Development and Characterization of Acrylonitrile (NBR)/ Styrene-Butadiene (SBR) Blends Reinforced with Halloysite Nanotubes
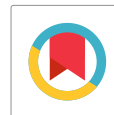
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ABSTRACT

Elastomeric blends based on Nitrile (NBR) and Styrene butadiene rubber (SBR) are compatibilized by 6% Chlorinated polyethylene (CPE) and further reinforced with Halloysite nanotubes in various % loading (1%, 2%, 3% & 4%) in a two roll mill mixer for preparation of nanocomposites with enhanced properties. Further to enhance the effect of nanofillers and to increase the interaction of nanofiller with rubber matrix, HNT's were functionalized by 30% H_2SO_4 by adopting the modification process. Tensile strength, elongation at break, modulas of elasticity, tear strength, hardness & thermal stability was studied. The result revealed that the blends reinforced with 3% modified HNT's showed better results as compared to blends with unmodified HNT's.

Keywords: Acrylonitrile; Styrene-butadiene rubber; Compatibilizer; Halloysite nanotubes; Thermal stability; Mechanical properties.

1. INTRODUCTION

Rubbers are special materials known for its elasticity. The usages of rubbers are seen in various industrial and domestic applications in terms of mechanical properties, large stretch ratios, resilience, water proofness etc. Natural rubber, Styrene butadiene rubber, silicone rubber, neoprene rubber, nitrile rubber are some of the examples of important rubber materials. SBR is a rubber with 75% styrene and 25% butadiene content as copolymer. SBR is cost effective and is resistant to abrasion. It is used in automotive sectors mainly but its disadvantage is its vulnerability to ozone, oxidation. Another rubber NBR is made by the polymerization of acrylonitrile and butadiene rubbers. NBR is resistant to temperature and swelling behaviour. SBR is non polar while NBR rubbers are polar in nature due to the presence of nitrile group. Blending of rubbers is an effective route to develop tailor made materials with desired set of properties (Akshay *et al.* 2021). The performance of rubber products is found to be increased when we blend the elastomers. New polymer materials with better properties can be developed by blending of rubbers (George *et al.* 2000). Rubber is organic and are arranged with repeating units of carbon atoms. In the present work, Nitrile butadiene rubber (NBR) and Styrene butadiene rubber (SBR) are used. Nitrile butadiene rubber (NBR) have high thermal conductivity and high tensile strength when compared to other rubber materials. Styrene butadiene rubber (SBR) is also a

thermoset elastomer. Styrene butadiene rubber (SBR) have low density and high ductile nature as compared to other materials. Some studies reveal that it is possible to use a blend of high acrylonitrile (NBR) content with Styrene butadiene rubber (SBR) to obtain a degree of oil resistance equal to that given by a low NBR within an overall reduction in cost. Products having high NBR content have a tendency to shrink in hot lubricating oils and replacement of part of it by SBR overcomes this defect. On the other hand, oil resistance, oil seals and gaskets sometimes require lower compression set at higher temperatures, and these can be improved by blending with SBR, blending also improves the processing properties. Generally, the pair of polymers (NBR/SBR) are immiscible in nature and can be made miscible by using compatibilizers because one being polar and other being non polar (Yeswin *et al.* 2022). To make immiscible blend miscible compatibilizer (CPE) is used to increase the compatibility of the polymers. Nitrile butadiene rubber (NBR) and Styrene butadiene rubber (SBR) cross links in the vulcanization process, and for this process dicumyl peroxide (DCP) is used as the vulcanizing agent. In this work, stearic acid and zinc oxide are used as coupling agent (Ramesan *et al.* 2001).

Most of the research work on elastomers-based nanocomposites reveal the use of carbon nanotubes and organoclay based nano fillers (Anand *et al.* 2016) which is very costly. To make it environmental friendly and also cost effective, halloysite nanotubes are used nowadays.

Halloysite ($Al_2Si_2O_5(OH)_4.2H_2O$), is a naturally occurring aluminosilicate nanotube. It is 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 aluminium, silicon, hydrogen and oxygen (Anand *et al.* 2016). Halloysite belongs to the family 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. HNTs when incorporated can give tremendous applications in various polymers as shown in a review article (Rooj *et al.* 2010; Anand *et al.* 2016) 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 modified & unmodified HNT's at different loading (1%, 2%, 3%, 4%) in compatibilized NBR/SBR blends. The mechanical & thermal properties of the blends reinforced with modified & unmodified HNT's are studied & analysed.

2. EXPERIMENTAL

2.1 Materials

SBR (SBR-1502, Sp.Gr. 0.945, styrene content 23.5%) and NBR (acrylonitrile content 34%, density 0.99 g/cm3) were used. Dicumyl peroxide (Mw 270.37) was supplied by Ottokemi. Halloysite nanotubes, $H_4Al_2O_9Si_2.2H_2O$ (Sp. Gr. 2.53, M= 294.19 g/mol) was from Sigma-Aldrich. Stearic acid & Chlorinated Polyethylene (CPE) were used in commercial grade.

2.2 Preparation of NBR/SBR Blends

Mixing of the blends were done using two roll mill having a friction ratio of 1:14. NBR/SBR blends were prepared in seven different combinations. These blends were vulcanized by dicumyl peroxide. The compounds were compression molded along the mill grain direction using hydraulic press at 150 °C. The vulcanization of the rubber compound was carried out in a hydraulically operated press at 150 °C for 10 minutes. The vulcanized samples were aged at 100 °C for 24 hrs in an air-circulating oven. Test specimens were punched out from the compression mould. The mechanical properties of the blends were analyzed. It was found that the NBR:SBR (60:40) formulations have shown the optimum properties, therefore this formulation was further used for the preparation of nanocomposites with different loading of HNT's.

2.3 Preparation of HNT Nanocomposites Using Compatibilizer (CPE)

The two rubbers i.e NBR / SBR (60:40) were masticated along with zinc stearate, Dicumyl peroxide (DCP), Chlorinated Polyethylene compatibilizer (CPE). In previous studies different loading of CPE was analysed and it was found that 6% loading of CPE in the NBR/SBR (60:40) is giving the optimized results. HNT was reinforced in the blends in various loading (1%, 2%, 3% & 4%) along with other ingredients in a two roll mill at 120 °C with a nip gap of 1mm. Vulcanization of rubber was done using hydraulic press at 150 °C for 10 min. The vulcanized samples were aged at 100 °C for 24 hrs in an air circulating oven.

Table 1. Compounding formulation of NBR: SBR (PHR) blend ratio (60:40) with compatibilizer (CPE 6%) & various loading of halloysite nanotubes (modified &unmodified HNT's)

Nomenclature	HNT1 %	HNT2%	HNT3%	HNT4 %
NBR/SBR (60:40)	60:40	60:40	60:40	60:40
HNT(%age)	1%	2%	3%	4%
DCP (w/w)%	1.75	1.75	1.75	1.75
Stearic Acid (w/w)%	2	2	2	2
Zinc Oxide (w/w)%	5	5	5	5
CPE (w/w)%	6	6	6	6

Table 2. Sample identification

Formulation	Sample Identification
NBR/SBR + compounding ingredients + Unmodified HNT 1%	UHNT1%
NBR/SBR + + compounding ingredients + Unmodified HNT 2%	UHNT2%
NBR/SBR + + compounding ingredients + Unmodified HNT 3%	UHNT3%
NBR/SBR++ compounding ingredients + Unmodified HNT 4%	UHNT4%
NBR/SBR ++ compounding ingredients + modified HNT 4%	MHNT1%
NBR/SBR ++ compounding ingredients + modified HNT 4%	MHNT2%
NBR/SBR ++ compounding ingredients + modified HNT 4%	MHNT3%
NBR/SBR ++ compounding ingredients + modified HNT 4%	MHNT4%

2.4 Modification of Halloysite Nanotubes (HNT's)

To increase the functionalization of HNT's they were treated with 30% sulphuric acid & stirred in a beaker on a heating plate at 80 °C for about 30 min. After 30 min the functionalized HNT's were washed with distilled water for about 3-4 times. After that excess water was removed by filtering in watsman paper for about 3 hrs. Then they were dried in an oven at about 80 °C for 24 hrs. The dried HNT's were used further in different percentage (1%, 2%, 3% & 4%) in rubber blends. The compounding formulation for modified & unmodified HNT's in rubber blends is given in Table 1.

Sample Identification for different blends with modified & unmodified HNT's is given in Table 2.

3. EXPERIMENTAL TECHNIQUES

3.1 Mechanical Properties

Tensile testing, %elongation & modulas of elasticity of the samples were performed using Universal Testing Machine (Tinius olsen, Model 25ST, capacity 25 KN) at 27 °C with a crosshead speed of 50 mm/min using dumble shaped tensile specimen according to ASTMD 412. The tear strength test was also conducted as per ASTMD 624 using 90° angle test specimen at 50 mm/min. The hardness of the samples was measured as per ASTMD 2240 by using Mitotoyo Shore a hardness tester.

3.2 Thermal Gravimetric Analysis (TGA)

The thermal stability and degradation behaviour of developed nanocomposites have been studied with the help of Perkin-Elmer TGA. The TGA measurements have been conducted with a constant heating rate of 10 °C/min under nitrogen atmosphere from 50 to 700 °C as per ASTMD 1131.

4. RESULTS AND DISCUSSION

4.1 Mechanical Properties Analysis

4.1.1 Tensile Strength, Modulus & % Elongation

The mechanical properties of optimized & compatibilized blend of NBR & SBR rubber with various loading (1%, 2%, 3% and 4%) of modified (30% H_2SO_4) and unmodified HNT are depicted in Table 3 and Figs. 1-3. It is evident from the Table 3 that there is a significant enhancement in tensile strength, modulus and % elongation of rubber nanocomposite with the increase of percentage reinforcement of HNT's up to 3 %. But the enhancement is more distinct in case of 3 % modified HNT when compared to unmodified HNT. It is obvious from the data that the maximum improvement in mechanical properties is observed at 3% modified HNTs loading in rubber matrix as compared to unmodified HNT rubber nanocomposites. The tensile strength of the modified HNT nanocomposites is found to increase with an increase in the weight fraction of HNT (Figs. 1-3). The tensile strength of 1% HNT was observed at 2.36 MPa, which increases to 2.66 and 2.94 MPa at 2% and 3% HNT compositions, respectively, and then decreases to 1.379 MPa for 4 %HNT. The highest value of tensile strength is 2.94 MPa which is 41% higher than the 3% unmodified HNT composition. Similarly there is enhancement of 275% in modulus. This increase in tensile strength and modulus of the developed rubber nanocomposites may be attributed to the stress transfer from the rubber matrix to the fillers. It is a well-known fact that the effective stress transfer between the rubber matrix and fillers entirely

depends upon the interfacial interaction between the rubber blend and fillers as well as on the dispersion of the fillers over the entire polymer matrix. The bridging effect of modified HNTs at the blend interface may also be responsible for improvement in tensile properties. % Elongation and increases from unmodified HNT rubber blend to modified HNT rubber blend may be because of increase in ductility.

Table 3. Mechanical properties of NBR/SBR nanocomposites with modified and unmodified HNT in different compositions

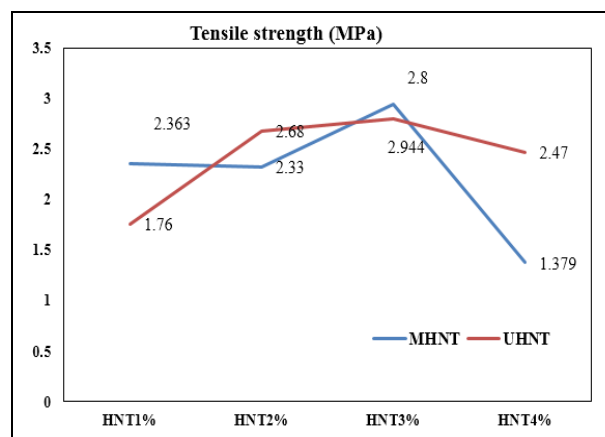| Sample Identification	Tensile Strength (MPa)	Modulus (MPa)	Elongation at break (%)	Tear Strength (N/mm)	Hardness (Shore - A)
MHNT 1%	2.363	0.565	1426	7.60	53
UHNT1%	1.76	0.1087	991	8.37	52
MHNT2%	2.66	0.595	1463	11.50	51
UHNT2%	2.68	0.1664	991	11.80	53
MHNT3%	2.944	0.6042	1759	15.84	54
UHNT3%	2.08	0.1681	1224	13.26	52
MHNT4%	1.379	0.555	1604	13.02	53
UHNT4%	2.47	0.0861	875	16.13	52

Fig. 1: Tensile properties of different rubber nanocomposites with modified and unmodified HNT
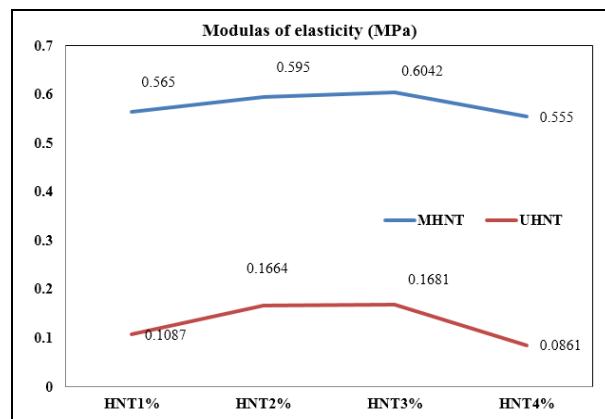

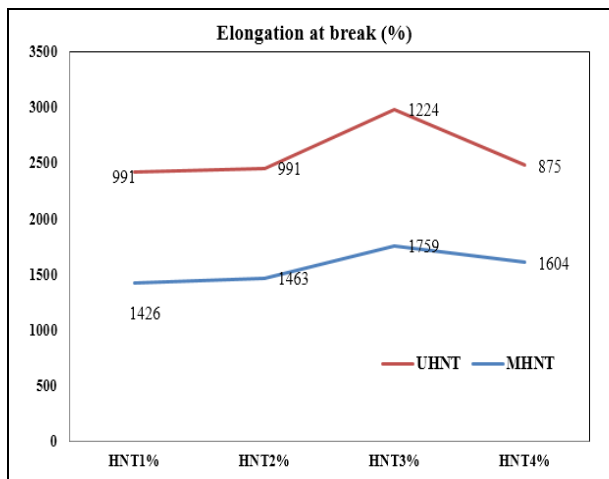Fig. 2: Elastic modulus of different rubber nanocomposites with modified and unmodified HNT

Fig. 3: Elastic modulus of different rubber nanocomposites with modified and unmodified HNT

4.1.2 Tear Strength

Tear Strength of rubber nanocomposite is the maximum force required to tear a test specimen in a direction normal to (perpendicular to) the direction of the stress. As depicted in Table 3 & Fig. 4, the tearing strength is initially found to increase with an increasing amount of HNT. The highest tear strength value is 15.84 N/mm for the 3% modified HNT composition, 20 % (approx.) higher than for 3% unmodified HNT composition. With a further increase in the HNT percentage, the tearing strength starts to decline and reaches 13.02 N/mm. A better uniform dispersion of the HNT could explain this in the matrix for the 3% modified HNT nanocomposite. Reduction in the tear strength for the 4% composition is attributed to the agglomeration in composite with an increase in the wt % of the HNT.
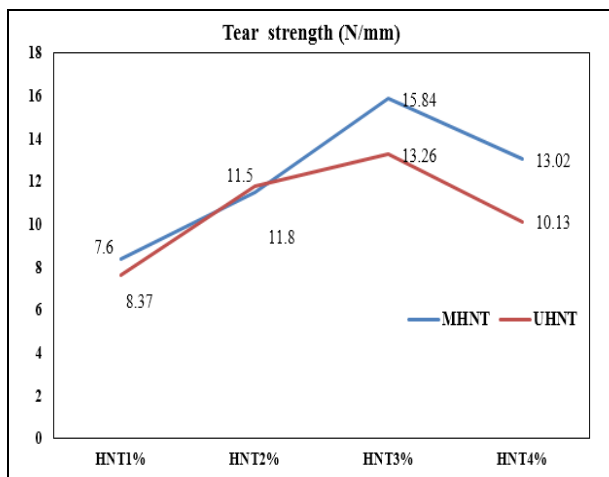

Fig. 4: Tear strength of different rubber nanocomposites with modified and unmodified HNT

4.1.3 Hardness

As shown in the Table 3, it is clear that not much significant changes is observed in the hardness of the blends. However, it is evident that maximum hardness (54) of rubber nanocomposites has been achieved at 3 wt% loading of modified HNT as compared to different compositions of unmodified HNT. It is, therefore, concluded that 3 wt% modified HNTs get dispersed uniformly and increase interfacial interaction that results in greater energy absorption by rubber nanocomposite, thus increasing the hardness.

4.2 Thermal Gravimetric Analysis (TGA)

Thermal stability of NBR/SBR/HNT's nano-composites are shown in Figs. 5-6 and Tables 4-5. It is evident that the reinforcement of HNT's in the rubber blends in 1%, 2%, 3% & 4% loading of nanofiller has a significant effect on the thermal degradation. In the NBR/SBR blends with unmodified HNT's it is clear that the thermal degradation has significantly increased to 449 °C in 3 wt % loading of nanofiller. However, when the HNT's are modified, and reinforced in the rubber matrix in various loading, it is clear that the remarkable increase in thermal degradation is observed in 3% wt loading of HNT's which is 456 °C. This can be attributed to the fact that by modification of HNT's no, of functional groups are enhanced which lead to good interaction of rubber matrix with the nanofiller. Also as per (Paran *et al.* 2024), molecular theory dispersion state of HNT's and its high aspect ratio prevents the emission of small gaseous molecules trapped into the polymer structure at higher temperatures.
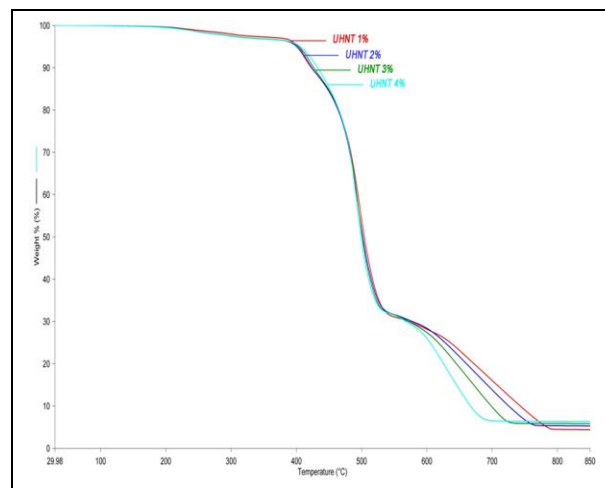

Fig. 5: TGA thermograph of rubber nanocomposites with unmodified HNT

Table 6. TGA results of NBR/SBR blends with varied loadings of UHNT's

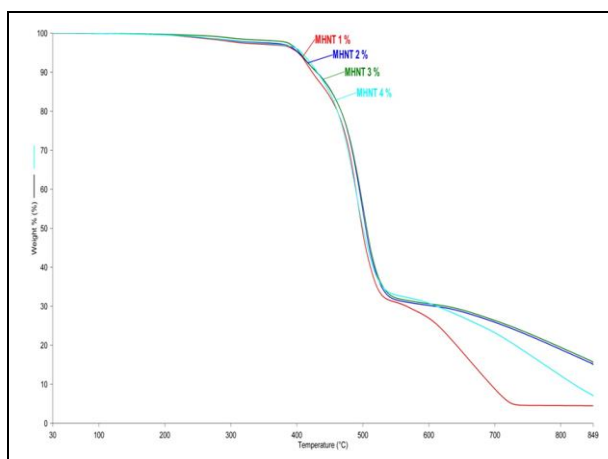| Sample code	Onset Degradation Temperature (°C)
HNT1%	379
HNT2%	400
HNT3%	449
HNT4 %	402

Fig. 6: TGA thermograph of rubber nanocomposites with modified HNT

Table 5. TGA results of NBR/SBR blends with varied loadings of modified HNT's (MHNT's)

Sample code	Onset Degradation Temperature (℃)
MHNT1 %	399
MHNT2 %	403
MHNT3 %	456
MHNT4 %	413

5. CONCLUSION

The mechanical properties analysis shows that there is a significant enhancement in tensile strength, modulus and % elongation of rubber nanocomposite with the increase of percentage reinforcement of HNT's up to 3 %. But the enhancement is more distinct in case of 3 % modified HNT when compared to unmodified HNT which is attributed to the good interaction of rubber & nanofillers in rubber matrix. The tearing strength is initially found to increase with an increasing amount of HNT. The highest tear strength value is 15.84 N/mm for the 3% modified HNT composition, which is 20% higher than for 3% unmodified HNT composition. With a further increase in the HNT percentage, the tearing strength starts to decline and reaches 13.02 N/mm. A better uniform dispersion of the HNT could explain this in the matrix for the 3% modified HNT nanocomposite. Reduction in the tear strength for the 4% composition is attributed to the agglomeration in composite with an increase in the wt % of the HNT. Remarkable increase in thermal degradation is observed in 3% wt loading of MHNT's which is 456 °C. This can be attributed to the fact that by modification of HNT's number of functional groups are enhanced which lead to good interaction of rubber matrix with the nanofiller. Also as per (Paran *et al.* 2024) molecular theory dispersion state of HNT's and its high aspect ratio prevents the emission of small gaseous molecules trapped into the polymer structure at higher temperatures leading to higher thermal degradation.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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