are formed by surface weathering of aluminosilicate minerals and comprise aluminum, silicon, hydrogen and oxygen(11-14). Halloysite is a member of the Kaolin group of clays. Halloysite natural tubules are ultra-tiny hollow tubes with diameters typically smaller than one tenth of a micron (100 billionths of a meter), with lengths typically ranging from about half of a micron to over 5 microns (millionths of a meter). Due to its high aspect ratio (L/D), it gives a large amount of filler–polymer interactions compared to other nanofillers(15).

HNTs when incorporated can give tremendous applications in various polymers as shown in a review article (11) and Sandip Rooj et al (3) have reported the work on HNT with NR at 10% loading and their properties . Halloysite Nanotubes (HNT) are least studied for elastomer based nanocomposites and hence this paper presents the effect of HNT at different loading level in natural rubber on various properties.

II. EXPERIMENTAL PROCEDURE

2.1 Materials

All the materials used in this study were purchased and used as such without further treatment. Natural rubber , RSS-3, TSR-10 was purchased from Namazie International Malaysia and Halloysite nano tubes(HNT) was bought from Natural Nano Inc. Rochester, Newyork having ultra-tiny hollow tubes with diameters typically smaller than 100 nanometers, with lengths typically ranging from about 500 nanometers to over 1.2 microns. In addition to this N-330 high abrasion furnace carbon black, TMQ (2,2,4-trimethyl-1,2dihydroquinoline) and TBBS (N-tert-Butyl-2-Benzothiazole sulfenamide), stearic acid and Zinc oxide as activators, 6-PPD (N(1,3-dimethyl-butyl)-N'-phenyl paraphenyline diamine) as antioxidant, soluble sulphur as curative, retarder-PVI(N-(cyclo hexyl thio) phthalimide) and anti ozonant wax were purchased and used in the rubber formulation.

2.2 Preparation of Nanocomposites

The HNT at varying concentrations 2, 4 & 6 parts per hundred parts of rubber (phr) was mixed with natural rubber under controlled condition in a lab scale Banbury mixer with rotor speed 50 rpm. (Make: Fam India Pvt Ltd) with fill factor of the mixer 0.8. Calculated maximum volume was found to be 2200cc and optimum for a good dispersed mixing is 1760cc. and the compounding was done with a laboratory two roll mill (Santosh Industries, India) cooled with cold water circulation. After mixing, the compound was passed through a tight nip (<1 mm) of the cold two roll mill to achieve a sheet of about 6 mm thickness and stored for 24 h. for making the sheet.

Experiments were conducted for preparing NR / HNT mixing formulation with various additives using the following three stages .

Stage 1:Natural rubber+ZnO+Stearic acid+HNT+6PPD+TMQ

Stage2: Stage 1masterbatch+Carbon black N330

Stage3: Stage 2 masterbatch+Sulphur+DCBS+ Retarder.

The mixed dough again was milled for getting a good dispersion of fillers in the mix and the sheet kept 24Hrs for the maturation. The optimum cure time for the composites was determined by Moving Die Rheometer (MDR 2000 Alpha Technologies USA) at 160°C 30 minutes.

The vulcanization of the rubber compound was carried out in a hydraulically operated press (Moor press UK) at 150°C for 10 minutes. The vulcanized samples were aged at 100°C for 48hrs in an air-circulating oven. Test specimens were punched out from the compression mould. The nanocomposites prepared with various compositions (Table 1) were tested for various properties.

Table 1. Composition of NR-HNT Nanocomposites

Material	Composite Composition, in phr			
	Control	2HNT	4HNT	6HNT
Natural Rubber	100	100	100	100
N330 HAF Carbon Black	45	35	35	35
Sulphur	1.40	1.40	1.40	1.40
Stearic Acid	2.00	2.00	2.00	2.00
TMQ	1.00	1.00	1.00	1.00
Zinc Oxide	4.50	4.50	4.50	4.50
TBBS	1.30	1.30	1.30	1.30
HNT	0.00	2.00	4.00	6.00

2.3 Characterization

Prevulcanizate properties such as Mooney viscosity as per ASTM D1646 and rheological properties as per ASTM D7271 are studied. After curing properties such as Hardness as per ASTM D2240, Tensile strength and percentage elongation at break of the nanocomposites as per ASTM D-412 were tested. Dynamic mechanical analysis with DMA machine (VA 4000 METRAVIB, France) was carried out as per ASTM D-7028. Thermo gravimetric analysis was carried out using a Sii TG-DTA 6500 thermal analyzer,Japan in a dry nitrogen atmosphere at a heating rate of 20 °C / min for determining the thermal stability of the NR-HNT nano composites. The abrasion testing was done by DIN abrasion tester-6012(Zwick Gmbh & Co, Germany) as per ISO4649 method. XRD and SEM studies were carried out using Rigaku Miniflex CN 2005 X-ray diffractometer equipped with CuKa radiator (30 kV, 10 mA, Rigaku Corporation, Tokyo, Japan) and FEI Quanta FEG 200-High Resolution Scanning Electron Microscope (SEM) respectively.

III.RESULTS AND DISCUSSION

3.1 Rheological Properties

The effect of HNT content on the pre-vulcanizate properties such as Viscosity, Cure indices are illustrated in Fig 1 to Fig 3

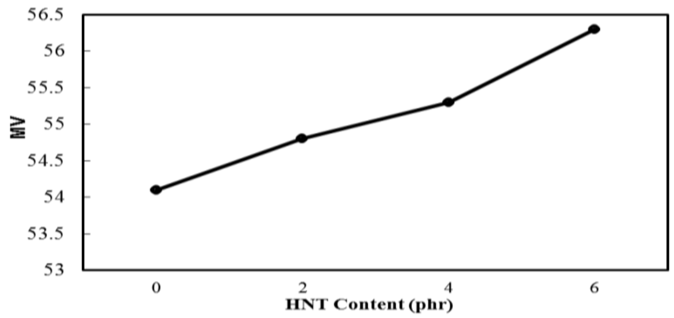

Fig.1 Effect of HNT content on viscosity (Mv) of NR nanocomposites

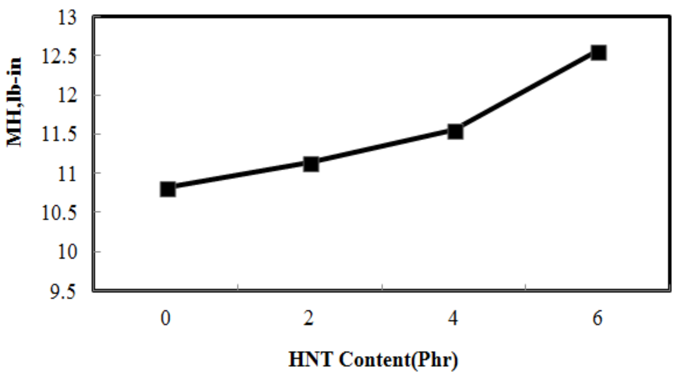

Fig.2 Effect of HNT content on Maximum torque(MH) of natural rubber nanocomposites

International Journal of Engineering Research & Technology (IJERT)
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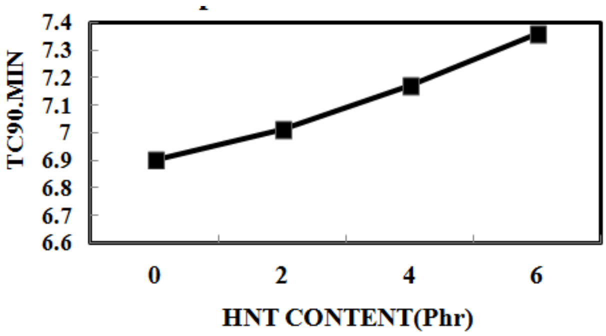

Fig.3 Optimum Cure time(TC90)

Mooney viscosity(MV) tested at 135°C fir 2.5min as in Fig.1 is found to increase with the increase in content of HNT and this will provide good green strength to the compound for better processability. Maximum torque MH (Fig.2) increases with the increase in HNT content compared to the control compound and this provides the stability of the tyre component in extrusion process. Optimum cure time (Fig 3) at is found to increase marginally with HNT content . Thus, in all the composites of NR the normal cure cycle of 10min @ 150˚C was followed.

3.2 Mechanical Properties

The effect of HNT content on the mechanical properties of NR - HNT nanocomposites was analysed (Fig 4 and 5). From the Fig. 4 and 5, the maximum value of tensile strength and percentage elongation was observed for the NR-nanocomposite containing HNT loading of 4 phr. Tensile strength of natural rubber HNT nanocomposites was found to increase by 20% for the addition of 4 phr of HNT. Percentage elongation at break was found to increase up to 34% at loading of 4 phr HNT. The values for tensile strength and percentage elongation decreased as the level of HNT content increased beyond 4phr.

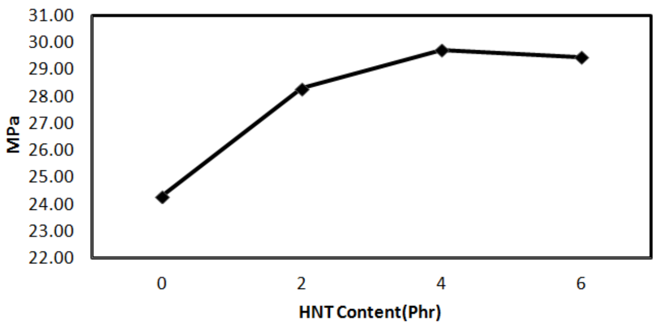

Fig.4 Effect of HNT content on Tensile strength of natural rubber nanocomposites.

Hardness of NR-HNT nanocomposites were plotted in Fig.6 which also reveals the increasing trend in the hardness values with HNT content.

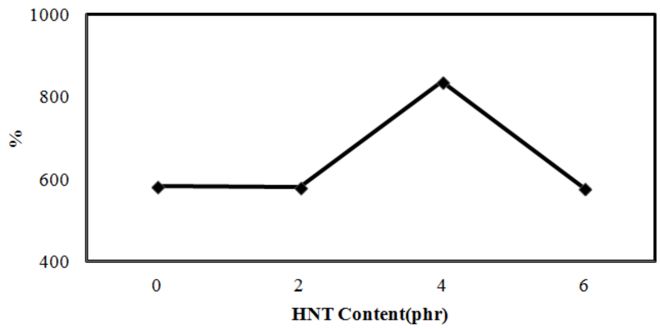

Fig.5 Effect of HNT content on % elongation at break of natural rubber nanocomposites

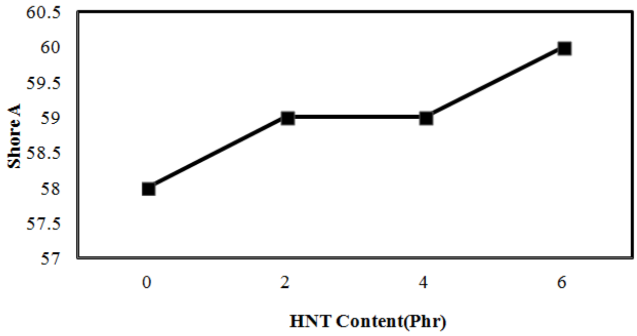

Fig.6 Effect of HNT content on Hardness of natural rubber nanocomposites

3.3. Dynamic mechanical analysis

The dynamic mechanical thermal analysis was conducted using parallelepiped samples with dimensions 25 x 310 x 32 mm in a DMA machine (VA 4000 METRAVIB, France) being operated in the tension mode. The dynamic temperature sweep tests were conducted within a temperature range of -30°C to 70°C at a heating rate of 28°C /min keeping fixed frequency as 10 Hz and strain at 0.25%.

In the dynamic mechanical analysis the NR-HNT nanocomposites show higher storage modulii than the regular composition. Figure.7 and 8 shows the tan δ versus the dynamic strain.

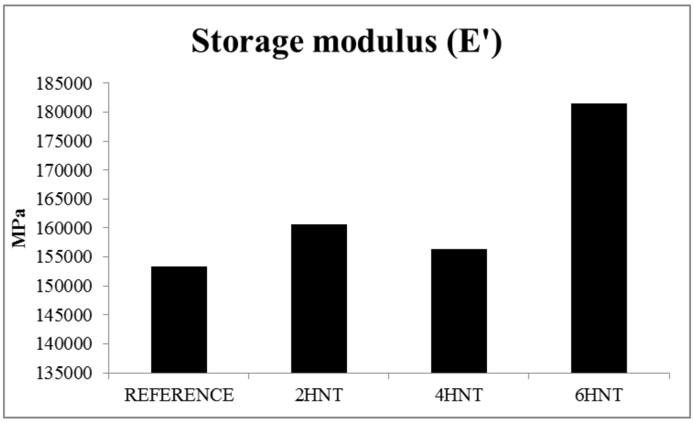

Fig.7 Effect of HNT content on Storage modulus

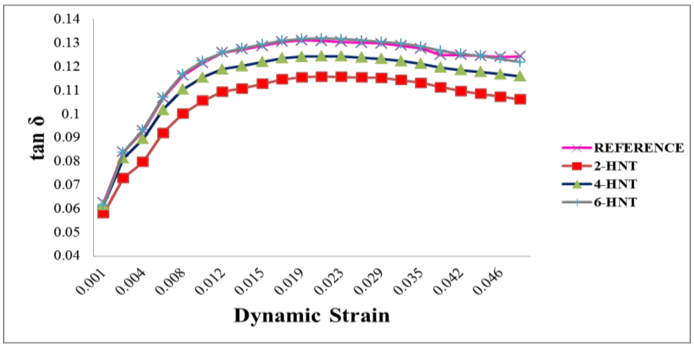

Fig.8 DMA analysis for HNT-Natural rubber nano composites

The tan δ level itself is a key indicator for most of the important properties of a tyre tread compound. The minimum value of tan **δ** indicates the better rubber-filler interaction as in 2phr & 4 phr of HNT than the control sample. This also indicates the higher dispersion at lower nano filler loading and increasing of tan δ shows lower dispersion as shown in the figure.

3.4 Wear characteristics

Wear characteristics was studied by Abrasion test with Din Abrader. Each sample was prepared using a three piece-sixteen cavity mould at 1608C maintaining a time span of 30 min. The testing was done by DIN abrasion tester-6012 (Zwick Gmbh & Co, Germany) as per ISO4649 method. Abrasion loss for each sample is expressed in terms of volume loss & abrasion resistance index (ARI). Abrasion resistance of NR vulcanizates was determined in terms of DIN volume loss. Fig. 8 shows DIN volume loss of NR/HNT vulcanizates containing various contents of HNT. DIN volume loss of NR/HNT vulcanizates reduced as HNT content increased and abrasion resistance index also shows a reducing trend as shown in Fig.8, which reveals that the abrasion resistance is good for the increase in HNT content for NR-HNT nanocomposite.

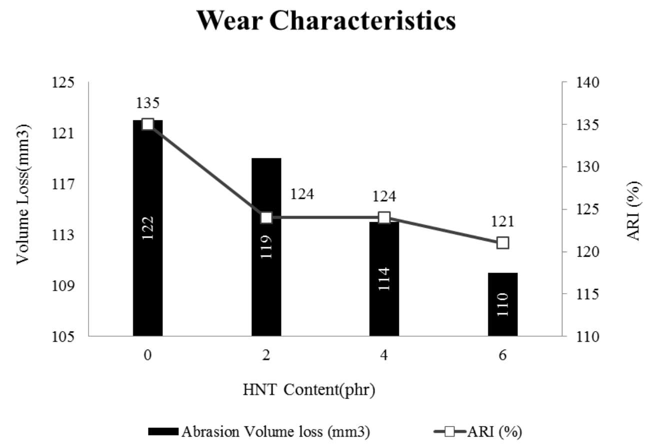

Fig.9 Wear characteristics of NR-HNT nano-composite

3.5 Thermal Analysis

The TGA study was conducted for the NR-HNT nanocomposites and compared with the control NR compound. (Fig 10 & 11). The data shows that the NR-HNT composites have better thermal stability for the nanocomposites than the control compound. The thermal stability (decomposition at 50% weight loss) improved from 399°C to 412°C with the increase in HNT content. The thermal stability improvement can be due to the strong interaction of NR & nonofiller by means of proper blending and homogeneous mixing of the NR-HNT nanocomposites.

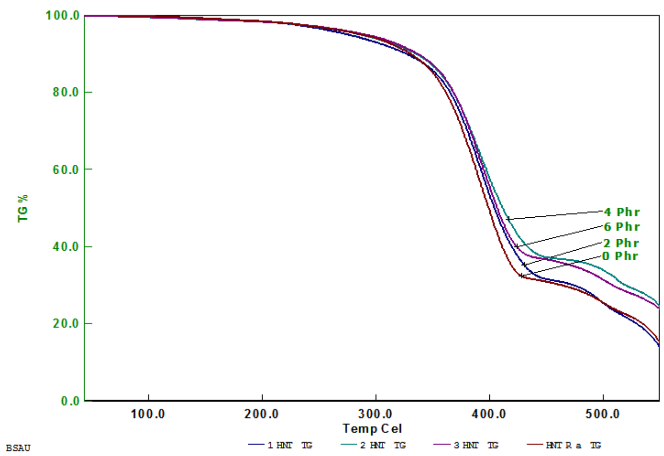

Fig.10 TGA thermogram for NR-HNT Nanocomposite

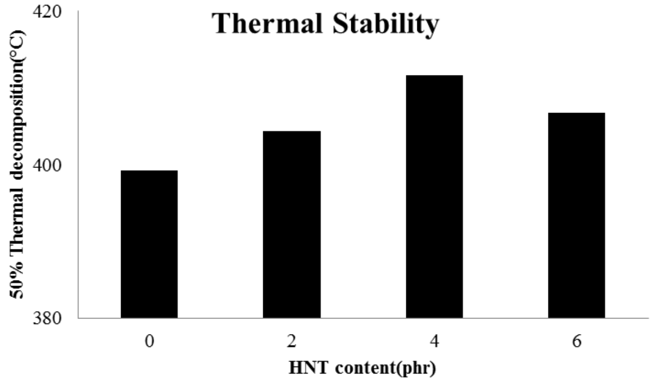

Fig.11 Thermal stability of NR-HNT NCs

3.6 X-ray Diffraction

To measure the change in gallery spacing of HNT, X-ray diffraction (XRD) test was conducted in a Rigaku Miniflex CN 2005 X-ray diffractometer equipped with CuKa radiator (30 kV, 10 mA, Rigaku Corporation, Tokyo, Japan). The diffraction data were obtained within a goniometer angle (2θ) range of 10°-30°.

The XRD peak for pure HNT found 12.385°where as the 4 phr HNT-NR nano composites shows a shift in the diffraction pattern to the lower angle of 11.675.(Fig 12) . It shows that the increase in basal length between the nanofiller. Basal length increased from 7.30 to 7.39 in nanofiller loading of 6phr shows the good dispersion of nanocomposite. Lower angle reveals the better exfoliation of the NR in to the nanofiller HNT.

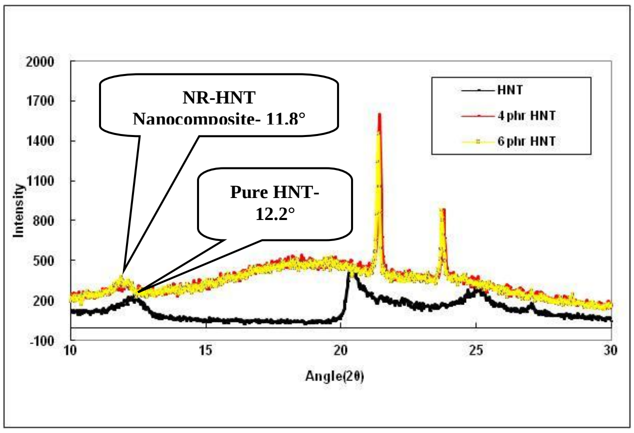

Fig.12 Diffraction peak shift for pure HNT and NR-HNT Nanocomposites

3.7 SEM Analysis

SEM analysis of NR-HNT nanocomposite with 4phr having good mechanical properties & thermal properties were analysed and found to have better dispersion.

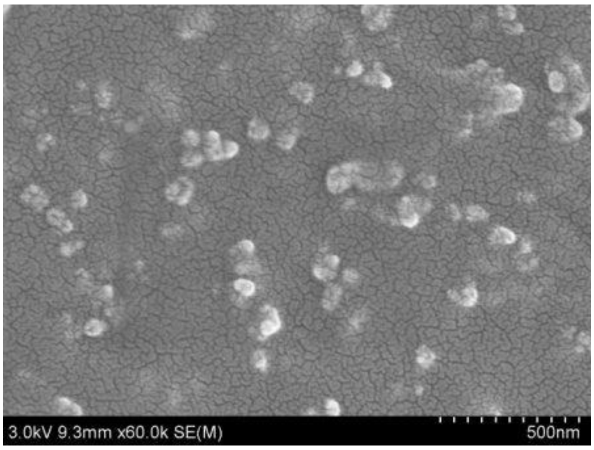

Fig.13 SEM image for 4phr HNT-NR nanocomposite

IV. CONCLUSIONS

Natural rubber nanocomposites were prepared with natural halloysite nanotubes filler upto 6 phr. Superior reinforcing activity of HNTs was realized in all the properties studied. The results obtained for mechanical properties showed a significant improvement in tensile strength and elongation at break of nanocomposites. Improved wear characteristics were found for the composites filled with HNTs. XRD results show that the composites with nanofiller have a slight shift in the 2θ angle compared to pure HNT. TGA studies of HNT-NR nanocomposites with 4phr HNT loading shows improved thermal stability. Wear characteristics studied using the Din Abrader gave lesser weight loss on increasing the HNT content revealing higher abrasion resistance. Finally, owing to the high reinforcing activity of the halloysite nanotubes as compared to silica , application of this filler can be extended to the green tyre formulation where a large amount of silica are being used to get a high performance, mileage of the tyre.

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