Research Article

Journal of Environmental Nanotechnology

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

Ambika Joshi[1*] A. B. Soni[1] and Alok Sahu[2]

[1]Department of Chemical Engineering, National Institute of Technology, Raipur, CG, India
[2]Central Institute of Petrochemicals Engineering and Technology, Raipur, CG, India
Received: 04.05.2024 Accepted: 19.06.2024 Published: 30.06.2024
*ambikajoshi123@gmail.com

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 (HNTs) in various % loading (1%, 2%, 3% and 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, the HNTs were functionalized by 30% H_2SO_4 by adopting the modification process. Tensile strength, elongation at break, modulus of elasticity, tear strength, hardness and thermal stability were studied. The results revealed that the blends reinforced with 3% modified HNTs showed better results as compared to blends with unmodified HNTs.

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

1. INTRODUCTION

Rubbers are special materials known for their elasticity. The usage of rubbers is seen in various industrial and domestic applications as they show favorable mechanical properties, large stretch ratios, resilience and waterproof property. Natural rubber, styrene butadiene rubber (SBR), silicone rubber, neoprene rubber, nitrile butadiene rubber (NBR) are some of the examples of important rubber materials. Styrene butadiene rubber is a rubber with 75% styrene and 25% butadiene content as copolymer. It is cost effective and 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. It is resistant to temperature and swelling behaviour. While SBR is non polar, NBR rubbers are polar in nature due to the presence of nitrile group. Blending of rubbers is an effective route to develop customized materials with desired set of properties (Akshay *et al.* 2021). The performance of rubber products is found to be increased when elastomers are blended. 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, NBR and SBR are used. Nitrile butadiene rubber has high thermal conductivity and high tensile strength when compared to other rubber materials. Styrene butadiene rubber is also a thermoset elastomer. It has low density and high ductile nature as compared to other materials. Some studies reveal that it is possible to use a blend of NBR (high nitrile content) and 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, which 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 and styrene butadiene rubber undergo crosslinking during the vulcanization process, in which 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 ecofriendly and also cost effective, halloysite nanotubes (HNTs) 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. When incorporated, HNTs can give tremendous applications in various polymers as discussed in review articles (Rooj *et al.* 2010; Anand *et al.* 2016). They are least studied for elastomer-based nanocomposites and hence this paper presents the effect of modified- and unmodified HNTs at different loading (1%, 2%, 3%, 4%) in compatibilized NBR/SBR blends. The mechanical and thermal properties of the blends reinforced with modified and unmodified HNTs are studied and 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/cm^3) were used in this work. 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 and Chlorinated Polyethylene (CPE) were used in commercial grade.

2.2 Preparation of NBR/SBR Blends

Mixing of the blends was 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 hours 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 HNTs.

2.3 Preparation of HNT Nanocomposites Using Compatibilizer (CPE)

The two rubbers i.e., NBR / SBR (60:40) were masticated along with zinc stearate, DCP and 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) gave the optimized results. Halloysite nanotubes were used as reinforcement in the blends in various loading (1%, 2%, 3% and 4%) along with other ingredients in a two-roll mill at 120 °C with a nip gap of 1 mm. Vulcanization of rubber was done using hydraulic press at 150 °C for 10 min. The vulcanized samples were aged at 100 °C for 24 hours in an air circulating oven.

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

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 (HNTs)

To increase the functionalization of HNTs, they were treated with 30% sulphuric acid and stirred in a beaker on a heating plate at 80 °C for about 30 min. After 30 min, the functionalized HNTs were washed with distilled water for about 3-4 times. After that, excess water was removed by filtering through a Whatman paper for about 3 hours. Then they were dried in an oven at about 80 °C for 24 hours. The dried HNTs were used

further in different percentage (1%, 2%, 3% and 4%) in rubber blends. The compounding formulation for modified and unmodified HNTs in rubber blends is given in Table 1. Sample identification for different blends with modified and unmodified HNTs is given in Table 2.

3. EXPERIMENTAL TECHNIQUES

3.1 Mechanical Properties

Tensile testing, % elongation and modulus of elasticity of the samples were evaluated using Universal Testing Machine (Tinius Olsen, Model 25ST, capacity 25 KN) at 27 °C with a crosshead speed of 50 mm/min using dumb-bell 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 Mitutoyo Shore A Hardness Tester.

3.2 Thermogravimetric 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

4.1.1 Tensile Strength, Modulus and % Elongation

The mechanical properties of optimized and compatibilized blend of NBR and 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 Fig. 1-3. It is evident from Table 3 that there is a significant enhancement in tensile strength, modulus and % elongation of rubber nanocomposite with the increase of percentage reinforcement of HNTs 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. 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 a 275% enhancement 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. The percentage elongation increased from the unmodified HNT rubber blend to the modified HNT rubber blend, which may be attributed to enhanced 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

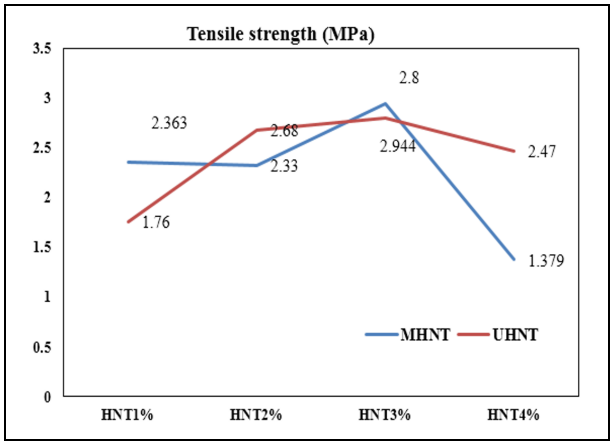


Fig. 1: Tensile properties of different rubber nanocomposites with modified and unmodified HNT

4.1.2 Tear Strength

The 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 and Fig. 4, the tear 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.

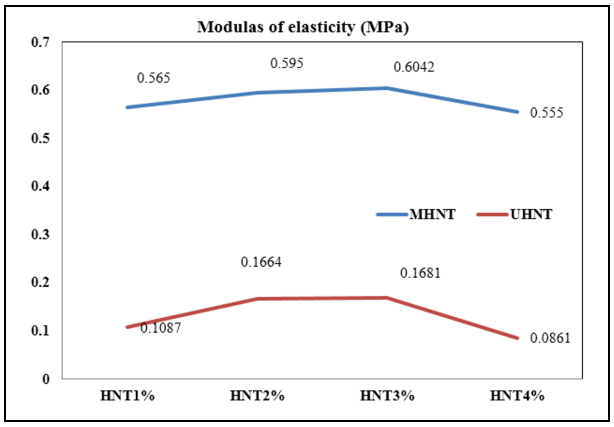


Fig. 2: Elastic modulus of different rubber nanocomposites with modified and unmodified HNT

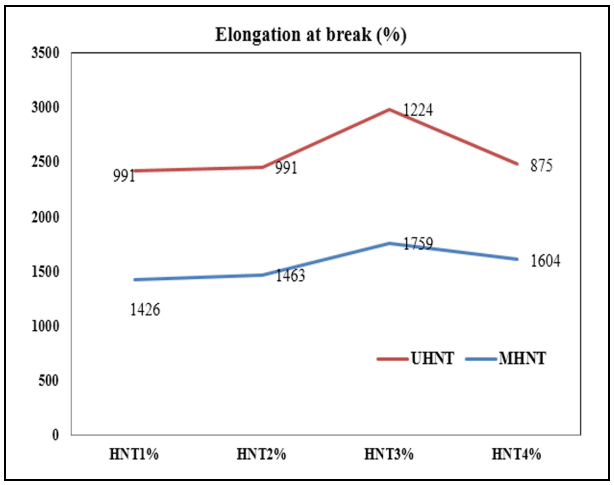


Fig. 3: Elastic modulus of different rubber nanocomposites with modified and unmodified HNT

4.1.3 Hardness

As shown in the Table 3, it is clear that not much significant changes are 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/HNTs nano-composites are shown in Fig. 5 and 6 and Tables 4 and 5. It is evident that the reinforcement of HNTs in the rubber blends in 1%, 2%, 3% and 4% loading of nanofiller has a significant effect on the thermal degradation. In the NBR/SBR blends with unmodified HNTs, the thermal degradation significantly increased to 449 °C in 3 wt % loading of nanofiller. However, when the HNTs are modified, and reinforced in the rubber matrix in various loadings, a remarkable increase in thermal degradation (456 °C) is observed in 3% wt loading of HNTs. This can be attributed to the fact that by modification of HNTs, the 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 HNTs and its high aspect ratio prevents the emission of small gaseous molecules trapped into the polymer structure at higher temperatures.

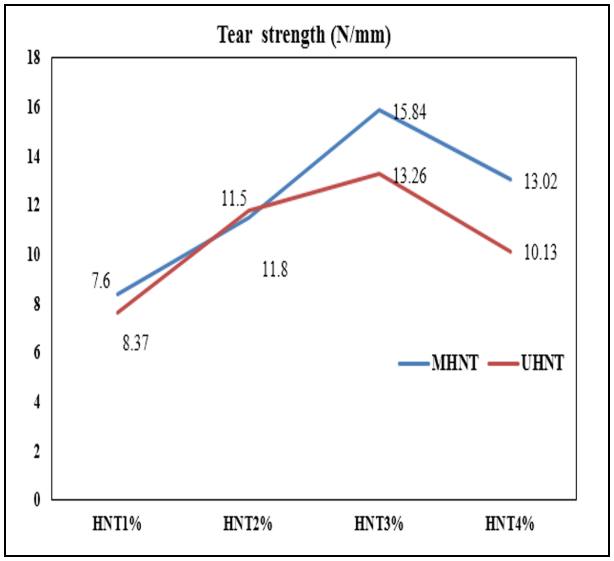


Fig. 4: Tear strength of different rubber nanocomposites with modified and unmodified HNT

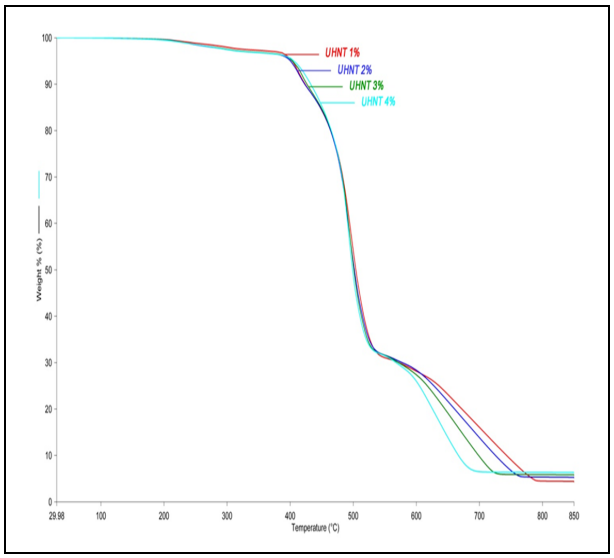


Fig. 5: TGA thermograph of rubber nanocomposites with unmodified HNT

Table 6. TGA results of NBR/SBR blends with varied loadings of UHNTs

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

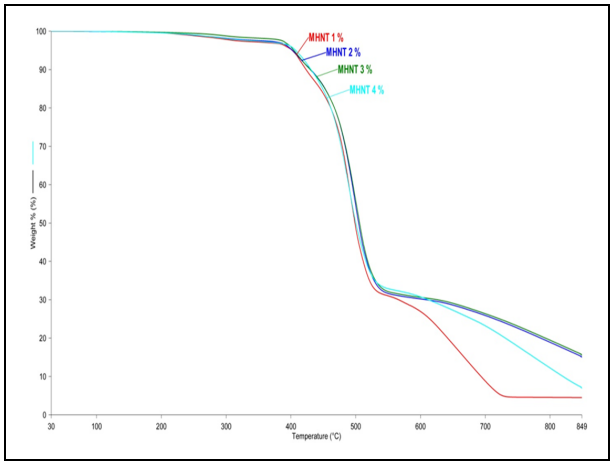


Fig. 6: TGA thermograph of rubber nanocomposites with modified HNT

Table 5. TGA results of NBR/SBR blends with varied loadings of modified HNTs (MHNTs)

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

5. CONCLUSION

The mechanical properties of rubber nanocomposites improved with increasing HNT content up to 3%, with modified HNT showing superior performance due to better filler-matrix interaction. Tensile strength, modulus, elongation, and tear strength increased, with a maximum tear strength of 15.84 N/mm for 3% modified HNT. Further increase to 4% reduced properties due to agglomeration. Thermal stability also improved, reaching 456 °C at 3% modified HNT, attributed to enhanced dispersion and strong interfacial bonding.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

COPYRIGHT

This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

REFERENCES

Akshay, K., Arjun, M., Govind, S. S., Hrithwik, V., Akhil, S., Rahulan, N., Mechanical behavior of silicon carbide filled SBR/NBR blends, *Mater. Today Proc.* 42, 1432–1436 (2021). https://doi.org/10.1016/j.matpr.2021.01.234

Anand, N. A. G., Rajesh Babu, R. Vasanthakumari, Studies on Halloysite Nanotubes(HNT) Natural Rubber Nanocomposites for Mechanical Thermal and Wear Properties, Int J Eng Res. https://doi.org/10.17577/IJERTV5IS030167

George, S. C., Ninan, K. N., Groeninckx, G., Thomas, S., Styrene-butadiene rubber/natural rubber blends: Morphology, transport behavior, and dynamic mechanical and mechanical properties, *J. Appl. Polym. Sci.* 78(6), 1280–1303 (2000). https://doi.org/10.1002/1097-4628(20001107)78:6<1280::AID-APP150>3.0.CO;2-S

Paran, S. M. R., Naderi, G., Mirzaee, M., Ghoreishy, M. H. R., Włoch, M., Esmaeili, A., Abida, O., Saeb, M. R., Microstructure–properties relationship in ethylene-propylene diene monomer (EPDM)/nitrile butadiene rubber (NBR)/halloysite nanotubes (HNTs) nanocomposites, *Polym. Bull.* 81(1), 755–772 (2024). https://doi.org/10.1007/s00289-023-04723-7

Ramesan, M. T., Alex, R., Compatibilization of SBR/NBR blends using chemically modified styrene- co -butadiene rubber Part 2. Effect of compatibilizer loading, *Polym. Int.* 50(12), 1298–1308 (2001). https://doi.org/10.1002/pi.775

Rooj, S., Das, A., Thakur, V., Mahaling, R. N., Bhowmick, A. K., Heinrich, G., Preparation and properties of natural nanocomposites based on natural rubber and naturally occurring halloysite nanotubes, *Mater. Des.* 31(4), 2151–2156 (2010). https://doi.org/10.1016/j.matdes.2009.11.009

Yeswin, C., Vamsi, D. B. S., Vijay, B. N., Naveen, I., Reddy, P. S. P., Rahulan, N., Physical properties of nano Al2O3 reinforced NBR/SBR blends, *Mater. Today Proc.* 52, 2273–2278 (2022). https://doi.org/10.1016/j.matpr.2021.08.241