Halloysite Nanotubes (HNTs)-Filled Ethylene-Propylene-Diene Monomer/Styrene-Butadiene Rubber (EPDM/SBR) Composites: Mechanical, Swelling, and Morphological Properties

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Received: 30 June 2021 / Accepted: 20 September 2021 / Published online: 9 October 2021
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Abstract

Halloysite nanotubes (HNTs) were incorporated into an EPDM/SBR rubber/styrene-butadiene rubber (SBR) composite by melt blending of HNTs into the EPDM/SBR blend. The mechanical properties, abrasion and swelling resistance of HNTs ranging from 2 parts per hundred rubber (phr) to 10 parts per hundred rubber (phr) were investigated in EPDM/SBR base rubber. Tensile strength, 100% modulus (modulus at 100% elongation), elongation at break and tear strength were evaluated at ambient temperature using electric universal tensile testing equipment in accordance with ASTM D-412. Hardness, abrasion and swelling resistance were determined using Shore-A Durometer, DIN abrader and immersion techniques, respectively. The results show that increasing HNT content increased tensile strength, tear strength, hardness (stiffness), and crosslink density. The surface morphology of tensile-fractured material was studied using field-emission scanning electron microscopy (FE-SEM). According to FE-SEM results, the most roughness of the surface was seen at HNTs filled rubber nano-composites.

Keywords EPDM/SBR · HNTs · Mechanical properties · Swelling resistance

1 Introduction

Polymers are lightweight, have a high specific strength/modulus, are easy to process, and are inexpensive [1]. Without some kind of reinforcement, a rubber substance, whether polar or non-polar, has weak physico-mechanical properties [2]. The addition of a number of ingredients with special roles, such as curatives (activator, catalyst, and vulcanization or cross-linking agents), aids in the enhancement of those properties. At the present days, rubber and curatives materials are well-known and are not becomes an issue to any further extent. However, many academicians and researchers have recently improved the problem of modifying or replacing traditional additives such as carbon black (CB) and silica [3–5]. Because of their unique particle form and hydrophobic surface, CB is recommended as a strong reinforcement particle with better dispersibility in rubber matrix [6]. In addition, CB particle caused pollution in atmosphere and displayed dark color in the composite [7, 8]. Due to its hydrophilic surface, silica is recognised as a white filler with similar reinforcement effect as CB and low dispersion in rubber matrices, which appears in natural rubber (NR) composite [6, 9]. As a result, a variety of researchers [10–14] have introduced new types of nano-fillers, such as clay particles, to enhance the mechanical and swelling properties of rubber composites. They are also layered silicates and belong to the phyllosilicate group, which includes montmorillonite, saponite, and hectorite. Silica, which is commonly used as a rubber reinforcing filler, is a non-carbon filler [15, 16], with usage second only to carbon black in the rubber reinforcing industry. The presence of many hydroxyl groups on the surface of silica, on the other hand, causes filler tendentious aggregation, which is unfavourable to rubber composite performance.

Carbon nanotubes (CNTs) are divided into single-walled carbon nanotubes (SWCNTs), which have a typical diameter of 1–2 nm, and multi-walled carbon nanotubes (MWCNTs),
which have an outer diameter of 3–30 nm or more, depending on the number of graphitic layers comprising their structure [17]. CNTs also have a low mass density and a large aspect ratio (length to diameter ratio of approx 1000) [18]. Mechanical (elastic modulus: 1–1.7 TPa), thermal (thermal conductivity greater than 3000 W·m⁻¹·K⁻¹), and electrical (electrical conductivity: 10⁵ S·m⁻¹ – 10⁷ S·m⁻¹) properties are all outstanding [19]. Carbon nanotubes, while their numerous benefits, have a few disadvantages. CNTs have a great inclination to aggregate due to their nanometric size. Carbon nanotubes are also rather costly [20, 21]. Natural halloysite nanotubes are another sort of nanotubular structure (HNTs). HNTs have been found to be effective as nanofillers in a variety of rubber materials [22, 23]. HNTs are a two-layered aluminosilicate (Al₂Si₂O₅(OH)₄·H₂O) with a hollow tubular structure in the micron range and chemically similar to kaolin particles [24, 25]. HNTs are a type of phyllosilicates material that consists of one octahedral sheet and one tetrahedral sheet with six-membered rings and 1:1 layers. The crystalline structure of HNTs is double layered. The outer layer surface of HNTs has Si-O groups, while the inner side surface and tube edges have Al(OH)₃ groups [26]. HNTs have a higher aspect ratio than clay minerals (montmorillonite, saponite, and hectorite) due to their tuber shape. HNTs have an aspect ratio ranging from 10 to 130, depending on the tube dimension. HNTs’ large surface area and aspect ratio are likely to have a unique reinforcing impact on the polymer matrix. For nanocomposites to improve their mechanical and thermal properties, good interaction and interfacial adhesion between the rubber matrix and nano-filler particles are essential [7]. The lengths of HNTs typically range from 300 to 1500 nm, with inner diameters of 15–100 nm and outside diameters of 40–120 nm [27, 28]. HNTs are a low-cost, environmentally acceptable substance that can be disseminated in a polymer matrix more easily than carbon nanotubes [29]. Because of the fact that HNTs materials are naturally occurring and much cheaper, yet structurally comparable to MWCNTs, the HNTs could be a best choice for more expensive CNTs for some applications. EPDM, SBR, and silicone rubber can all endure temperatures as low as −40 degrees Celsius, making them ideal for low-temperature applications. Both materials have the same degree of compression set, making them suitable for applications requiring a high level of durability. EPDM and SBR have high tensile strength and abrasion resistance, making them ideal materials for dynamical loading and force applications that require a lot of physical effort [30, 31].

The addition of HNTs to the EPDM/SBR matrix results in a new material. Because of the high aspect ratio and low density, HNTs nanofiller materials combine the features of matrix and filler, and may also display additional properties. Nano-reinforcement has been the focus of recent nanocomposites manufacturing research in order to produce improved or tailored mechanical performance. This usually refers to gaining some unique tensile qualities, as well as abrasion and swelling resistance, in the case of nano-reinforcements. This work is an important accountability in the creating of new material of EPDM/SBR nanocomposites filled with various contents of HNTs. The objective of this paper is to explain the reinforcing ability of EPDM/SBR nanocomposites on the mechanical and swelling properties.

2 Experimental

2.1 Materials

Sigma-Aldrich supplied the halloysite nanotubes (HNTs) and swelling chemicals. The HNTs had a relative density of 2.53 g/cm³ and a basic surface area of 65 m²/g. The tubes had a diameter of 40–80 nm and a length of 1 to 4 μm. Arihant Reclamation Private Limited, Delhi, India, provided ethylene-propylene-diene monomer (EPDM) rubber (KEP-270; Mooney viscosity 71 ML1+4, 125 °C; ENB content 4.5 wt.%; ethylene content 57 wt.%, volatile content 0.4 wt.%; specific gravity 0.86) and styrene-butadiene rubber (SBR-1502; bound styrene 23.5 wt.%; volatile matter 0.3 wt.% ash 0.2 wt.%; organic acid 5.8 wt.%; specific gravity 0.94; Mooney viscosity 52 ML1+4, 100 °C). The zinc oxide and stearic acid used as activator, sulphur used as vulcanizing agent, tetramethylthiuram disulfide (TMTD) and mercaptobenzothiazyl disulfide (MBTS) used as accelerator and was purchased from Sigma-Aldrich. Without any further purification, all chemicals were utilised as received.

2.2 Preparation of Nanocomposites

In an open mill mixer, EPDM rubber, styrene-butadiene rubber (SBR), Halloysite nanotubes (HNTs), and other ingredients (zinc oxide, stearic acid, tetramethylthiuram disulfide (TMTD), mercaptobenzothiazyl disulfide (MBTS), and sulphur) were mixed together (50 °C). The friction ratio is maintained in mixer is 1:1.4. Stage 1: Before mixing, rubber was passed 9–10 times between the mill rollers having a less than 1 mm nip gap. Stage 2: After homogenization of both the rubber (i.e., EPDM and SBR), the other ingredients like activator (zinc oxide and stearic acid), accelerator (TMTD and MBTS), and curing agent (sulphur) were added according to Table 1. For preparing various samples of EPDM/SBR blends, the amount of HNTs were different proportion as shown in Table 1. A semi-automated electrically powered hydraulic press was used to shape the composites sheet with a thickness of 2 mm. At a pressure of 30 MPa, the press temperature was held at 160 °C for a 10 min cure time.
2.3 Testing and Characterization of Rubber Composites

EPDM/SBR nanocomposites were tested for tensile properties (tensile strength, elongation at break, and modulus) according to ASTM D-412. At ambient temperature, the tensile properties were calculated using a Universal Testing Machine (UTM) model Dak System Inc., T-72102, series 7200 with a crosshead speed of 500 mm/min. The tear strength is also measured in the same machine and conduction as per ASTM D-624 [10]. The hardness of the composites has been performed as per ASTM D-2240 by the Shore-A Durometer hardness tester. The abrasion characteristics of the rubber composite were measured using a DIN abrader according to ASTM D-5963 and are expressed in terms of volume loss. The swelling resistance was measured using the ASTM D-471 immersion process [12]. At different temperatures of 30 °C, different penetrates such as aromatic, aliphatic, and chlorinated hydrocarbons are used to analyse the swelling properties of the composites. The mole percent uptake was calculated by this Eq. (1)

\[
Q_t (\text{mol}%) = \frac{(M_f - M_i)/MW}{M_i} \times 100
\]  

where, \(M_f\) = Final mass of the composite,
\(M_i\) = Initial mass of the composite.
MW = Molecular weight of the penetrate.

The following eq. (2) [32–34] was used to measure the degree of crosslinking density:

\[
\vartheta (\text{mol/cm}^3) = \frac{1}{2M_c}
\]  

where, \(M_c\) = Molar mass of the polymer between crosslinks.

The Flory-Rehner eq. (3) was used to measure the molar mass between the crosslinks of the composites [32–35]:

\[
M_c (\text{g/mol}) = \frac{-\rho_p V_s V_r^{1/3}}{\ln(1-V_r) + V_r + \chi V_r^2}
\]  

where, \(\rho_p\) = Polymer Density.

\(V_s\) = Molar volume of the solvent (106.3 mL/gmol),
\(V_r\) = Volume fraction of the solvent-swollen filled polymer compound,
\(\chi\) = Interaction parameter of the polymer (0.3) [36], and.
\(V_r\) can be determined by the following eq. (4) [37]:

\[
V_r = \frac{1}{1 + Q_m}
\]  

where, \(Q_m\) = Weight swell of the composites in toluene.

The tensile fractured surface of composites were observed with a Sigma with Gemini Column, CARL ZEISS FE-SEM, USA at the acceleration voltage of 10 kV. The specimen surfaces were coated with gold with thickness of 10–20 nm.

3 Results and Discussion

Figure 1 depicts the stress-strain curves of EPDM/SBR-HNTs nanocomposites. The addition of 2 phr of HNTs to an EPDM/SBR blend resulted in stresses of roughly 8.15 MPa, a 33% increase over the base EPDM/SBR blend, whereas the addition of 10 phr of HNTs to an EPDM/SBR blend led in a

| Sample code | EPDM (phr) | SBR (phr) | HNTs (phr) | Zinc oxide (phr) | Stearic acid (phr) | MBTS (phr) | TMTD (phr) | Sulphur (phr) |
|-------------|------------|-----------|------------|-----------------|-------------------|-----------|-----------|-------------|
| H0          | 80         | 20        | 0          | 4               | 1.5               | 1.2       | 1         | 2.5         |
| H2          | 80         | 20        | 2          | 4               | 1.5               | 1.2       | 1         | 2.5         |
| H4          | 80         | 20        | 4          | 4               | 1.5               | 1.2       | 1         | 2.5         |
| H6          | 80         | 20        | 6          | 4               | 1.5               | 1.2       | 1         | 2.5         |
| H8          | 80         | 20        | 8          | 4               | 1.5               | 1.2       | 1         | 2.5         |
| H10         | 80         | 20        | 10         | 4               | 1.5               | 1.2       | 1         | 2.5         |
stress of 12.78 MPa, a 109% increase over the base EPDM/SBR blend. Furthermore, because to the increased discontinuity in the rubber composite material, the addition of HNTs has reduced the strain % of EPDM/SBR-HNTs composites. Figures 2, 3, 4, 5, 6, and 7 show the mechanical properties of EPDM/SBR-HNTs nanocomposites, with information of mechanical properties such as tensile strength, 100% modulus, elongation at break, tear strength, hardness, and abrasion resistance. From Fig. 2, it is observed that the tensile strength of base rubber is very low strength, which is ineffective in practical application and is why desires to be incorporated by nano-materials. The addition of HNTs to EPDM/SBR-HNTs nanocomposites will increase their tensile strength. When the addition of HNTs is about 10 phr, the tensile strength of rubber nanocomposites is about 109% of that of base rubber blends. Furthermore, as the content of HNTs increased from 0 to 6 phr, the tensile strength increased rapidly due to better dispersion of nano-particles within the EPDM/SBR rubber matrix, and from 8 to 10 phr due to poor interaction, lesser agglomeration, and bonding between HNTs and EPDM/SBR matrix, which is responsible for the slight improvement in HNTs and rubber properties. As a result, the rubber-filler interfacial region’s reinforcing effect of HNTs becomes extremely effective in influencing the tensile strength of EPDM/SBR-HNTs nanocomposites, resulting in increased tensile strength.

Figure 3 shows the modulus with different proportions of HNTs, calculated at 100% elongation. Figure 3 shows that as the HNTs loading in the EPDM/SBR composites increased, the modulus calculated at 100% elongation increased. The modulus at 100% elongation was used to determine the stiffness of the rubber composite. The 100% modulus was primarily influenced by the surface area, scale, and structure of HNTs. As a result, the composite with 6 phr of HNTs had a higher degree of cross-linking (as shown by the crosslinking density test), resulting in a higher 100% modulus. Since the composites filled with a higher amount of HNTs had a lower degree of chemical cross-linking, as shown by the cross-link density property in Fig. 8, the composites filled with a higher amount of HNTs had lower values. Low structural integrity, which is a significant parameter that can affect the characteristics of HNTs’ reinforcing capacity, is also a result of high HNTs material. As a result, when compared to higher amounts of HNTs, the reinforcing impact of HNTs was reduced. The moduli were mostly impacted by the structure and surface area. EPDM/SBR composites filled with 8 phr of HNTs had a 3% decrease in modulus compared to EPDM/SBR composites filled with 6 phr of HNTs filler. However, because a change in modulus frequently has negative effects for applications, the reduced modulus is regarded as a positive.
The effect of HNT loading on elongation at break is depicted in Fig. 4. With the addition of HNTs to the EPDM/SBR composites, the elongation at break decreased. The inter-tubular and interfacial bonding between the HNTs and the EPDM/SBR rubber matrix, as well as the better contact of the HNTs within the rubber matrix, play a key role in reducing the elongation at break. The improved interactions between the nano-filler and the rubber matrix increased the composites' strength and stiffness, reducing their ductility.

Figure 5 shows that as the HNTs were increased, the tear strength of the EPDM/SBR composites increased. The high crosslinking density of the HNTs-loaded composites was responsible for the steady increase in tear strength with the inclusion of HNTs in the composite. As a result, it can be inferred that HNTs inhibited crack propagation, thereby increasing the composites’ resistance. As a result, HNTs with high structural integrity have a fair resistance to crack propagation.

The mechanical property of rubber composites that is most significant is their hardness. Figure 6 illustrates the hardness of EPDM/SBR-HNT composites. The hardness of the composites varies depending on the amount of HNTs present. It begins at 53 Shore-A for unloaded compounds and steadily increases as the amount of HNTs in the HNTs nanofiller filled EPDM/SBR composites increases. The degree of cross-linking has a significant effect on the hardness of a compound. Furthermore, the HNTs’ lower active surface area may have increased cross-links, which increased the composites hardness. The mechano-chemical grafting of EPDM/SBR molecular chains on the HNTs surfaces and the stretching orientation of HNT in EPDM/SBR-HNTs composites may be responsible for the enhancement of characteristics.

The abrasion loss of EPDM/SBR composites reinforced with HNTs is shown in Fig. 7. The abrasion resistance increases as the content of HNTs increases. This is due to the reinforcing effect of HNTs, which resulted in a stronger...
rubber-filler network. Furthermore, increasing the crosslinking density made the composites stiffer and more abrasion resistant.

The mole percent uptake of the rubber composites in different solvent (aromatic, aliphatic and chlorinated) at 30 °C are shown in Table 2. The mole percent uptake was considerably decreased for HNTs reinforced composites as compared to neat EPDM/SBR blends. The higher HNT reinforcement in the EPDM/SBR rubber matrix limits the swelling-induced expansion of the rubber chains. This makes it very difficult for the solvent to penetrate the gaps between the rubber molecules, lowering the mole percent uptake. Hence, the rubber blend composites have higher solvent barrier properties compared to neat EPDM/SBR blends. The trend was in the order of: dichloromethane > chloroform > benzene > toluene > xylene > mesitylene > n-pentane > n-hexane > carbon tetrachloride > n-heptane > n-octane. The higher molecular weight of solvent exhibited the lowest absorption and vice-versa. From the Table 2, mole percent uptake trend was in order of: chlorinated > aromatic > aliphatic.

The crosslinking density was calculated by the help of equilibrium swelling measurement. A sample dimension about 250x250x2 mm was cut from the rubber sample. To assess the crosslinking density, EPDM/SBR composites were soaked in toluene for three days at 23 °C, with the toluene being replaced with new solvent (toluene) every day. An immersion test is performed to examine the nanofiller-rubber matrix interaction. Figure 8, shows the molecular weight of the polymer between the crosslinks (M_c) and crosslinking density of EPDM/SBR blend composites with different proportion of HNTs. The obtained result shows an increasing trend in crosslinking density after loading the HNTs. The crosslinking density is determined in part by the molecular weight of the polymer between the crosslinks (M_c). The M_c values of HNTs filler filled EPDM/SBR nanocomposites are lower than those of unfilled EPDM/SBR nanocomposites. With increased HNTs content, the molar mass between crosslinks (M_c) decreased. The accessible volume between consecutive crosslinks reduced as the M_c values declined. As the amount of HNTs in the EPDM/SBR-HNTs nanocomposites increased, the crosslinking density also increased. Tensile strength, tear strength, hardness, and abrasion resistance are all improved by increasing crosslinking density.

The FE-SEM micrograph of the fractured tensile surface are shown in Fig. 9 (a) HNTs Fig. 9 (b) EPDM/SBR blends, (c) EPDM/SBR composites containing 6 phr HNTs and (d) EPDM/SBR composites containing 10 phr HNTs. The image of HNTs is shown in Fig. 9 (a), showing the tube-like dimension and the nature of the tubes. It can be concluded that the tensile fractured morphology surface of unfilled EPDM/SBR was relatively smooth (Fig. 9 (b)). For EPDM/SBR reinforced with 10 phr composite, the tensile fractured surface exhibited notable undulating stripes and rough characteristics (Fig. 9 (d)). In comparison, the tensile fractured surface of EPDM/SBR reinforced with 6 phr HNT shows large deformation and many tear folds (Fig. 9(c)), and no noticeable curatives (zinc oxide, stearic acid, sulphur, etc) particles were observed, showing excellent compatibility and good interfacial bond strength between HNTs and EPDM/SBR compound due to the

| Sample code | Mole percent uptake (mol%) | Aromatic | Aliphatic | Chlorinated |
|-------------|---------------------------|----------|-----------|-------------|
|              | Benzene | Toluene | Xylene | Mesitylene | n-pentane | n-hexane | n-heptane | n-octane | Dichloromethane | Chloroform | Carbon tetrachloride |
| H0          | 3.95    | 3.57    | 3.46    | 3.03      | 2.42      | 2.34      | 2.28      | 2.24      | 5.42           | 4.56       | 2.26              |
| H2          | 3.65    | 3.28    | 2.71    | 2.46      | 2.16      | 2.02      | 1.95      | 1.87      | 4.86           | 4.17       | 1.94              |
| H4          | 3.63    | 3.25    | 2.67    | 2.39      | 2.03      | 1.98      | 1.81      | 1.756     | 4.62           | 4.17       | 1.86              |
| H6          | 3.59    | 3.17    | 2.63    | 2.36      | 1.96      | 1.95      | 1.83      | 1.72      | 4.56           | 4.08       | 1.75              |
| H8          | 3.58    | 3.14    | 2.65    | 2.35      | 2.04      | 1.92      | 1.86      | 1.8       | 4.54           | 4.03       | 1.87              |
| H10         | 3.52    | 3.09    | 2.59    | 2.28      | 1.92      | 1.87      | 1.78      | 1.74      | 4.42           | 3.86       | 1.76              |
SiO$_2$-Al$_2$O$_3$ present in the HNTs filler, which was reliable with the improved tensile strength of the composite.

4 Conclusions

EPDM/SBR with various HNT loadings was prepared in this research, tensile properties, tear strength, hardness, abrasion, and swelling resistance tests were conducted and analyzed. Compared with EPDM/SBR blend, addition of HNTs resulted in 109% increase of tensile strength, 45% increase of 100% modulus and 11% increase of hardness. The improved interactions between the nano-filler and the rubber matrix increased the composites’ strength and stiffness, reducing their ductility. The HNTs were found to act as a reinforcing agent in the crosslinking process.
Acknowledgements The authors thank Dr. G. Anand, Department of Mechanical Engineering, MVJ College of Engineering, Bangalore, India for her continuous support and encouragement throughout the work. We are grateful to MAEON Laboratories Section, Chennai for her help in preparing the materials and Technical Support for providing the set-up of all testing.

Authors’ Contributions All authors of this research paper have directly participated in the planning, execution, or analysis of this study.

Availability of Data and Materials Not Applicable.

(c) EPDM/SBR-HNTs composites containing 6 phr HNTs

(d) EPDM/SBR-HNTs composites containing 10 phr HNTs

Fig. 9 (continued)
Declarations

Ethics Approval and Consent to Participate  Research involving No Human Participants and Animals.

Consent for Publication  The contents of this manuscript have not been copyrighted or published previously. The contents of this manuscript are not now under consideration for publication elsewhere.

Competing Interests  The authors declare no conflict of interest.

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