Journal of Nano Research
ISSN: 1661-9897, Vol. 45, pp 208-217
doi:10.4028/www.scientific.net/JNanoR.45.208

Submitted: 2016-07-13
Revised: 2016-10-07
Accepted: 2016-10-13
Online: 2017-01-13

Synthesis and Characterization of Carbon Black-Halloysite Nanotube Hybrid Composites Using XRD and SEM

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Keywords: Carbon Black, Halloysite Nanotubes, Mechanical Properties, XRD, SEM

Abstract: Composite materials are the leading emerging materials over the past twenty years since its introduction. Among the natural composites, carbon black-halloysite nanotubes hybrid composite is one of the recent emerging sector in the composite field, because of its high strength with less density as compared to the metal matrix composite. In this research carbon black-halloysite nanotubes hybrid composites based on synthetic rubber copolymer of acrylonitrile and butadiene were prepared and tested. The carbon black loading was kept fixed at sixty per hour and halloysite nanotube loading was varied from zero to ten parts per hundred rubbers per hour. The effect of carbon black-halloysite nanotube hybrid fillers on the curing behaviour, mechanical properties and morphology of the high nitrile rubber nanocomposites were investigated. The cure characteristics showed that the scorch time and cure time increased with the halloysite nanotube loading. The maximum torque exhibited an increasing trend from zero to six per hour. The tensile properties which exhibited an increasing trend until an optimum loading of six per hour were mainly influenced by the high nitrile rubber-carbon black-halloysite nanotube interaction and the intercalation of rubber and carbon black into the tubules. X-ray diffraction test and scanning electron microscope studies were supported to the results obtained.

Introduction

The natural composites are providing numerous advantages because of their better corrosion resistance, excellent mechanical properties and high strength to weight ratio and also the composite materials play an important role in maintaining the ecofriendly environment. Polymer nanocomposites with reinforced rubber are a remarkable development in the field of engineering materials. The applications of composite materials have significantly increased in Defense, Aeronautical Automobiles etc. In composite material development, nano particles reinforcement and reinforcement rubber are the most recent methods developed [1]. In order to acquire desired results natural materials alone do not meet requirements, but along with the composite materials challenges should be met. Strength properties in natural composites are slightly higher than the metal matrix such as steel and aluminum and it also provides less vibration transmission than the metals [2]. Reinforcement of rubber is expressed by the enhancement of modulus, failure properties and abrasion resistance of the vulcanisates. Fillers are mainly added to improve certain properties. Among the various fillers, carbon black and silica are the main reinforcing agents widely used in rubber industries [3-4]. However continued demand for lower cost, low weight and environmentally friendly reinforcing fillers still poses a big challenge to the rubber industries. Very recently the concept of hybrid fillers especially with the inclusion of nanosized particle has drawn the attention of many researchers [5]. It has been demonstrated that the multiphase hybrid filler not only retains the advantages of all fillers but also exhibits processing synergistic effect in polymers and elastomer due to co-operative interaction at nanoscale. Recently Halloysite Nanotubes (HNT) has become the topic of research attention as a new category of additive for improving the mechanical and thermal performance of polymers [6-10].

Polymer materials like polypropylene, epoxy resin, polyethylene, nylon, polyvinyl chloride, polyvinyl alcohol, natural rubber and various synthetic rubbers are used in these nanocomposites [11-12]. A number of experimental results showed that the amalgamation of Carbon Nanotubes (CNT) with polymers signifies an attractive path to tailor electrical properties. Tensile strength as well as electrical conductivity improvement in multiwall carbon nanotube elastomers was demonstrated [13-17]. A thermo-mechanical model was developed to illustrate the hyper-elastic response of filled rubbers over a wide range of temperatures. In addition, the prediction ability of this proposed constitutive model is verified by comparison with test data issued from the mechanical experiments [18-19]. In recent time's halloysite nanotubes, a naturally occurring aluminosilicate has been used as potential nano reinforcement for elastomers such as natural rubber, styrene butadiene rubber and nitrile rubber to improve the mechanical and thermal properties of the composites [20-21]. Xu Li et al, have credited enhanced tensile properties in Natural Rubber (NR)/ Carbon Black (CB) nano components to the strain induced crystallization of NR by clay layers [22]. In earlier studies the effects of silicone rubber hardness and HNT loading on the cure characteristics, dynamic mechanical, thermal and mechanical properties of the resulting rubber compounds were systematically studied and the results were correlated with the microstructure of the samples as investigated by XRD and SEM analyses [23-25].
Based on the above literature in this research carbon black/HNT hybrid nanocomposites were prepared and the combined effect of CB/HNT hybrid filler system on the mechanical properties of nitrile rubber composites were investigated by ASTM standards and characterized by XRD and SEM.

Experimental

Materials and Sample Preparation: Acrylonitrile butadiene rubber (NBR) with acrylonitrile content of 41% is a medium high nitrile rubber and Mooney viscosity ML (1+4) at 100ºc of 35 Mooney units was used as the matrix. The halloysite nanotubes with an average tube diameter of 50 nm were procured from Sigma Aldrich and carbon black (N550), zinc oxide, stearic acid, sulphur, tetramethylthiuram disulphide and 2-mercaptobenzathiazole were purchased from local markets. The nanocomposites were prepared by mixing using a two-roll open mill. The composition of NBR, CB, HNT and other elements was done on a laboratory scale of 160 mm x 320 mm by open two roll mill at the room temperature and at a speed ratio of 1:1.4 as per the ASTM method A370-12 according to the compositions listed in Table 1. Initially the processing supports and rubber were mixed together and then HNT, CB and curatives were added. The samples were then cured at 160ºc in an electrically heated hydraulic press for their respective cure times (t90) determined by an oscillatory disk rheometer measurement.

Strength Measurements: As per the dimensions of ASTM standards the tensile, compressive, modulus and hardness test were carried out for the above fabricated material in our laboratory. Oscillating disc rheometer (Ekt-100h) was used to determine the cure characteristics of each NBR hybrid nanocomposites at 160ºC. The cure time (t90), scorch time (ts2) and maximum torque were obtained according to ASTM A370-12. Tensile testing of prepared specimen according to ASTM A370-12 type dumbbell shaped samples were carried out using Instron 5566 universal testing machine at a crosshead speed of 500mm/min. Hardness is a measure of how resistant the solid matter could change the various kinds of permanent shape when force is applied. The hardness test was carried out for the NBR hybrid composites as per ASTM standard test method. Dimension of 12.5 mm thick and 29mm diameter of NBR hybrid composite specimen should be enough for hardness testing and there is no ASTM standard for specimen cutting. Similarly the compression of the NBR hybrid composites was determined with a sample size of 12.5 mm thickness and 29 mm diameter.

X-Ray Diffraction Test (XRD): The test was performed on X ray diffractometer (X pert Phillips) for nitrile rubber hybrid composite samples to study the interlayer separation. XRD is the best tool to characterize the structure of high nitrile rubber hybrid composites. The test was carried out with a current of 100 mA and a voltage of 30kV. The prepared composite samples were subjected to XRD 2θ scanning range from 5° to 40°.

Scanning Electron Microscope (SEM) Test: The morphologies of the nanocomposites samples were observed by SEM (HITACHI S- 3000N) at different magnifications. The Morphology of halloysite nanotubes and the tensile fracture surface of nitrile rubber-carbon black-halloysite nanotube composites were observed under field emission SEM.

Table 1. Composition of Nitrile Rubber, Carbon Black, HNT and Other Elements

Elements	Quantity (per hour)					
	HN_0	HN_1	HN_2	HN_3	HN_4	HN_5
High Nitrile Rubber (NBR)	100	100	100	100	100	100
Carbon Black (C)	60	60	60	60	60	60
Halloysite Nanotubes (HNT)	0	2	4	6	[illegible]	10
Zinc Oxide (ZnO)	5	5	5	5	5	5
Stearic Acid ($C_{18}H_{36}O_2$)	1	1	1	1	1	1
Dioctyl Phthalate ($C_{24}H_{38}O_4$)	6	6	6	6	6	6
Sulphur (S)	1.5	1.5	1.5	1.5	1.5	1.5
Dibenzothiazyl Disulfide ($C_{14}H_8N_2S_4$)	1.5	1.5	1.5	1.5	1.5	1.5
Trimethyltryptamine ($C_{13}H_{18}N_2$)	0.15	0.15	0.15	0.15	0.15	0.15

Results and Discussion:

Cure characteristics: It can be seen that the cure characteristics of carbon black/ halloysite nanotubes filled with NBR composites, cure time t90 and scorch time ts2 of NBR hybrid composites increases when halloysite Nanotube content increases. This is due to the absorption of curatives by halloysite nanotubes onto its surface and additionally into its lumen which resulted in longer scorch and cure time. The minimum torque of NBR hybrid composites increases with increasing HNT content nearly by about 1%. This is most likely due to the interactions between nitrile rubber-carbon black- halloysite nanotubes. It can also be seen that the maximum torque of NBR hybrid composites increases gradually as HNT content increases up to six per hour. This may be due to the reduction in the mobility of the macromolecular chains caused by the occurrence of both the fillers. The cure characteristics of carbon black-halloysite nanotubes hybrid composites are given in Table 2.

Table 2. Cure Characteristics of Carbon Black-Halloysite Nanotubes Hybrid Composites

Element Sample	Cure Time (t90) (Secs)	Burn Time (ts2) (Secs)	Minimum Torque in deci Newton meter (dNm)	Maximum Torque (dNm)
HN_1	2.21	0.57	1.51	16.01
HN_2	2.25	0.573	1.58	16.08
HN_3	2.27	0.59	1.64	16.11
HN_4	2.28	0.591	1.71	16.07
HN_5	2.39	0.605	1.80	16.04

Mechanical Properties: Based on the test and experimental analysis, the following results and discussions were made with the help of the following charts. The tensile strength of carbon black-halloysite nanotubes hybrid composites for different samples is shown in Figure 1. The tensile strength increased as the HNT loading increased from 0 to 6 per hour. This is due to enhanced Nitrile rubber-carbon black-halloysite nanotube interaction and formation of filler network due to the association of carbon black particles with halloysite nanotubes. Normally strong interactions allow more efficient load transfer and hence better mechanical performance as stated in the earlier research reports. However the tensile strength decreased after 6 per hour loading due to aggregation of fillers. The elongation at break of high nitrile rubber hybrids also increased as the halloysite nanotubes loading increased from 0 to 6 per hour as shown in Figure 2. This is due to the unique behavior of halloysite nanotubes and enhanced filler polymer interactions, which improves both the stiffness and ductility of the composites.

Fig. 1. Tensile Strength for High Nitrile Rubber Hybrids

Fig. 2. Percentage of Elongation at Break for High Nitrile Rubber Hybrids

The 100% of tensile modulus of NBR hybrid composites were calculated for all the samples as per the ASTM standards and the results were shown in following Figure 3. From the results it was found that there is an increasing trend from 0 to 6 per hour and after an optimum loading of 6 per hour, the tensile modulus decreased. The improvement in the modulus of the composites is due to strong Nitrile rubber-carbon black-halloysite nanotube interaction on the surface and inner wall of halloysite nanotubes as well as intercalated structure of Nitrile rubber-carbon black-halloysite nanotube.

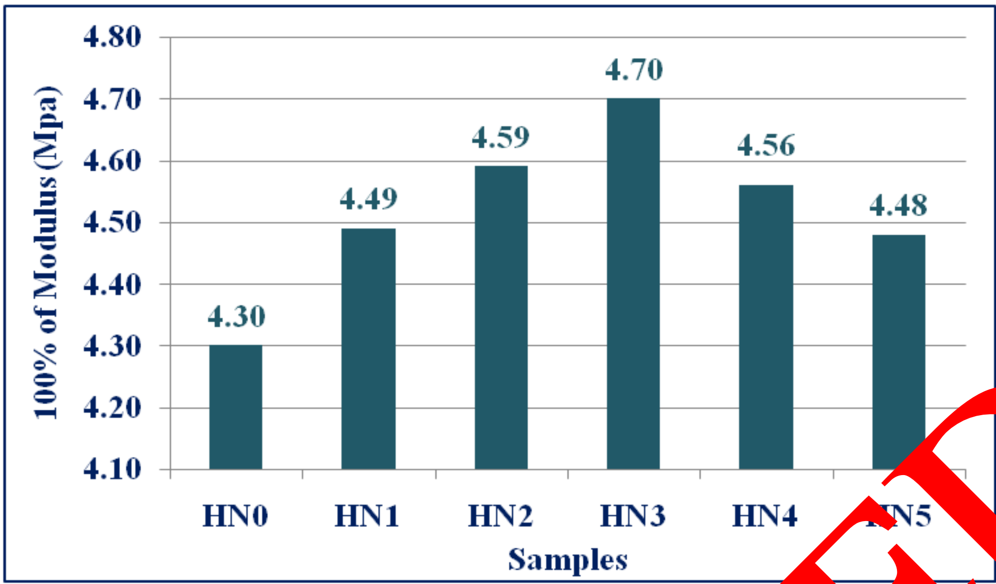

Fig. 3. 100% of Modulus for High Nitrile Rubber Hybrids

Hardness of NBR hybrid composites was tested using International Rubber Hardness Degree (IRHD) testing machine and the results are given in Figure 4. It is explored that the hardness of the composites depends upon their crosslink density. In our analysis the HNT content in the hybrid filler composites increases from 0 to 6 per hour, the crosslink density also increases consequently causing an increase in hardness.

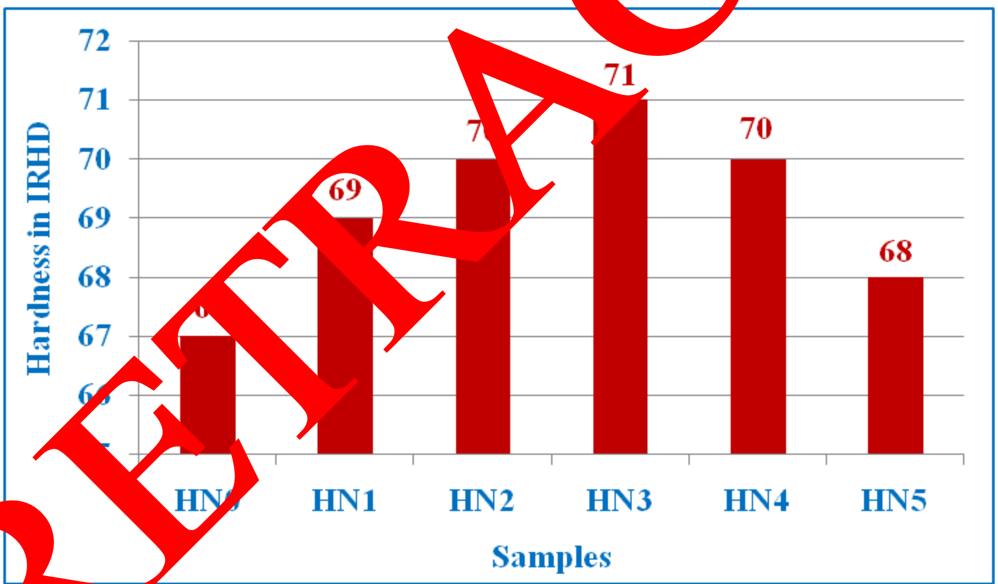

Fig. 4. IRHD Hardness for High Nitrile Rubber Hybrids

The compression set of NBR hybrid composites is analyzed and the results are given in Figure 5. Compression set is a measure of the ability of rubber vulcanizes to retain its elastic properties after pro-longed compression at constant strain under a specific set of condition. From the observed results, it is clearly evident that the compression set of the NBR hybrid composite decreases with increase in HNT loading from 0 to 6 per hour. The better performances of rubber compounds in terms of compression set is accredited to cross linked chains forming a permanent network and are unable to relax during the compression stage.

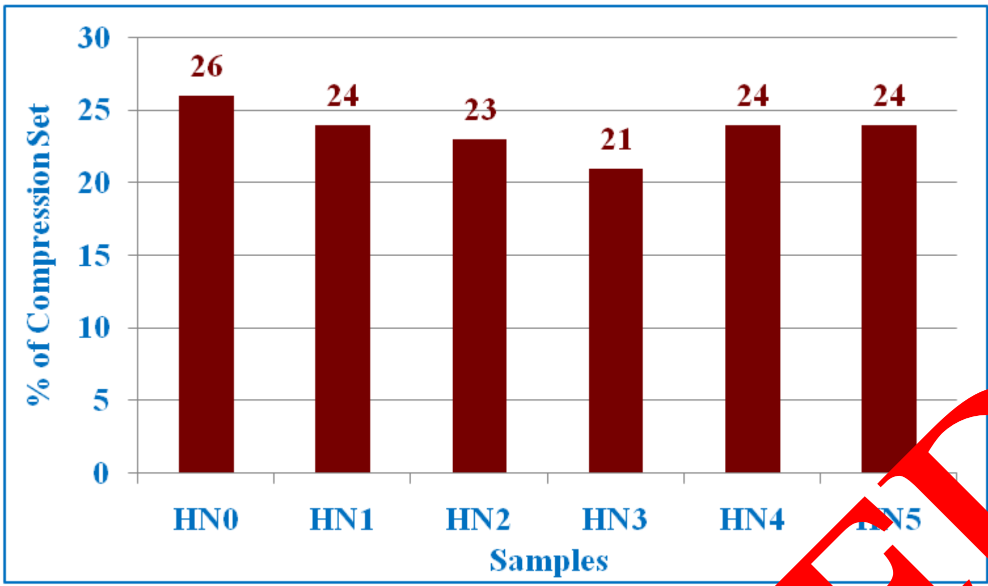

Fig. 5. Percentage of Compression Set for High Nitrile Rubber Hybrid

XRD Test: XRD was carried out to assess the degree of intercalation/exfoliation of nanocomposites. The values of 2θ and their relative basal spacing of halloysite nanotubes and NBR hybrid composites are given in Table 3. XRD patterns of the halloysite nanotubes and NBR hybrid composites are presented in Figure 6.

Table 3. Characteristics of HNT and High Nitrile Rubber Hybrids for Sample Diffraction

Sample Differaction	2θ		d-spacing	
HNT	**12.01**		**0.733**	
HN_1	9.677	12.403	0.901	0.705
HN_2	9.585	12.318	0.910	0.710
HN_3	8.775	12.302	0.992	0.711
HN_4	9.602	12.346	0.909	0.708
HN_5	9.631	12.473	0.905	0.700

The halloysite nanotubes and NBR hybrid composites demonstrate a diffraction peak at 2θ=12.01 which is related to the 0.733 nm basal spacing for the 001peak. There were two reflection (001) peaks for halloysite nanotubes and NBR hybrid composites which were dispersed in NBR nanocomposites which are clearly showed in table 3. The first peak for the nanocomposites (HN_1 to HN_5) is attributed to the displacement of the (001) peak to lower angles which confirm the presence of structures with limited intercalation and can be accredited to the formation of nanocomposites. Further the inter layer spacing increases from HN_1 to HN_3 composites. This layer expansion may be accredited to the adsorption of curatives such as Zinc oxide and Stearic acid in the HNT galleries and inter tubular diffusion of NBR and CB into the HNT tubules .There is one more peak with 2θ=(12.403,12.318,12.302,12.346,12.473) for HN_1 to HN_5 composites with distance less than that of halloysite nanotubes. This occurs due to re-aggregation of layers which is due to reaction between the hydrogen bonds of rubber and the hydroxyl groups at the interlay space which results in their exit from the space between the layers.

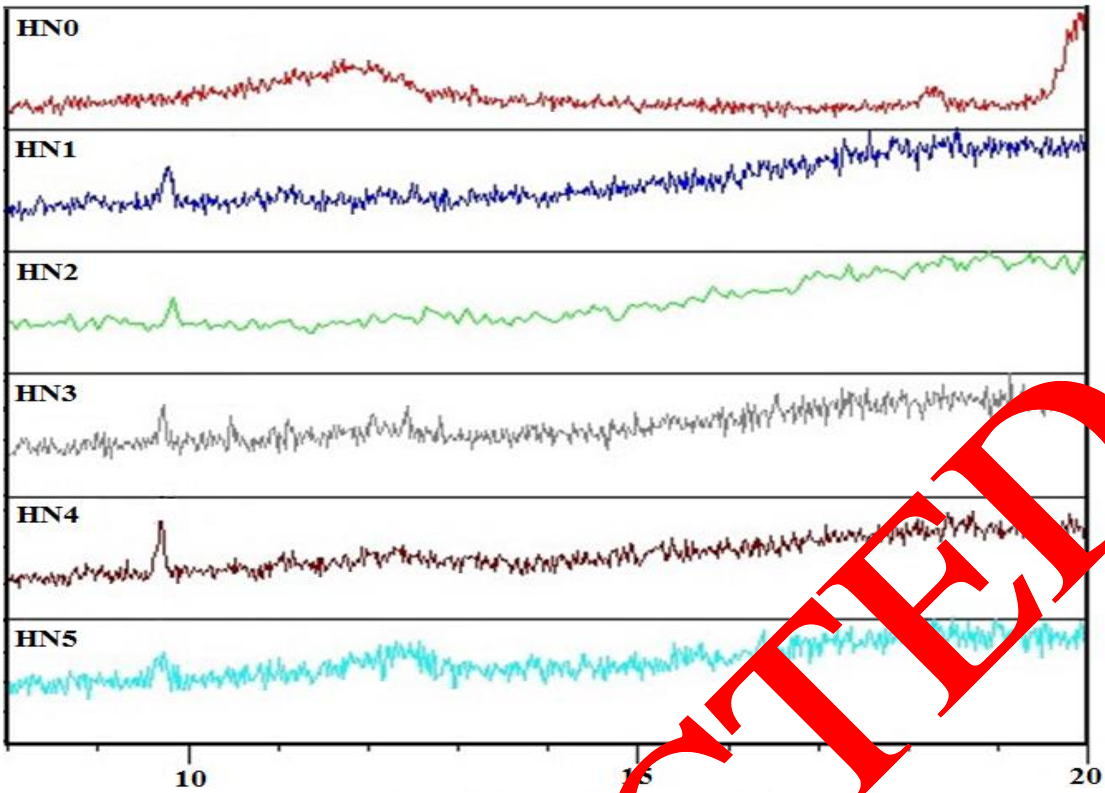

Fig. 6 . XRD Pattern of High Nitrile Rubber Hybrids

SEM Test: Scanning electron microscope results of halloysite nanotubes and NBR hybrid composites under different loading conditions are clearly shown in the following Figure 7. The SEM images illustrate the difference in the structure of the halloysite nanotubes and NBR hybrid composites when compared with the structure of the fibre and the polymer matrix individually. The fracture surfaces of tensile specimens at low magnification (x100) are clearly illustrated. When comparing Figures 7(a) and (e) it is seen that the roughness and twisted path of fracture surfaces increased with increase of the HNT loading up to six per hour. The increasing surface roughness indicated that the rubber received a lot of deformation and hence it should posses a higher strength before it breaks. Hence NBR nanocomposites with six per hour loading exhibited higher tensile strength. After six per hour loading the surface roughness decreased and hence the tensile strength also decreased.

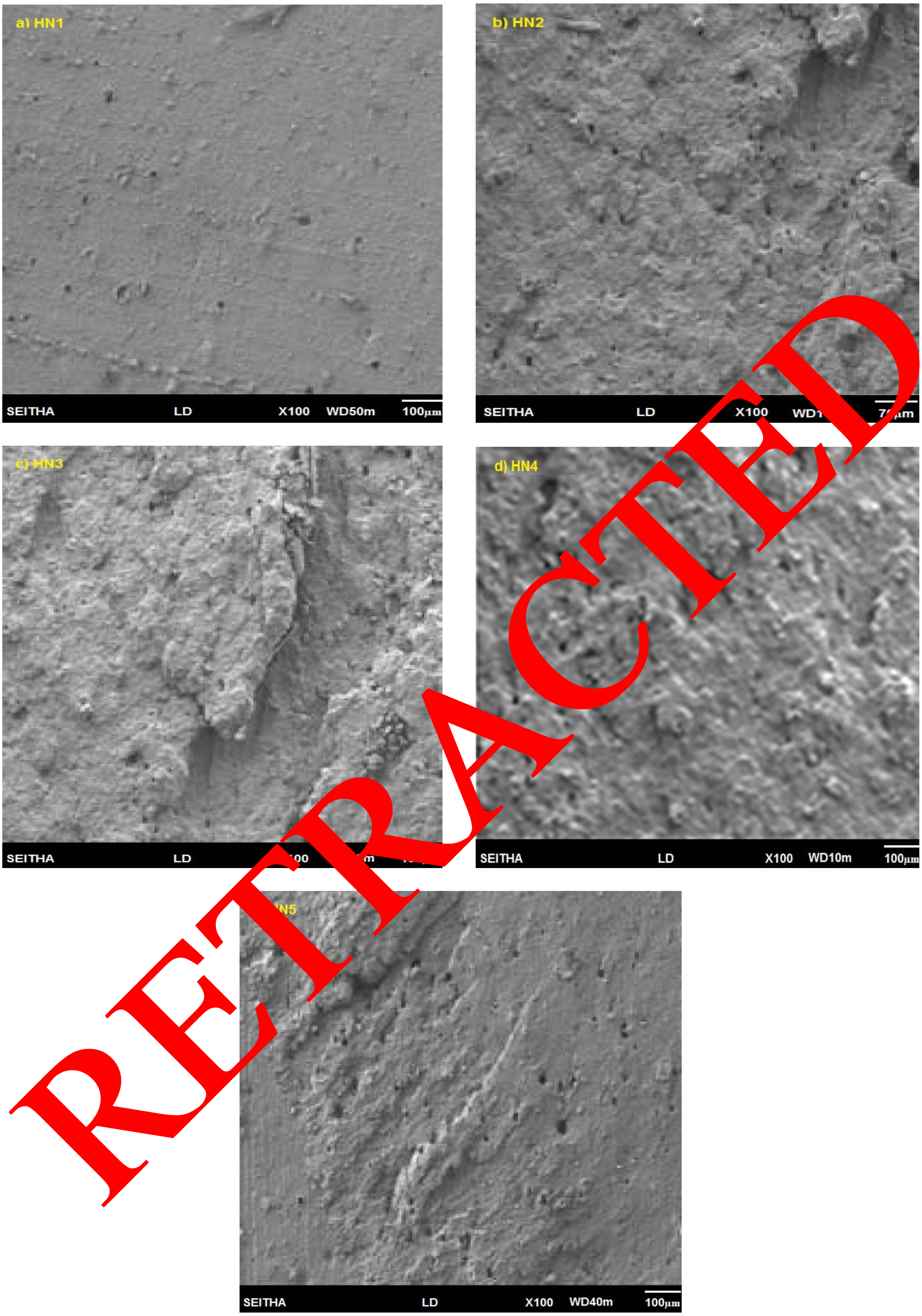

Fig. 7. SEM Images of High Nitrile Rubber Hybrids (x100)

Conclusions

Natural polymer composites are more environmental friendly. Nitrile rubber-carbon black-halloysite nanotube composites were prepared with different loading of HNTs from 0 to 6 per hour. The strength properties of halloysite nanotubes and NBR hybrid composites were analyzed with ASTM Standards. The XRD and SEM test was also carried out for the hybrid composite and the results were analysed. From the above experimental results the following have been concluded:

- There were strong interfacial interactions and inter-tubular diffusion of NBR, CB and other ingredients into the halloysite nanotube which provides simultaneous increases in tensile strength, stiffness and ductility and better performance in terms of compression set of nitrile rubber-carbon black-halloysite nanotube nanocomposites.
- Scorch time and cure time increases with increase in halloysite nanotube loading. Maximum torque increases up to six per hour loading and then decreases.
- Increase in tensile strength, modulus and elongation of break up to six per hour of halloysite nanotube loading which makes the composite more stiff and ductile.
- X-ray diffraction analysis indicated limited intercalation of halloysite nanotube in the NBR.
- As per SEM analysis NBR nanocomposites with six per hour loading exhibited higher tensile strength.

Further research on nitrile rubber-carbon black-halloysite nanotube composites may be possible on account of the huge requirement of composites for engineering applications.

Reference:

[1] M.W. Kusmono, Wildan and Z.A. Mohd Ishak, (2013), "preparation and properties of clay-reinforced epoxy nanocomposites", International Journal of Polymer Science Vol. 201, pp. 01-07

[2] N. Selvi and S. Sankar, (2014), "Effect of shells ZnO; SiO_2 on SnO_2 hybrid core-shell nano spheres and their structural, morphological and magnetic properties", International Journal of Chemical Technology Research, Vol. 6, No.14, pp 5665-5671

[3] S. Nallusamy, (2016), "Characterization of epoxy composites with TiO_2 additives and E-glass fibers as reinforcement agent", Journal of Nano Research, Vol. 40, pp 99-104

[4] Arcudi F et al., (2014), "Selective functionalization of halloysite cavity by click reaction: Structured filler for enhancing mechanical properties of bio nano composite films", Journal of Physical Chemistry C, Vol. 118, pp. 15095-15101

[5] S. Nallusamy, (2016), "A review on the effects of casting quality, microstructure and mechanical properties of cast Al-Si-0.3mg alloy", International Journal of Performability Engineering, Vol. 12(2), pp. 143-154

[6] Reyhaneh Berahman, Maryam Raiati, M M Mazidi and S M Reza Paran, (2016), "Preparation and characterization of vulcanized silicone rubber/halloysite nanotube nanocomposites: Effect of matrix hardness and HNT content", Materials and Design, Vol. 104, pp. 333-345

[7] S. Nallusamy and Gautam Majumdar, (2016), "Effect of stacking sequence and hybridization on mechanical properties of jute-glass fiber composites", International Journal of Performability Engineering, Vol. 12(3), pp. 229-239

[8] M.X. Liu, B.C. Guo, M.L. Du and D.M. Jia, (2014), "Recent advance in research on halloysite nanotubes-polymer nano composite", Polymer Science, Vol. 39, pp. 1498-1525

[9] Z. Jia, B. Guo and D. Jia, (2014), "Advances in rubber/halloysite nanotubes nanocomposites", Journal of Nanoscience and Nanotechnology, Vol. 14, pp. 1758-1771

[10] S. Nallusamy, N. Manikanda Prabu, K. Balakannan, and Gautam Majumdar, (2015), "Analysis of static stress in an alloy wheel of the passenger car" International Journal of Engineering Research in Africa, Vol. 16, pp. 17-25

[11] Liu C et al., (2013), "Thermal degradation behaviors of poly(vinyl chloride)/halloysite nanotubes nanocomposites", International Journal of Polymeric Materials and Polymeric Biomaterials, Vol. 62 (3), pp. 128-132

[12] S. Nallusamy, (2016), "Analysis of MRR and TWR on OHNS die steel with different electrodes using electrical discharge machining", International Journal of Engineering Research in Africa, Vol. 22, pp. 112-120

[13] Grimaldi C, Mionic M, Gaal, Forro and Magrez, (2013), "Electrical conductivity of multi-walled carbon nanotubes-SU8 epoxy composites", Applied Physics Letters, Vol. 102(22), pp. 223114

[14] S. Nallusamy, A. Manoj Babu and N. Manikanda Prabu, (2015), "Investigation on carbon nanotubes over review on other heat transfer nano fluids", International Journal of Applied Engineering Research, Vol. 10, No. 62, pp. 112- 117µ

[15] Yunlong Li, Shijie Wang, Quan Wang and Malcolm Xing, (2016), "Molecular dynamics simulations of tribology properties of NBR (Nitrile-Butadiene Rubber) /carbon nanotube composites", Composites Part B, Vol. 97, pp. 62-67

[16] Xu Lia, Tao Baia, Ziran Lib and Lisheng Liu, (2016), "Influence of the temperature on the hyper- elastic mechanical behavior of carbon black filled natural rubbers", Mechanics of Materials, Vol. 95, pp. 136-145

[17] S. Nallusamy, (2016), "Thermal conductivity analysis and characterization of Copper oxide nanofluids through different techniques", Journal of Nano Research, Vol. 40, pp 105-112

[18] Renata L. Sala et al., (2016), "Dynamic and structural correlations in nanocomposites of silica with modified surface and carboxylated nitrile rubber", Journal of Colloid and Interface Science, Vol. 466, pp. 247-253

[19] S. Nallusamy and A. Karthikeyan, (2016), "Analysis of wear resistance, cracks and frictional properties of metal matrix composites with SiC additives and Al_2O_3 as reinforcement", Indian Journal of Science and Technology, Vol. 9([illegible]), pp. 1-6

[20] Yan Wu, Zongliang Du, Haibo [illegible]ang and Xu Cheng, (2016), "Preparation of waterborne polyurethane nanocomposites reinforced with halloysite nanotubes for coating applications", Journal of Applied Polymer Science, Vol. 133(37), pp. 43949

[21] Xu Li, Tao Bai, Ziran Li and Lisheng Liu, (2016), "Corrigendum to Influence of the temperature on the hyper-elastic mechanical behavior of carbon black filled natural rubbers", Mechanics of Materials, Vol. 95, pp.136-145

[22] Rui Zou, C[illegible]i Li, Liqun Zhang and Dongmei Yue, (2016), "Selective hydrogenation of nitrile butadiene rubber (NBR) with rhodium nanoparticles supported on carbon nanotubes at room temperature", Catalysis Communications, Vol. 81, pp. 4-9

[23] S. Nallusamy, (20[illegible]), "Analysis of welding properties in FSW aluminium 6351 alloy plates added with silicon carbide particles", International Journal of Engineering Research in Africa, Vol. [illegible], pp. [illegible]-117

[24] G. Cavallaro, G. Lazzara, S. Milioto, F. Parisi and V. Sanzillo, (2014), "Modified halloysite nanotubes: Nanoarchitectures for enhancing the capture of oils from vapor and liquid phases", ACS Applied Materials and Interfaces, Vol. 6, pp. 606-612

[25] S. Nallusamy and Manoj Babu, (2015), "X-Ray differaction and FESEM analysis for mixture of hybrid nano particles in heat transfer applications", Journal of Nano Research, Vol. 37, pp. 58-67