

Studies on the mechanical properties of carbon black-halloysite nanotube hybrid fillers in nitrile /PVC nanocomposites for oil seal applications

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Abstract— In the present work ,NBR/PVC conventional composites containing 70phr Carbon black(CB) and NBR/PVC hybrid nanocomposites containing a fixed amount of CB (60phr) and varying amount of halloysite nanotubes(HNT) with 0 to 6phr were prepared by melt -mixing method using a two roll open mill. The effect of CB-HNT hybrid fillers on the morphology and mechanical properties of the NBR/PVC composites have been investigated. The tensile strength ,elongation at break, 100% modulus, swelling ratio and tear strength of the NBR/PVC hybrid nanocomposites are increased by 12.87%,13.91 %,14.54%, 25.97 % and 33.72 % respectively compared to the conventional composites .Hardness and Compression set have significantly improved compared to the conventional composites .XRD studies reveal the intercalation of NBR/PVC chains ,CB and other ingredients into the HNT galleries and formation of intercalated structures. Synergistic effect of CB-HNT hybrid fillers, improved NBR/PVC-CB-HNT interfacial interactions and formation of intercalated structures are believed to be responsible for the superior mechanical properties of the NBR/PVC hybrid nanocomposites.

Keywords—Oil seal,NBR/PVC,Halloysite nanotube,Intercalation,Mechanical properties.

I. INTRODUCTION

Carbon black is the oldest and most promising reinforcing filler in the rubber industry. Its depleting and hazardous nature, consumption in larger amounts and black colour to achieve optimum mechanical properties have prompted the scientists to develop alternative fillers, either partially or wholly these conventional fillers. However the continued demand for novel, cheap, weightless environmentally-friendly fillers have become a serious threat to the industries and researchers. Very recently the concept of hybrid fillers especially with the embodiment of nanofillers is gaining momentum. It was divulged that the multiphase hybrid filler was able to conserve the superior properties of all fillers, as well as exhibited process synergistic effect in polymeric and elastomeric systems due to compatibility and co-operative interactions at the nanoscale level[1]. As a result, hybrid filler systems containing CB and CNT[2],CB and nanoclay[3] and CB and nanographene/graphene oxide[4]were developed and the resulting rubber nanocomposites demonstrated remarkable improvement in properties taken for their studies.

Halloysite nanotubes (HNT) are naturally occurring aluminosilicates with the molecular formula of $Al_2Si_2O_5(OH)_4.nH_2O$.They are multi walled kaolinite

nanotubes with high aspect ratio, low surface energy(due to the presence of low density hydroxyl groups on its surface) with reduced filler/filler aggregation. Owing to these unique attributes, HNT has received growing interest as promising filler for several rubber matrices including natural rubber[5],styrene butadiene rubber[6],ethylene propylene diene monomer[7],silicone rubber[8],fluoroelastomers[9] and nitrile rubber[10].

Studies pertaining to the synergistic effect of CB and HNT in rubber systems is scarce. Ismail et al.[11-12] have studied the effect of partial replacement of CB with HNT in natural rubber and nitrile rubber. The authors in their previous works have demonstrated that strong NBR-CB-HNT interactions have resulted in better mechanical properties in NBR-CN-HNT hybrid nanocomposites[13].

Acrylonitrile butadiene copolymer(NBR)/Polyvinyl chloride (PVC) blend is a miscible physical mixture of commercial importance. The elastomeric component NBR acts a permanent plasticizer for PVC applications in which PVC improves the chemical resistance, thermal aging and abrasion resistance of NBR which enables the use of this blend as gasket, wires and cables, manufacture of soles, footwear, leather and artificial leather[14].In recent years, NBR/PVC nanocomposite systems containing CNT[15],

nanoclay[16], nano graphite and nano copper[17] has been extensively used. To the best of the knowledge of the authors, there is no work in the literature concerning the effect of CB-HNT hybrid filler system on NBR/PVC nanocomposites.

The aim of this present work to prepare NBR/PVC hybrid nanocomposite by partially replacing 10phr of CB in NBR/PVC conventional composite(containing 70phr of CB) with 2,4 and 6phr of HNT loading. The synergistic effect of CB and HNT hybrid fillers on the morphology and mechanical properties of NBR/PVC hybrid nanocomposites is also reported in this article.

II. MATERIALS AND METHODS

2.1 Materials

NBR/PVC(70:30),Vinoprene-731 [Mooney viscosity ML (1 + 4) at 100°C: 45] is purchased from BP Chemicals, India. HNT with an average tube diameter of 50 nm are received from Sigma Aldrich, Germany. Carbon black(N550),Zinc oxide(ZnO), Sulphur, Stearic acid, tetramethyl thiuram disulphide (TMTD) and 2-Mercapto benzothiazole(MBTS) of industrial grade are supplied by Ramcharan Chemicals, India and used as received

2.2 Preparation of NBR/PVC conventional and hybrid composites

Table:2

Ingredients (Phr ^a)	CB70	CB60- HNT2	CB60- HNT4	CB60- HNT6
NBR /PVC	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
TDQ	1	1	1	1
FEF N550	70	60	60	60
HNT	0	2	4	6
DOP	8	8	8	8
Sulphur MC	1.5	1.5	1.5	1.5
MC Wax	2	2	2	2
MBTS	1.5	1.5	1.5	1.5
TMT	0.15	0.15	0.15	0.15

The compounding of NBR/PVC,CB,HNT and other ingredients is done on a laboratory sized open two roll mill(160 mm x 320 mm) at room temperature and at a speed ratio of 1:1.4as per ASTM D3182 according to the formulation listed in Table 1.Processing aids and rubber are first blended. Then HNT, CB and curatives are added orderly. The samples are then cured at 160°C in an electrically heated hydraulic press for their respective cure times (t_{90}) determined from oscillatory disk rheometer measurements.The samples are designated as NBR-CBx-HNTy respectively according to the content of CB and HNT in the composites .

2.3 X-ray Diffraction studies

The XRD measurements of HNT and hybrid nanocomposites were performed using Rigaku Ultima IV X-ray diffractometer (Rikagu, Japan)with CuK α radiation ($\lambda=1.54016\text{\AA}$)operating at 60kV over the range of 2θ varying from 5° to 20° with a scanning rate of 2°/min.

2.4 Field Emission Scanning Electron Microscopy

Morphology of HNT and tensile fracture surface of NBR conventional and hybrid composites are observed under a SUPRA – 55 (CARC ZEISS, Germany) Field Emission Scanning Electron Microscope (FESEM) with energy dispersive X-ray (EDX) attachment. The samples are sputter coated with gold before analysis.

2.5 Swelling test

Samples with dimensions of 50 x 30 x 2 mm³ were immersed in toluene at room temperature for 72 h. The swelling percentage is given

Where w_1 is the weight of the samples before swelling and w_2 is the weight of the samples after swelling.

2.6 Tensile properties

Dumbbell shaped samples are cut from compression moulded sheets according to ASTM D412 for tensile testing . The tests were conducted on a universal testing machine (Dak system Inc.,7200) at a crosshead speed of 500mm/min. Five samples are taken for each compound and their averages were reported.

2.7 Tear strength

Tear tests were conducted according to ASTM D-624 on a universal testing machine (Dak system Inc.,7200) at a crosshead speed of 500mm/min. Five samples are taken for each compound and their averages were reported.

2.8 Hardness

The hardness of NBR hybrid composites are measured as per ASTM D 2240 test method with a shore A hardness tester. Six readings are taken from different areas of the testing samples and the average value is determined.

2.8 Compression set

Compression set of NBR hybrid composites are determined using cylindrical samples of 29 mm diameter and 12.5 mm thickness in accordance with ASTM D395.

III. RESULTS AND DISCUSSION

3.1 Microstructure of NBR conventional and hybrid composites

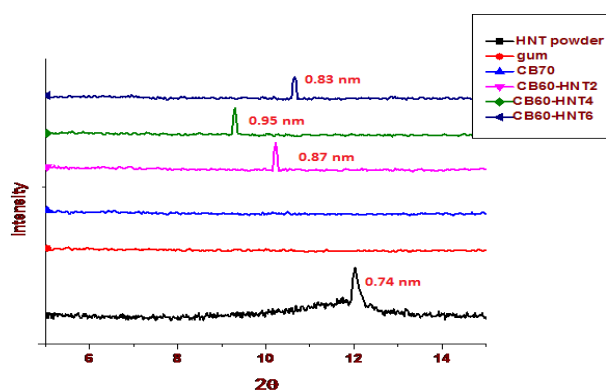


Figure:1

XRD patterns of HNT and NBR/PVC conventional and hybrid composites are represented in Fig.1. The values of 2θ and their relative basal spacing are also given in Table. 2. The HNT shows a diffraction peak at $2\theta = 12.02^\circ$ and the corresponding d_{001} basal spacing is 0.735nm. Further it can be noted from the Fig.1 for the NBR/PVC hybrid composites, the 001 reflection peak for HNT is shifted to lower angles with d_{001} basal respectively for 2,4 and 6phr of HNT content. This peak located at a lower angle confirms the formation of limited intercalated structures. This reduction of 2θ and increase in interlayer spacing can be attributed to the adsorption of curatives such as ZnO and stearic acid in HNT galleries and inter tubular diffusion of NBR/PVC and CB into HNT tubules. Similar observations are reported in EPDM/HNT[7] and NBR-CB-HNT systems[13].In comparison, no peak was found in the XRD curve of NBR/PVC conventional composites containing CB within the range of 1~ 15 because the characteristic length of CB ordering is beyond such range[18].

Table 2. X-ray diffraction pattern of HNT & NBR/PVC hybrid composites

Sample	0 0 1	
	2θ(degrees)	d(nm)
HNT powder	12.01	0.74
CB60-HNT2	10.22	0.87
CB60-HNT4	9.29	0.95
CB60-HNT6	10.64	0.83

3.2 Morphological characteristics

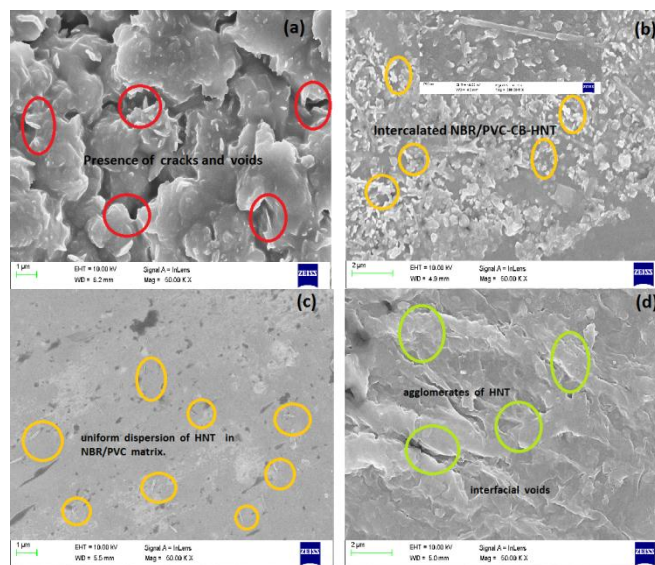


Fig. 2. FESEM images of a) NBR –PVC-CB70, (b)NBR-PVC-CB60-HNT2(c)NBR-PVC-CB60-HNT4 and (d)NBR-CB60-HNT8

To verify the interfacial interactions in NBR/PVC hybrid composites, the morphology of the tensile fracture surface were characterized by FESEM. Fig.2(a) shows a flat surface for NBR conventional composites with some cracks and void with good adhesion of CB particles to NBR /PVC matrix. Fig.2(b-c) exhibits a relatively rough surface for NBR/PVC hybrid composites with no cracks and voids and better dispersion of HNT in the NBR/PVC matrix. With the incorporation of CB particles into the NBR/PVC matrix, there is a susceptibility for inter-tubular diffusion for CB particles and other ingredients into the HNT lumen. As a result HNT forms an intercalated structure with CB and NBR/PVC which can be validated by XRD peaks at lower angles. Further it can be noticed that intercalated structures are projected as ruptured fibres as shown in Fig.2(b) suggesting the formation of local CB-HNT filler network and strong NBR/PVC-CB-HNT interfacial adhesion[19]. Formation of intercalated structure and good interfacial NBR/PVC-CB-HNT interaction promote efficient stress transfer resulting in a relatively rough surface without cracks in hybrid composites. Increase in HNT loading beyond 4phr causes formation of large agglomerates of HNT and interfacial voids in the NBR/PVC matrix as can be seen from fig 2(d) .Thus it can be concluded that the concentration, dispersion and interfacial characteristics of the filler particles with the surrounding matrix are the most crucial factors in determining ultimate properties of resulting composites.

3.3 Swelling behaviour

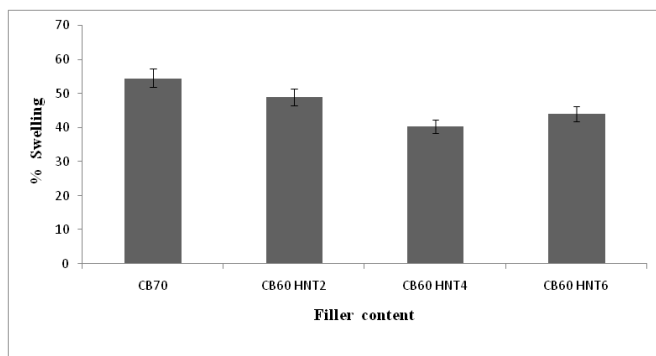


Fig.3. Percentage swelling of NBR/PVC conventional and hybrid nanocomposites.

The swelling percentage (Q_s) is an indication of cross link density of NBR/PVC conventional and hybrid nanocomposites and the Q_s curve is shown in Fig. 3. It can be seen that Q_s of NBR/PVC hybrid nanocomposites decreases with addition of HNT loading up to 4phr and then increases. However, it can also be observed that all NBR/PVC hybrid composites have lower Q_s values compared to that of NBR/PVC conventional composite. This indicates increment in the crosslink density of the hybrid nanocomposites[11]. This can be attributed to strong NBR/PVC-CB-HNT interactions which promotes a tortuous path for the diffusion of solvent and hence lower Q_s .

3.4 Tensile properties

The tensile strength of NBR/PVC conventional composites and hybrid nano composites are shown in Fig.4. From the Figure, it is evident that tensile strength of hybrid nanocomposites increases with the partial replacement of CB by HNT in the NBR/PVC matrix. The tensile strength of NBR/PVC-CB60-HNT4 has increased by 12.87 % compared with the NBR/PVC conventional composite. This improved performance of nanocomposites in terms of tensile strength is attributed to enhanced NBR/PVC -CB and NBR/PVC-CB-HNT interactions. Further high aspect ratio(L/D) and large surface area of HNT promote strong physical interaction with CB particles and favours formation of cross links. Moreover as HNTs were added prior to CB particles in NBR/PVC matrix, there might be more chance for diffusion of CB particles, NBR/PVC and other ingredients into HNTs. As a result CB particles and HNTs may form local hybrid filler networks confining the rubber to form more entangled structures which is responsible for high performance of NBR/PVC hybrid nanocomposites. Similar results were observed in Natural rubber-CB-organoclay systems[20].

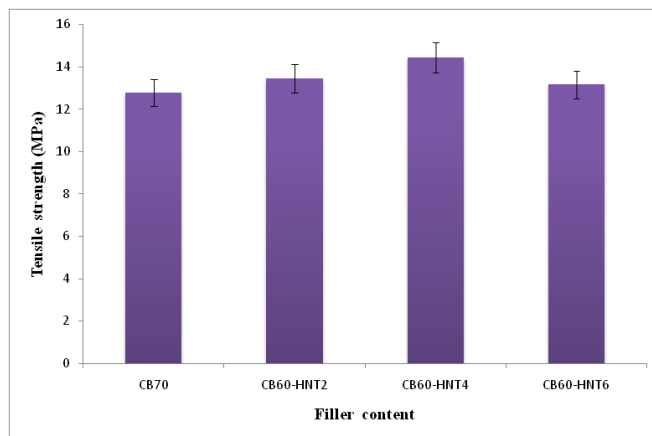


Fig.4. Tensile strength of NBR/PVC conventional and hybrid nanocomposites.

The % elongation at break of CB filled conventional composite is 160.64. Addition of 4phr HNT loading to conventional composites enhanced the elongation at break to 182.04 (an increase of 13.91 %).

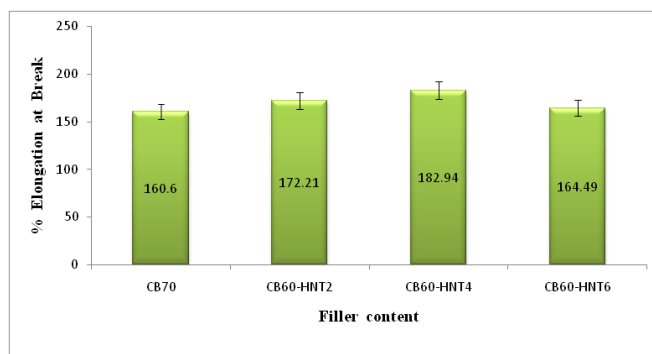


Fig.5. Percentage elongation at break of NBR/PVC conventional and hybrid nano composites.

This enhancement is attributed to improved rubber-filler interactions causing rubber to absorb more energy which can be used to decoil chains to a greater extent thus giving the hybrid composite a higher value of percentage elongation at break[21].

100 % modulus of the hybrid nanocomposites shown in Fig.6 demonstrates an increasing trend as the HNT content increases from 0 to 6phr. This enhancement in modulus is due to strong NBR/PVC-CB-HNT interfacial interactions and formation of intercalated structures[13].

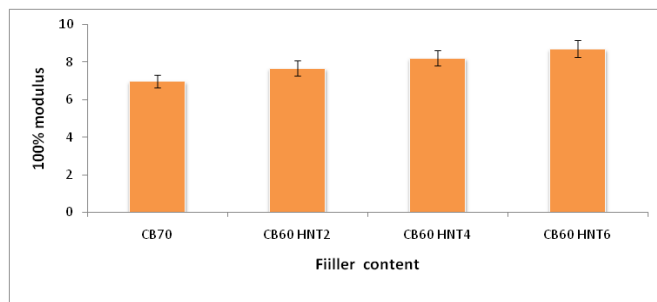


Fig.6. 100 % modulus of NBR/PVC conventional and hybrid nanocomposites.

3.5 Tear strength

In case of tear strength of the NBR-CB-HNT nanocomposites presented in Fig.7, it is observed that the tear strength increases from 30.17 N/mm to 37.14 N/mm (an increase of 23%) as the HNT loading increases from 0 to 4phr. This effect can be attributed to the randomly oriented HNTs act as bridging elements offering strong resistance to crack initiation and crack propagation and thereby prevent failure at low stresses[22]

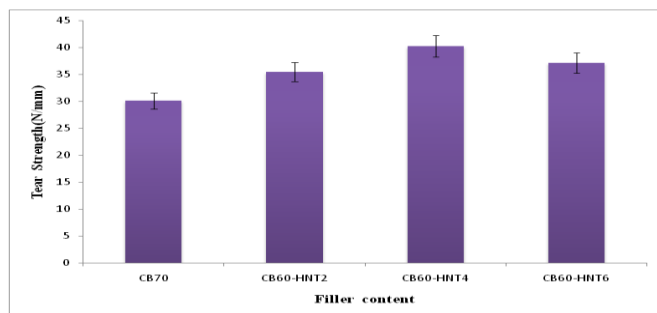


Fig.7. Tear strength of NBR/PVC conventional and hybrid nanocomposites.

3.6 Hardness

Hardness of the composites are presented in Fig.8. Hardness depends upon the crosslink density. With the addition of HNT upto 4phr into the NBR hybrid nanocomposites, the crosslink density increases consequently causing an increase in hardness[23].

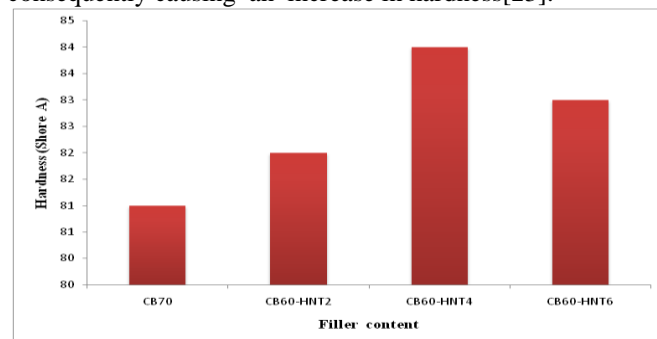


Fig.8. Hardness(Shore A) of NBR/PVC conventional and hybrid nanocomposites.

3.7 Compression set

From Fig.9, it is clearly evident that compression set of the NBR/PVC hybrid composites decreases with increase in HNT loading from 0 to 4 phr. The better performance of NBR-CB-HNT nanocomposites in terms of compression set can be attributed to formation of permanent cross-linked chains networks. These networks which are unable to relax during compression state cause elastic recovery during recovery stage[24].

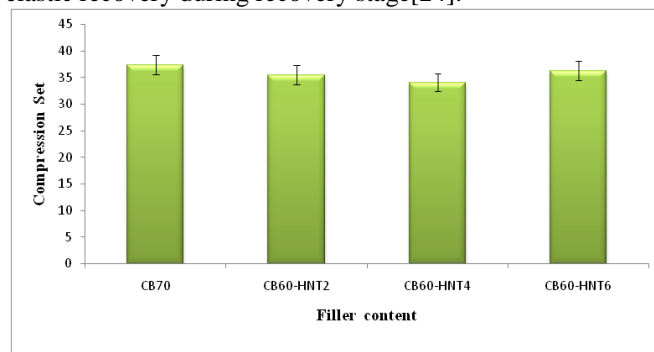


Fig.9. Compression set of NBR/PVC conventional and hybrid nanocomposites

IV. CONCLUSION AND FUTURE SCOPE

In this work NBR/PVC hybrid nanocomposites were prepared with different loading from 0 to 6phr. X-ray diffraction studies revealed inter-tubular diffusion of NBR/PVC and CB and other ingredients into the lumen of HNT and formation of limited intercalated structures. Improved NBR/PVC-CB-HNT interfacial interactions and formation of intercalated structures are the main reasons for the simultaneous improvement in tensile strength, tear strength, stiffness and ductility and superior performance in terms of compression set. The following conclusions are derived from the studies of CB-HNT hybrid fillers on NBR/PVC chains.

1. Tensile strength increases by 12.87 %
2. Elongation at break increases by 13.91%
3. 100 % modulus improves by 23.22 %
4. Tear strength enhances by 33.72 %
5. Swelling ratio improves by 25.97 %
6. Improvement in hardness and compression set

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