

Morphology and Mechanical Properties of NBR/PVC Hybrid Nanocomposites



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Abstract: In this present work NBR/PVC conventional composite containing 70phr carbon black (CB) is taken for study. In order to reduce the utilization of CB, new hybrid nanocomposites containing varied content of both CB(40phr-55phr) and graphenenanoplatelets (GNP) (3phr-9phr) were developed by melt-mixing on a two roll mill and their morphology and mechanical properties were tested and compared with conventional composite. FESEM studies evident that the formation of exfoliated structures of GNP and formation of local CB-GNP hybrid filler network which ensures proper and compatible mixing in the composites. It is also found that mechanical properties such as tensile strength, elongation at break, swelling resistance, hardness and compression set increases with increase in GNP content from 3 to 6phr and whereas tensile modulus and tear strength increases with increase in GNP content from 3 to 9phr. Further the developed NBR/PVC hybrid nanocomposites containing 55phr of CB and 3phr of GNP exhibited an improvement of 6.8%, 27.9% +1 shore A and 4.1% in tensile strength, tensile modulus, hardness, swelling resistance in comparison to the conventional composite containing 70phr CB. The better performance of NBR/PVC hybrid nanocomposites can be mainly attributed to high surface area of functionalized nanographene and its enhanced interactions with the NBR/PVC matrix, enhanced CB-GNP interactions, improved dispersion of graphene in the rubber blend due the presence of COOH group on the surface of graphene layers and formation of more cross-links between rubber and fillers with increase in nanofiller content. These newly developed hybrid nanocomposites can be used in automotive sector especially for oil seal applications where low compression set and high solvent resistance are of prime importance.

Keywords: Hybrid nanocomposites, NBR/PVC, graphene nanoplatelets, Mechanical properties, swelling resistance .

I. INTRODUCTION

The quest for smart rubber products have inspired the

Manuscript received on April 30, 2020.

Revised Manuscript received on May 06, 2020.

Manuscript published on May 30, 2020.

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academia and industries to explore novel high performance reinforcing materials. In this context, nano sized reinforcements such as carbon nanotubes(CNT), nanoclay, halloysite nanotubes(HNT), nanosilica and poly oligomeric sesquioxanes(POSS) have received considerable attention attributable to their superior aspect ratio, high specific surface area and their capability to achieve noteworthy properties at very low content. As a single filler cannot meet the comprehensive requirements of rubber products, the practice of hybrid fillers containing combination of two or more fillers as reinforcements in rubber composites has been widely adopted[1]. Carbon black(CB), the ultimate and cost effective reinforcement, is used especially in large quantities (>30phr) to achieve optimum properties in all commercially viable rubber. Nonetheless, carbon black particles have an inclination to form aggregates due to poor dispersion in processing[2]. Subsequently elastomeric composites containing traditional black filler hybridized with nano sized reinforcements(CNT, HNT, nanoclay) have been widely acknowledged among the academia and industries[3-5].

Recently, multi-layered graphene as graphene nanoplatelets (GNP) has enthralled a overwhelming amount of consideration and has emanated to be an fascinating material with promising applications as a reinforcing material for polymer nanocomposites. Accomplished from the expansion of graphite, GNP are characterized with superior mechanical strength, massive contact surface area and remarkable thermal conductivity[6]. Nevertheless, the inclination of GNP to aggregate hamper their utilization as reinforcement in polymer composites[7]. Consequently the surface of GNPs is modified either physically or chemically to ameliorate their dispersion in the polymer matrix and thereby augment the properties of the resulting composites[8].

Nonetheless studies pertaining to the synergy of GNP and carbon black in rubber composites are sparse. Cai et al.[9] have reported exceptional electrical conductivity and piezo-resistivity in Silicon rubber nanocomposites reinforced with CB/GNP hybrid fillers. Valentini et al. [10] have reported significant improvement in mechanical properties and thermal conductivity of ethylene propylene diene monomer rubber composites reinforced with GNP and CB.

Acrylonitrile butadiene copolymer(NBR)/Polyvinyl chloride (PVC) blend is a miscible physical mixture of commercial significance widely used in manufacturing gasket, shoe soles, footwear, and artificial leather[11]. Further studies illustrating the synergy of CB and GNP hybrid fillers in NBR/PVC composites are scarce.



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Hence in the present work, an attempt is made to study the mechanical properties of NBR/PVC rubber composites used in real time application. NBR/PVC rubber composites(reinforced with 70phr CB) used as oil seal in automotive applications is taken for study.

Novel NBR/PVC hybrid nanocomposites are developed with the aforementioned fillers. The morphology of these developed composites are examined using FESEM techniques. Further these composites are examined for their tensile and tear properties, hardness and compression set

II. MATERIALS

NBR/PVC (70:30), called as Vinoprene 731 with Mooney viscosity of 45Mooney unit supplied by BP chemical, India was used as the matrix material. COOH functionalized GNP (thickness: 0.8-1.6 nm) was purchased from United nanotech Pvt. Ltd., Bangalore, India. Other compounding ingredients as listed in Table 1 were procured from Ramcharan chemicals, chennai, India.

TABLE 1. Formulation of NBR /PVC conventional and hybrid composites (Phr)

Ingredients (Phr ^a)	CB70	CB55-GNP3	CB55-GNP6	CB55-GNP9
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	55	55	55
HNT	0	3	6	9
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

III. EXPERIMENTAL SET UP

3.1 Melt blending Process

NBR/PVC are prepared as per the formulations displayed in Table 1. Originally NBR/PVC rubber was masticated on an open two roll mill (160 mm X 320 mm) shown in Figure 1 .



Fig.1.Two Roll mill.

After 2-3 min of mastication, the COOH functionalized GNP was added and the blending was continued for 10min. Then antioxidant and activators(Zinc oxide and stearic acid), CB and plasticiser were included

into the blend and the mixing was carried out for another 20min. In the conventional compound, only 70phr of CB was loaded. For GNP reinforced composites, 15phr of CB was partially replaced by 3,6 and 9phr of the nanofiller. Finally the curatives (sulphur, potassium stearate and sodium stearate) were added and blended for further 2-3 min. A homogenous compound was obtained.

3.2 Curing Process

These compounds are cured at 160° C using an electric press shown in Figure 2 . Then test specimens were prepared from these compounds maintained at ambient conditions for 24 hours..



Fig.2. Electric Press

3.3 Mechanical Characterisation

Tensile tests were performed using dumbbell shaped samples in accordance with ASTM D412. Tear strength was determined using crescent shaped specimens in accordance with ASTM D673. Both the tests were conducted on a universal testing machine (shown in Figure 3) at a crosshead speed of 500mm/min. Hardness is assessed using a shore A hardness tester according to ASTM D2240. Compression set is determined using cylindrical button samples at 100°C for 22 hours as per ASTM D395 (shown in Figure 4).



Fig.3. UTM Testing



Fig.4. Compression set fixture

3.4 Morphology

The morphology of the tensile fracture surface of NBR/PVC composites were analysed by using a SUPRA-55 field emission scanning electron microscope(FESEM).

Ahead of the investigation, the specimens were gold sputtered to impede charging effect and to intensify secondary electron emanation

IV. RESULT AND DISCUSSION

NBR/PVC traditional and hybrid composites are tested for their mechanical properties and their results are summarised in Table .2

TABLE 2. Mechanical properties of NBR/PVC traditional and hybrid composites

Property	NBR/P VC-CB 70	NBR/P VC-CB 55-GNP 3	NBR/P VC-CB 55-GNP 6	NBR/P VC-CB 55-GNP 9
Tensile strength (Mpa)	12.99	13.88	14.68	13.55
Elongation at break (%)	159	177	153	258
300% modulus (Mpa)	5.81	8.06	8.2	8.58
Tear strength (N/mm)	30.13	33.22	38.84	34.46
Compression set	37	37	36	38
Hardness	83	84	87	85

4.1 Tensile test

. Fig 5 presents the stress at break of the NBR/PVC composites. It is vivid that the stress at break of NBR/PVC composites augments with increase in nano GNP content upto 6phr in the polymer matrix and then decreases. Further all the NBR/PVC hybrid nanocomposites demonstrate superior tensile strength in comparison to traditional composite. It can be noticed that incorporation of 6phr of GNP in the NBR/PVC hybrid nanocomposites improves the tensile strength by 13% in comparison to traditional composite. Such an enhancement in tensile strength is can be attributed to (i) high surface area of functionalized nanographene and its enhanced interactions with the NBR/PVC matrix, (ii) enhanced CB-GNP interactions, (iii) improved dispersion of graphene in the rubber blend due the presence of COOH group on the surface of graphene layers and (iv) formation of more cross-links between rubber and filler with increase in nanofiller content[12]. Strong interactions allow more efficient load transfer and hence better mechanical performance, as reported by Yang et al. [13].Beyond 9 phr of GNP content,formation of more agglomerates of graphene layers was observed and they act as stress concentrated zones in NBR/PVC matrix, and there by hinders the stress transfer and eventually cause reduction in tensile strength[13].

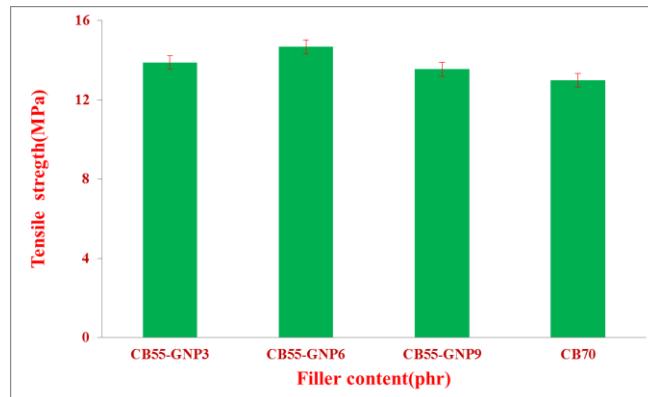


Fig.5(a). Effect on Tensile Strength due to variation of GNP and CB content of the developed Hybrid new composites in comparison with conventional composite.

From the Fig. 5(b), further it can be observed that % elongation at rupture of NBR/PVC composites reinforced with dual fillers increases with increase in GNP content from 3 to 6phr and then decreases with further increase in GNP content. In fact, during application of load on NBR/PVC-CB-GNP composites both stress and strain transfer happens between fillers and the matrix. While stretching beyond certain limit, break down of some filler-polymers bond may happens along with the formation of new filler-polymer bonds. These newly generated surfaces of GNP due to interlayer slippage under stress can form bonds with polymer chains, and this process continues, eventually increases the value of elongation at break of the newly developed composite[14]. However all the NBR/PVC composites reinforced with dual fillers present an inferior elongation at break in comparison to traditional composites. NBR/PVC composites with 6phr GNP demonstrate a reduction in elongation at break of 32% in comparison to traditional composite.This may be ascribed to increase in stiffness of the composites due to the presence of both the fillers[15]

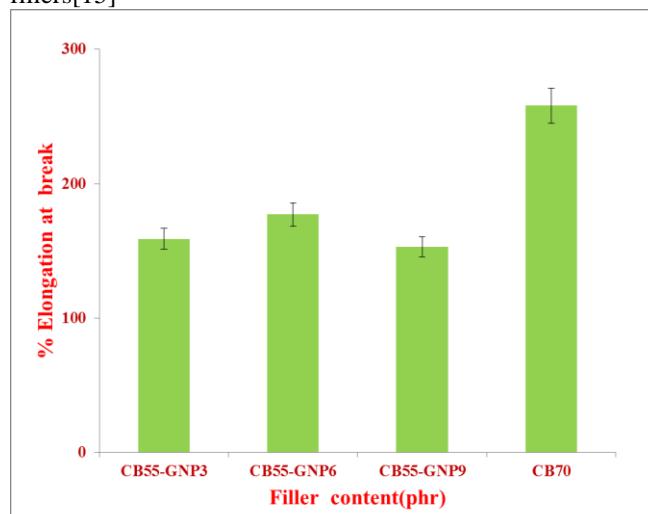


Fig. 5(b).Effect on Elongation at Break due to variation of GNP and CB content of the developed Hybrid new composites in comparison with conventional composite.

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The 100 % modulus of NBR/PVC hybrid nanocomposites at a particular CB content increases with increase in GNP content as shown in Fig. 5(c). NBR/PVC hybrid nanocomposite with 55phr CB and 6phr GNP exhibit an increase of 33% in 100% modulus in comparison with conventional composite. Such an improvement in tensile modulus of NBR/PVC hybrid nanocomposites can be attributed due to the improved COOH functionalized graphene interactions which reduces the free volume space between matrix molecules and its reduced molecular mobility around the graphene sheets thereby making the composites more stiff [16].

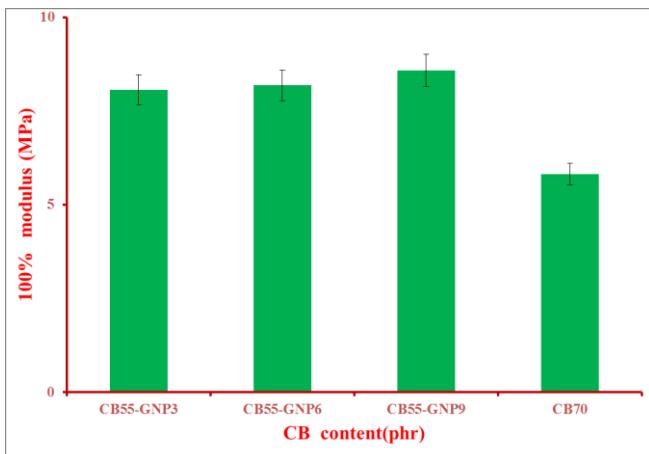


Fig. 5(c).Effect on Tensile Modulus due to variation of GNP and CB content of the developed Hybrid new composites in comparison with conventional composite.

4.2 Tear test

The tear strength of PVC composites reinforced with dual fillers increases inherently and reaches a maximum at a loading of 6phr of HNT ACM (shown in Figure 9). The noteworthy performance of NBR/PVC hybrid nanocomposites in terms of tear strength is accredited to the arbitrarily aligned GNP acting as connecting elements, which offer substantial defiance to inception and proliferation of crack and subsequently preventing collapse at inferior load. Additionally these GNP connect aggregates of carbon black to establish a local filler network, which affirms efficient transfer of stress from the matrix to the reinforcements and eventually leading to improved tear strength values [17].

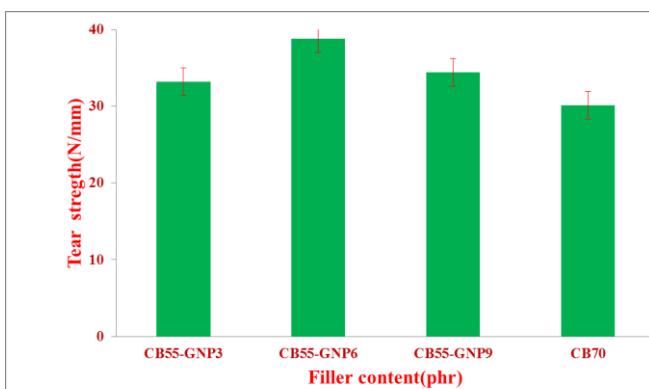


Fig. 6 Effect on Tear strength due to variation of GNP and CB content of the developed Hybrid new composites in comparison with conventional composite.

4.3 Hardness

The observed Hardness of NBR/PVC composites is displayed in Fig. 4. It is interesting to note that NBR/PVC hybrid nanocomposites have outperformed the conventional composite in terms of hardness. NBR/PVC hybrid nanocomposites with 6phr loading of GNP demonstrates the ultimate hardness among the various composites taken for study. Addition of GNP nanofiller causes the NBR/PVC rubber to become more rigid and hence a corresponding increase in hardness value is noticed in all NBR/PVC hybrid composites[18].

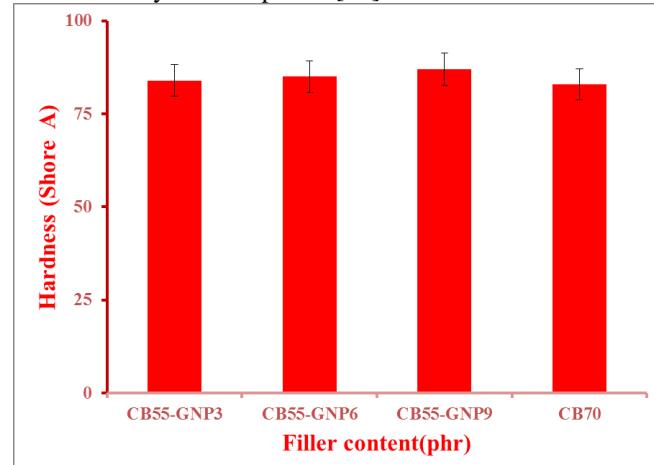


Fig. 7..Effect on Harrdness due to variation of GNP and CB content of the developed Hybrid new composites in comparison with conventional composite.

4.4 Compression set

Compression set exemplifies the capability of rubber vulcanizes to preserve their elastic characteristics after extended compression at constant strain under a specific set of condition. From the Fig. 5,it is clearly evident that compression set of the NBR/PVC composites reinforced with dual fillers decreases with increase in GNP content upto6phr and then increases with further increase in GNP content Further, it is very interesting to note that NBR/PVC hybrid nanocomposites(CB55 3phr GNP and CB55 GNP6) exhibited better compression set values of 37 and 36 in comparison to traditional composite whose value is 38. The remarkable performance of NBR/PVC hybrid nanocomposites in terms of compression set can be ascribed to enhanced NBR/PVC-GNP-CB interactions and development of enduring networks of cross-linked chain. These networks which are incompetent to relax during compression stage cause elastic resurgence during recovery phase and eventually resulting in lower compression set values [19].

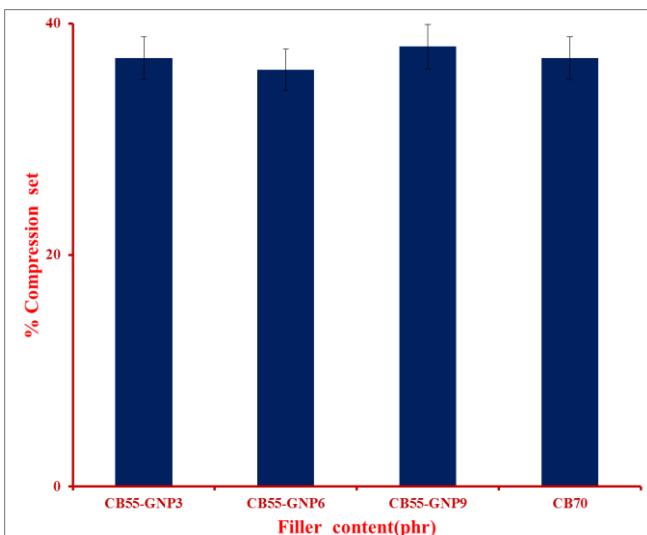


Fig. 8.Effect on Compression set due to variation of GNP and CB content of the developed Hybrid new composites in comparison with conventional composite.

4.5 Field emission scanning electron microscopy

The degree dispersion and its state of fillers in the rubber matrix are the cardinal factors in determining the properties of the composite and it can be visualized from the morphological studies. In the present work, the FESEM micrographs of tensile fracture surface of NBR/PVC conventional and hybrid nanocomposites are shown in Fig.1. Figure 1a displays the image of tensile fracture surface of the NBR/PVC conventional composites which indicates that there is good adhesion of CB particles with NBR /PVC matrix having some voids and cracks because of incorporation of GNP particles which results in the morphology change of matrix from smooth to rough one. On the other hand, NBR/PVC-CB55-GNP3 and NBR/PVC-CB55-GNP6 samples display a relatively high rough surface with no cracks and voids and better dispersion of GNP along with CB particles in the NBR/PVC matrix as evident from Fig. 1(b)&(c). It can also be noticed that some GNP sheets with reduced thickness are seen to be protruding out from the polymer matrix. Further the addition of CB particles in NBR-GNP composites aids in exfoliation of GNP layers as if CB particles act as bonding agent by entering in between individual GNP layers at varied degree of exfoliation. Above factors suggest that there is a good formation of local CB-GNP filler networks with strong NBR/PVC-CB-GNP interfacial adhesion. Formation of exfoliated structure and good interfacial NBR/PVC-CB-GNP interactions promote efficient stress transfer resulting in a relatively rough surface without cracks in hybrid nanocomposites[13]. In the case of NBR/PVC-CB55-GNP9 more agglomerated GNP particles(Fig. 1(d))were noticed, which indicates that there was a poor compatibility with NBR/PVC matrix and absence of bonding of layers[7].

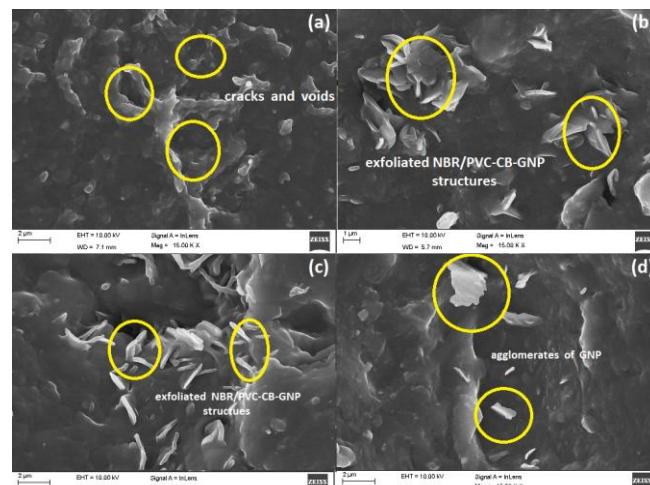


Fig. 9. FESEM images of a) NBR/PVC-CB70, (b) NBR/PVC-CB55-GNP3 (c) NBR/PVC-CB55-GNP6 and (d)NBR/PVC-CB55-GNP9

V. CONCLUSION

The following conclusions are derived based on the experimental works carried out on NBR/PVC-CB-GNP hybrid composites developed.

1. The morphological analysis based on FESEM studies confirmed the presence of exfoliated structures and formation of a local CB-GNP hybrid filler networks in NBR/PVC matrix.
2. Both the good dispersion of GNP filler in NBR/PVC matrix, synergy between CB and GNP, had enhanced the NBR/PVC-CB-GNP interfacial interactions and thereby improved the mechanical properties of the developed hybrid nanocomposites.
3. Tensile strength, tensile modulus(% 100) and tear strength of NBR/PVC composites with 6phr GNP are improved by 13%, 33% and 29% respectively in comparison to NBR/PVC traditional composite
4. Hardness and Compression set of the developed NBR/PVC hybrid composites are better than that of NBR/PVC conventional composite.
5. This research work it is suggested that NBR/PVC composite containing 55phr and 6GNP can be considered as the suitable material for oil seals to be used in automotive applications.

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