

Research Article

Evaluation of Effect of Various Nanofillers on Technological Properties of NBR/NR Blend Vulcanized Using BIAT-CBS System

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Owing to processing ease and resistance to oils and chemicals, NBR is widely used in many industries. But since neat NBR has only poor tensile properties, it is better to use suitable blends of NR and NBR after incorporating appropriate nanoingredients before vulcanization. It is well established that nanoparticles can be easily dispersed in a more uniform pattern in polymer matrix, thereby enhancing the technological properties of the elastomer vulcanizate. Since there are no systematic comparative studies on technological properties of NBR/NR blend containing different nanoingredients, efforts have been made in this study to investigate cure and technological properties like tensile properties, tear resistance, compression set, hardness, abrasion loss and swelling value of NBR/NR (80/20) blend vulcanizates containing stearic acid-coated nano-zinc oxide (ZOS), nano-BIAT, nano-silicate-coated CaCO₃, PEO-coated calcium silicate, and surface-modified carbon nanotubes (CNT). XRD and electron microscopy have been used for morphological analysis. The nano ingredients were effective in enhancing the technological properties of the vulcanizates. Among the nanofillers, modified CNT was found to impart superior properties to NBR/NR blend due to more intercalation.

1. Introduction

Owing to processing ease and resistance to oils and chemicals, NBR is widely used in many industries. However, neat NBR exhibits only poor tensile properties and oil resistance. A considerable amount of research has been made over the last several years with a view to obtaining new polymeric materials with enhanced specific attributes for specific applications. Much attention is devoted to the simplest route for combining outstanding properties of different existing polymers, that is, by blending polymers. Although increasing numbers of miscible blends are reported [1–5], most polymers are almost immiscible, thus leading to heterophase polymer blends. There are two widely used types of elastomer blends: miscible single-phase blends and immiscible two-phase blends.

It is scientifically proved that the presence of certain polymeric species with the right structure can result in

compatibilization of an immiscible elastomer blend by virtue of their ability to change interfacial situation [6–8]. Such materials, known as compatibilizers, are added or in situ formed during blending of elastomers. The compatibilizers in elastomer blends perform many roles like reducing interfacial energy between the phases, permitting finer dispersion during mixing, providing stability against gross segregation, and improving interfacial adhesion. Two elastomers can form a compatible blend when they have (1) segmental structural identity, (2) miscibility/partial miscibility with each other, and (3) functional groups capable of forming covalent or other bonds between the polymers [9].

Kader et al. prepared (50/50) NR/NBR blend using trans-polyacetylene rubber (TOR) as a compatibilizer [10]. They showed that inclusion of TOR in the blend altered the phase morphology by reducing the size of the NBR phase. In another study, Sirisinha et al. [11] have reported that oil

resistance of 20/80 NR/NBR blend depended mainly on the phase morphology of the blend. The resistance to oil was higher when the size of the NR dispersed phase was smaller. Mathai et al. [12] also investigated that the equilibrium solvent uptake decreases with an increase in the concentration of NBR. Li et al. [13] investigated the effect of polysiloxane-*g*-octane and polysiloxane-*g*-(3, 7-dimethyl-6-octylene) as compatibilizers in NR/SR blend system and showed that mechanical properties of the blend improved considerably when the compatibilizers were used. In another study, Angnanon et al. [14] investigated the effect of graft NR as a compatibilizer in the NR/NBR blend system. They also obtained a similar result as in the study conducted by Mingjun et al.

Polychloroprene (CR) has a backbone structure similar to that of NR, but it is more polar due to the presence of chlorine. The solubility parameter value of CR is an intermediate of that of NR and NBR. Also the presence of dipole within the repeat unit allows the possibility of interaction of acrylonitrile repeat unit of NBR.

Fillers like carbon black, metals, and ceramics were used to improve the technological properties of NBR [15–19]. For example, carbon blacks are excellent fillers because of their strong interaction with NBR, but the resulting materials have limitations associated with decreased processability at higher loading. Recently, silica has been used in NBR because of its good interaction and environmental issues caused by carbon black [20, 21]. However, it is difficult to get uniform dispersion of silica particles in NBR matrix due to particle agglomeration probably caused by the polar groups on the surface of silica particles [22].

Fillers like CaCO_3 , clay, and so forth with average particle size of 1–100 nm can be used in relatively small quantities (5%–10%) in order to provide substantial improvements in technological properties of elastomers. Nanoparticles can form fine and homogeneous dispersion in the polymer matrix. As compared with micron-sized particles, the nanoparticles can occupy substantially greater number of sites in the polymer matrix. Such particles increase the barrier properties by creating tortuous path that slows the progress of gas molecules through polymer matrix. Also these particles in the polymer matrix improve surface properties like gloss, surface finish, grip, and so forth. S. N. Chakravarty and A. Chakravarty reported the reinforcing and air retention effect of nano- CaCO_3 in (70/30) NBR/NR blend [23]. Effect of different nanoparticles on thermal, mechanical, and dynamic mechanical properties of HNBR nanocomposites was studied by Choudhury et al. [24]. Thomas also investigated the effect of calcium phosphate, titanium dioxide, and layered silicate on the technological properties of NBR nanocomposites [25]. Recently carbon nanotubes (CNTs) have become attractive due to the possibility of large-scale production of these materials. CNTs possess several advantages in industries like cost effectiveness and light weight of the article produced due to the requirement of these fillers in much lower dosages to achieve good technological properties [24–34]. The exceptional properties of CNTs like high mechanical strength, flexibility, and impressive electrical and thermal conductivity make them attractive and potential candidates

for various applications [35–37]. Despite these outstanding properties, there are two main limitations which prevent their easy use. The surface energy of CNTs is significantly different from that of the matrix of polymer or similar organic compounds, and as a result, the finer dispersion of CNTs into the matrix is quite a difficult task [38]. Also, the seamless surface of CNTs cannot provide physical interaction between CNTs and the matrix [39]. The modification of CNTs using suitable compounds makes them interesting and apt candidates for a plethora of applications including nanoelectronics [40]. In a study by Ali et al. [41], it was observed that the presence of nanoclay influenced the morphology of HNBR/NR blend to the extent that a change from the cocontinuous phase morphology into the island-matrix morphology occurred. Although better dispersion of CNTs in elastomer is possible by solution mixing [42, 43], it is not suitable for industrial applications owing to the requirement of hazardous solvents in large quantities which in turn makes the method less economic. Better dispersion of comparatively lower dosage of nanofillers in elastomers is also possible by two-roll mixing. The shear force developed at 80°C in the two-roll mill is sufficient to cause uniform dispersion.

Since there are no systematic and comparative studies on the use and effect of nanomodified accelerator, stearic acid-coated nano-zinc oxide (ZOS), silicate-coated nano- CaCO_3 (SCC), PEO-coated calcium silicate (PCS), and carbon nanotubes (CNTs) on vulcanizate properties of NBR/NR blend, efforts have been made in this study to compare the technological properties of 80/20 NBR/NR blend nanocomposites containing these nanoparticles. This particular blend has been taken for the study because an earlier study [11] reported better oil resistance for it. XRD and electron microscopy have been used for morphological analysis.

2. Experimental

Different NR/NBR blend (20/80) compounds were prepared using the ingredients as shown in Table 1, on a laboratory-size two-roll mill (15.3 × 30.5 cm, Indian Expeller) as per ASTM designation D3182-89. NBR (33% acrylonitrile content, grade N-684) was masticated for 2 min, and the nanofiller/compatibilizer/antioxidant were added to the masticated NBR. The mixing was continued for 5 min and previously masticated NR (ISNR-5) and ZOS were added to this NBR, and again mixing was continued for another 3 min. Finally, accelerators followed by sulfur were also added, and mixing was continued to get a homogeneous rubber compound.

All the mixes from NBCNT₁ to NB₀ contain NBR and NR in 80 : 20 proportion, 5 phr of ZOS, 1.32 phr (5 mmols) of CBS, 1.3425 phr (7.5 mmols) of BIAT, and 1.5 phr of sulfur. The mix NBCNT₁ to NBCNT₄ contains 1, 3, 5, and 7 phr of CNT as nanofiller. NB_{CS} contains 7 phr of nano-PCS as filler. NB_{CC} contains 7 phr of nano-SCC as filler. The mix NB₀ contains 2 phr of CR as compatibilizer, and no nanofiller is present in it. Since the maximum concentration of CNT has been limited as 7 phr, other prepared nanofillers (PCS and SCC) have also been taken in the limiting concentrations of 7 phr.

TABLE I: NBR/NR blend formulations containing nano-SCC, -PCS, and CNT.

Ingredients in phr	Mixes						
	NBCNT ₁	NBCNT ₂	NBCNT ₃	NBCNT ₄	NBCC	NBCS	NB ₀
NR	20	20	20	20	20	20	20
NBR	80	80	80	80	80	80	80
CR	0	0	0	0	0	0	2
ZOS	5	5	5	5	5	5	5
TDQ	1	1	1	1	1	1	1
CNT	1	3	5	7	0	0	0
n-SCC	0	0	0	0	7	0	0
n-PCS	0	0	0	0	0	7	0
CBS	1.32	1.32	1.32	1.32	1.32	1.32	1.32
n-BIAT	1.3425	1.3425	1.3425	1.3425	1.3425	1.3425	1.3425
S	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Accelerators are taken in phr corresponding to mols.

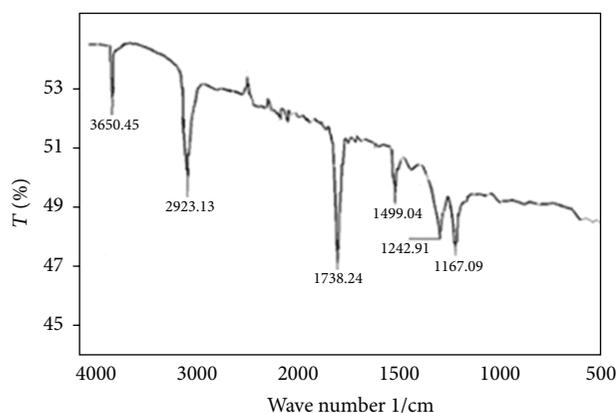


FIGURE 1: FTIR spectrum of modified MWCNT.

3. Results and Discussion

3.1. Characterization

3.1.1. FTIR Spectroscopy. The FTIR spectrum of CNT is given in Figure 1. The IR spectrum of the compound was taken on Shimadzu FTIR spectrometer. About 5 mg of the pure sample was pelletized with KBr, and then, the spectrum was taken. The peak at 1738 cm^{-1} is due to carbonyl group. The peak at 3650.45 cm^{-1} can be assigned to $-\text{OH}$ group. The peaks at 2857 and 2928 cm^{-1} are due to $\text{C}-\text{H}$ stretching of aromatic ring attached to CNT by modification [44].

3.1.2. XRD Analysis. The XRD spectra are given in Figure 2. X-ray diffraction patterns of the samples were taken on Bruker AXS D₈ advance model XRD instrument, with source Cu, wavelength 1.5406 \AA , and Si (Li) PSD detector. The peaks at 28.5 and 38.5 in Figure 2(f) are due to nano-calcium carbonate intercalated into polymer matrix. Tavangar et al. [45] and Mishra and Shimpi [46] reported peaks at angles 29 , 39 , 47.5 , and 48.5° (2θ scale) for (104), (113), (018), and (116) planes, respectively, for free nano- CaCO_3 (Figure 2(g)). The

slight shift from these values in the case of the XRD spectrum of NBCC (Figure 2(f)) could be due to intercalation. Other peaks are due to ZnO. Gupta et al. reported peaks at 31.7 , 34.4 , 36.2 , 47.5 , 56.6 , and 62.9° for the various planes of ZnO [47].

In the XRD spectra of all of the CNT-filled NBR/NR blend vulcanizates (Figures 2(b)–2(e)), less intense peak at 24.7° is due to the intercalated CNT. Khairurrijal et al. reported a peak at 25.5° for (002) planes of CNT fabricated using spray pyrolysis [48]. Li et al. also reported a peak at 25.9° for pure CNT (Figure 2(a)) [49]. The reduction in intensity and also the shift from the expected angle from 25.9° to 24.7° in the present case could be due to intercalation as evident from the SEM and TEM images (Figure 3). The peak at 24.7° becomes broader and less intense as the concentration of CNT increases due to more intercalation.

3.1.3. Microscopic Analysis. The morphological analysis of representative vulcanizates of NBR/NR blend mixes was done using microscopic methods like SEM, TEM, and AFM and the micrographs are given in Figure 3. Scanning electron microscopic images of the samples were taken using Jeol SEM (10 KV). The foldings found in the SEM image of NBCNT₁ (Figure 3(a)) could be due to the lower NBR/NR miscibility. The white patches are due to agglomerated nanoparticles of ZnO and BIAT. These types of foldings are not found in the SEM image of NBCNT₄ (Figure 3(b)), due to the enhanced compatibilizing action of carboxylated CNT as its concentration increases. The white patches found in the SEM image of NBCC (Figure 3(c)) are also due to the nanoparticles of SCC, ZnO, and BIAT dispersed in the rubber matrix. The SEM images of the fractured surface of NBCNT₁ and NBCNT₄ (Figures 3(d) and 3(e)) show the sliding of rubber chains over CNTs.

Transmission electron microscopic images of the samples were taken on Jeol JEM-2100 HRTEM (200 kV, beam current $104.2\text{ }\mu\text{A}$). The TEM images of vulcanized rubber samples were taken after preparing ultrathin sections of samples using ultramicrotome (Leica EM FCS Ultracut) with cryosystem. The TEM image of NBCNT₁ (Figure 3(f)) shows well-dispersed curled CNTs. As the concentration of CNTs reaches

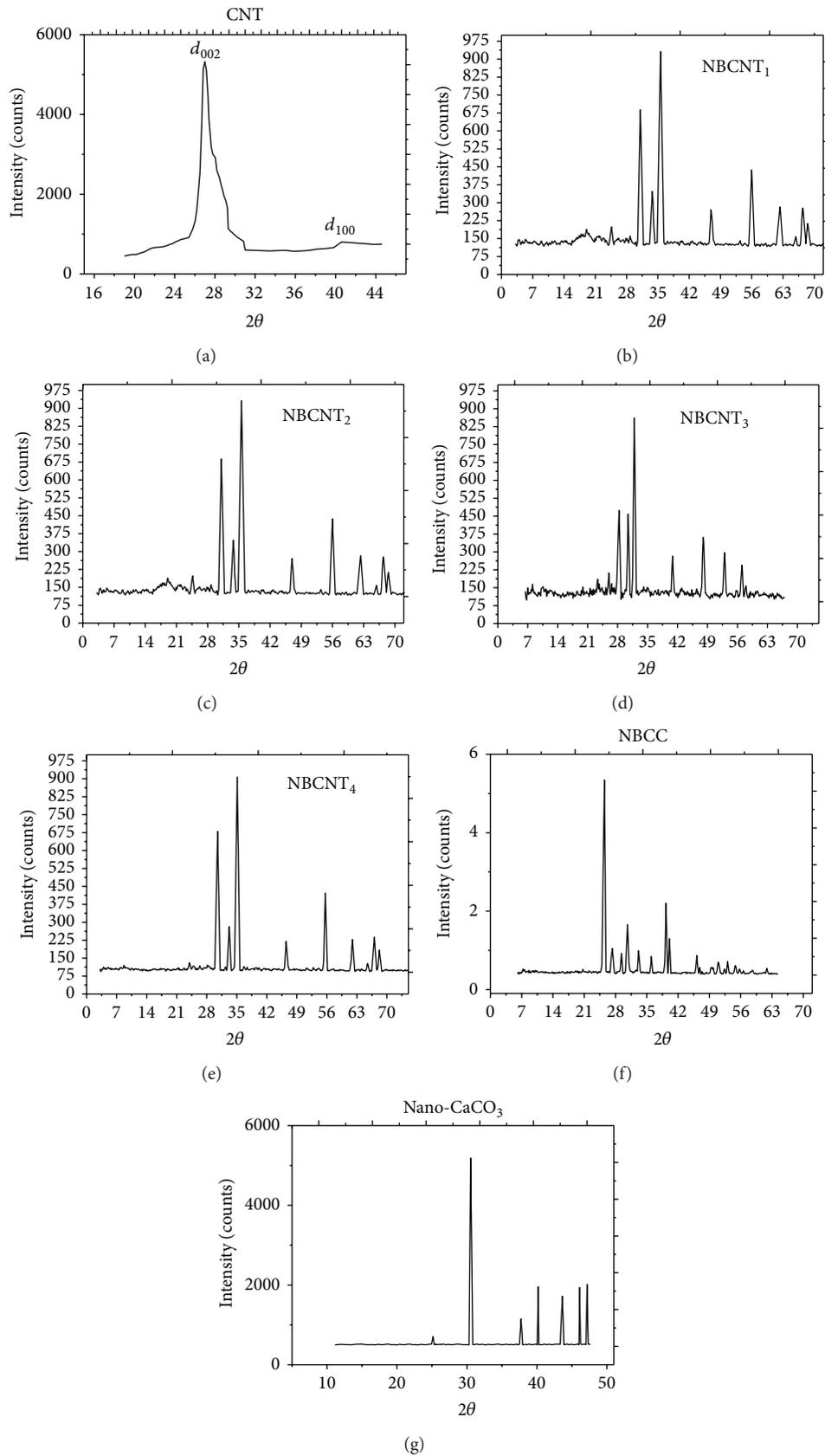


FIGURE 2: XRD curves of (a) pure CNT, (b) NBCNT₁, (c) NBCNT₂, (d) NBCNT₃, (e) NBCNT₄, (f) NBCC, and (g) nano-CaCO₃.

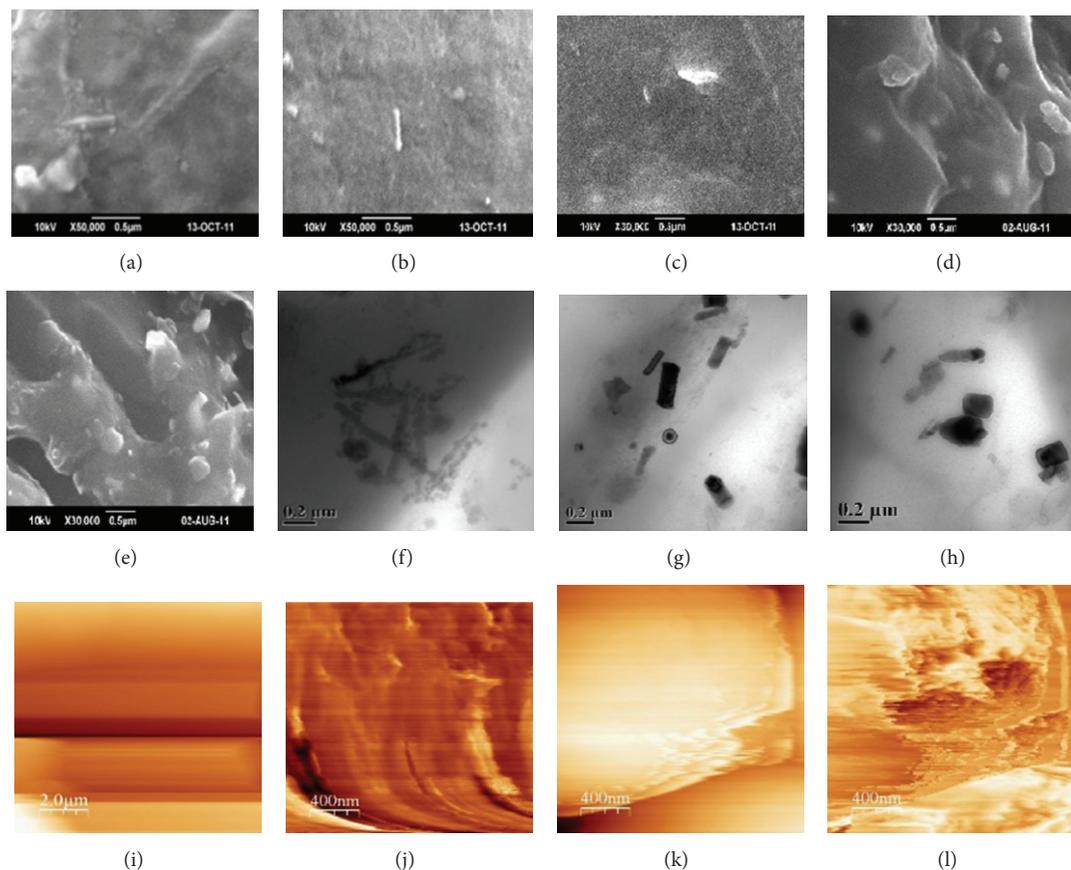


FIGURE 3: (a) SEM image of NBCNT₁. (b) SEM image of NBCNT₄. (c) SEM image of NBCC. (d) SEM image of fractured NBCNT₁. (e) SEM image of fractured NBCNT₄. (f) TEM image of NBCNT₁. (g) TEM image of NBCNT₄. (h) TEM image of NBCC. (i) AFM height image of NBCNT₁. (j) AFM phase image of NBCNT₁. (k) AFM height image of NBCNT₄. (l) AFM phase image of NBCNT₄.

7 phr in NBCNT₄, fracturing and agglomeration of CNTs occur as shown in the TEM image (Figure 3(g)). The TEM image of NBCC (Figure 3(h)) shows that the average length of the nano-SCC polygons is 113 nm and the breadth is 66 nm. Agglomeration of the nanoparticles is also seen in the TEM image.

AFM images of the vulcanized rubber samples were taken on Multiview-1000 SPM (Nanonics Imaging, Ltd., Malcha, Jerusalem), in tapping mode. The AFM topographic (height) and phase images were taken in tapping mode. The height images barely show (Figures 3(i) and 3(k)) the dark and bright regions corresponding to the valleys and hills in the surface [50–54]. But the phase images (Figure 3(j)) reveal the microstructure of the composites. The phase image of NBCNT₄ (Figure 3(l)) shows more roughness than the phase image of NBCC (Figure 3(j)), indicating greater rubber-filler interaction in NBCNT₄. The hills and valleys are due to the dispersion of filler particles.

3.1.4. Cure Properties. The curing behavior of rubber compound was measured using the automated Goettfert elastograph, model Vario 67.98 (German) at 150°C. The cure properties of the NBR/NR nanocomposites containing different fillers are given in Table 2. Optimum cure time of the CNT-filled NBR/NR blend mixes decreased with the increase in the

dosage of CNT from 1 phr in NBCNT₁ to 7 phr in NBCNT₄ as given in Table 2. The carboxyl groups on CNT could reduce the cure time compared with the SCC-filled mix NBCC. Like silica, PCS-filled mix (NBCS) showed a slight reduction in cure time, and the value was close to that of unfilled mix NB₀. The scorch time slightly decreased with the increase in concentration of CNT as reported for NR [55]. The delta torque values of the mixes also exhibited an increase as the concentration of CNT was increased, indicating better cure state. Cure rate index values were in agreement with other results shown by the mixes.

Considering the various cure properties, it can be inferred that CNTs filled mixes are slightly superior to nano-SCC and nano-PCS-filled mixes. This can be due to more efficient dispersion of carboxyl-modified CNTs in the polymer matrix leading to intercalation when compared with SCC and PCS. The smaller particle size and larger surface area of CNTs could increase their dispersion in the polymer matrix. The polar groups on the CNT increased the interfacial interaction between polar NBR and nonpolar NR (Figure 4).

3.1.5. Tensile Properties. Studies on the effect of filler addition on tensile strength of natural and synthetic rubbers are available. Tensile strength provides information about strength and toughness of a material [56, 57]. Tensile properties

TABLE 2: Cure properties of NBR/NR blend mixes containing nano-SCC, -PCS, and CNT.

Mixes	Optimum cure time t_{90} min.	Scorch time t_{s2} min.	Minimum torque dNm	Maximum torque dNm	Cure rate index (CRI)
NBCNT ₁	8.20	1.38	0.2	5.1	14.7
NBCNT ₂	6.95	1.37	0.3	5.5	17.9
NBCNT ₃	6.71	1.20	0.4	5.7	18.2
NBCNT ₄	5.74	1.11	0.8	6.2	21.6
NBCC	8.14	1.28	0.5	5.2	14.6
NBCS	5.81	1.48	0.3	5.2	23.1
NB ₀	5.9	1.21	0.5	5.4	21.3

TABLE 3: Technological properties of NBR/NR blend mixes containing nano-SCC, -PCS, and CNT.

Mixes	TS MPa	300% M MPa	EB %	TR N/mm	Hardness Shore A	AL mm ³	CS %	ΔG J/mol	ΔS J/mol/K
NBCNT ₁	4.36	2.54	463	21.52	37	161.13	3.85	-27.08	0.0902
NBCNT ₂	6.64	3.33	490	28.5	41	139.76	3.91	-27.96	0.0932
NBCNT ₃	7.83	4.12	519	36.49	43	137.12	4.08	-30.0	0.100
NBCNT ₄	8.45	4.76	542	37.21	48	135.32	4.14	-31.01	0.1034
NBCC	3.86	2.21	445	20.71	40	175.26	3.32	-26.12	0.0871
NBCS	5.81	2.60	429	18.11	37	179.19	3.46	-26.08	0.0869
NB ₀	3.79	2.11	379	14.97	34	191.09	3.95	-26.54	0.0885

TS: tensile strength, M: modulus, EB: elongation at break, TR: tear resistance, CS: compression set, AL: abrasion loss, and SV: swelling value.

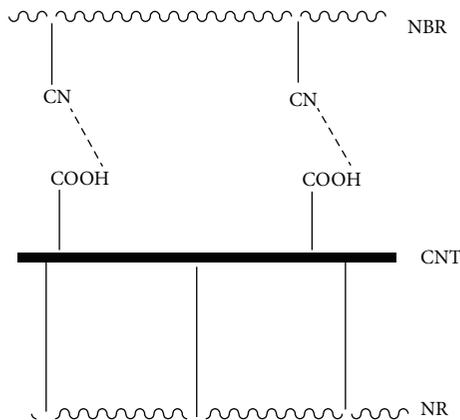


FIGURE 4: NR/NBR compatibilization by carboxylated CNT.

of the vulcanizates were measured on a Universal Testing Machine, Instron Corporation, series IX model 1034, using a crosshead speed of 500 mm/min as ASTM procedure D412-87 and using dumbbell specimen. Five samples of each vulcanized sheet were used for the measurement. The values were directly obtained from the instrument. Tensile strength and modulus were reported in MPa and elongation at break in percentage. Table 3 shows that tensile strength is higher for vulcanizates containing modified CNT compared with those containing silicate-coated calcium carbonate and PEO-coated calcium silicate indicating that polymer-filler interaction is more for the mixes containing CNT, as evident from the bound rubber content (Figure 5). Compatibilization and miscibility between NR and NBR is also more for CNT mixes, as clear from the SEM and TEM images (Figure 3);

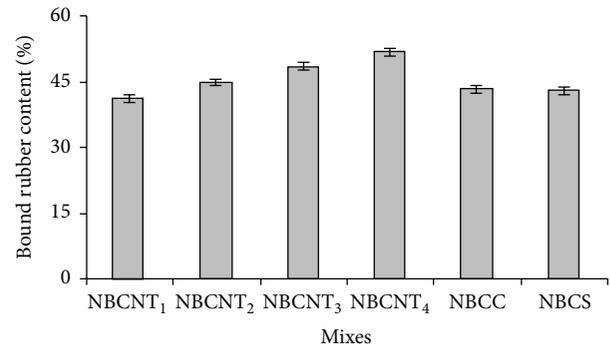


FIGURE 5: Variation of bound rubber content with filler.

that is, foldings are minimum in the images. As the dosage of the modified CNT having much higher aspect ratio increases, surface area available to the polymer will increase, resulting in high polymer-filler interaction and intercalation of polymer into the CNTs. The spherical shape and lower aspect ratio of SCC and PCS caused lower polymer-filler interaction in NBCC and NBCS, as evident from the microscopic images (Figure 3).

Table 3 shows that the elongation at break (EB) percent was higher for CNT-filled mixes compared with those containing SCC and PCS due to superior polymer-filler interaction possible in CNT mixes. As the dosage of CNT increased from 1 phr in NBCNT₁ to 7 phr in NBCNT₄, EB percent also increased unlike in conventional composites probably due to the plasticizing or sliding effect [58], as clear from the SEM images (Figures 3(d) and 3(e)). Also, miscibility of NR in NBR was increased due to the binding

action of CNT containing polar groups. The nonpolar part of CNT interacts with the nonpolar NR, and the polar groups on CNT interact with polar end of NBR, causing an improvement in miscibility of the two rubbers.

Modulus of the CNT-filled mixes was also higher compared with SCC- and PCS-filled mixes. Also, an increase in modulus was observed (Table 3) when the dosage of CNT was increased from 1 phr in NBCNT₁ to 7 phr in NBCNT₄. This can be attributed to the high polymer-filler interaction in these vulcanizates as described above.

3.1.6. Other Mechanical Properties. Tear resistance values of the NBR/NR nanocomposites are given in Table 3. The test samples were cut from the vulcanized sheets parallel to the grain direction. The test pieces were mounted on a Universal Testing Machine, Instron Corporation, series IX, model 1034, using a crosshead speed of 500 mm/min as per ASTM method D624-98. Five samples of each vulcanized sheet were used for the measurement. Tear resistance was directly obtained in N/mm. All of the CNT-filled vulcanizates exhibited superior tear resistance compared with SCC- and PCS-filled vulcanizates. Also, as the dosage of CNT was increased from 1 phr in NBCNT₁ to 7 phr in NBCNT₄, there was a 73% increase in tear resistance. This is because of the better dispersion of CNTs in the polymer matrix and the higher filler-polymer interaction, as evident from the bound rubber content (Figure 5) and microscopic images (Figure 3). The CNTs have suitable shape and geometry to prevent crack propagation more effectively than NBCC and NBCS [59].

Hardness values (Shore A) of the vulcanizates are also given in Table 3. The CNT-filled mixes exhibited more hardness than the SCC- and PCS-filled mixes, particularly at 5 and 7 phr of CNTs. This is due to the extra strength of CNT and also due to the superior polymer-filler interaction possible for CNT-NBR/NR systems. The high bound rubber content of CNT-filled mixes (Figure 5) is an indication of high polymer-filler interaction.

Compression set was determined as per ASTM D395-89 (method B) using the apparatus manufactured by Prolific Engineers India, Ltd. The moulded samples (1.25 cm thick and 2.8 cm in diameter) compressed to constant deflection (25%) were kept for 22 hrs at 27°C. The samples were taken out, and after keeping for 30 min, the final thickness was measured. Three samples of each mix were used for compression set determination. The CNT-filled vulcanizates showed high compression set values as given in Table 3, compared with the NBCC and NBCS. This can be attributed to the reduction in the elasticity of the composites with an increase in MWNT dosage [60].

Abrasion loss was measured using DIN abrader (DIN 53516). A moulded sample having a diameter of 6 ± 0.2 mm and a thickness of 6 mm was inserted into the sample holder so that 2 mm of the sample remained exposed and was allowed to move across the surface of an abrasive sheet mounted on a rotating drum. Weight of the test specimen was noted before and after the test. The difference in weight was converted into volume loss by dividing the weight loss with the density of the specimen. Three moulded samples

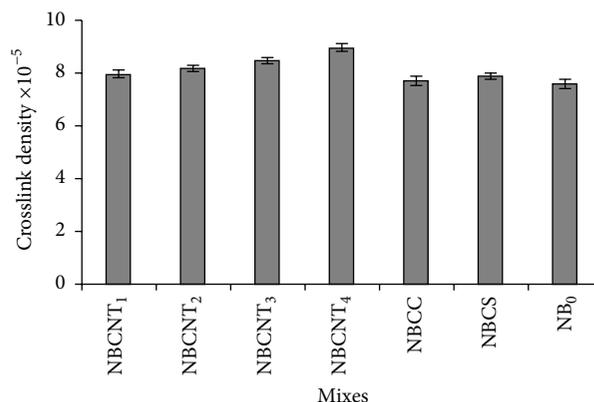


FIGURE 6: Variation of crosslink density with filler dosage.

of each mix were used for the determination of abrasion loss, and the final result was expressed as the average of these results. Abrasion resistance of CNT-filled vulcanizates was superior to that of the SCC- and PCS-filled vulcanizates (Table 3). As the dosage of CNT was increased, abrasion loss decreased (abrasion resistance increased). The reinforcing action of CNT has improved the abrasion resistance of CNT-filled mixes.

3.2. Extent of Reinforcement: Thermodynamic Parameter Analysis. Cross-link density (CD) values of the vulcanizates estimated using toluene are represented in Figure 6. Circular samples of approximately 1 cm diameter and 0.2 cm thickness were punched out from the central portions of the vulcanizate and weighed. These samples were allowed to swell in toluene at room temperature to allow the swelling to reach equilibrium. The CNT-filled nanocomposites possessed higher CD than the gum and those filled with SCC and PCS. As the dosage of CNT was increased from 1 phr in NBCNT₁ to 7 phr in NBCNT₄, crosslink density also increased. The higher cross-link density of the CNT-filled mixes shows the reinforcing action of CNT in the NBR/NR blend. The blend became more cross-linked in presence of the modified CNT due to the intercalation of polymer chain segments into the tube space of CNT. The increased crosslink density puts restraint on the network which could result in enhanced tensile properties. The lower aspect ratio and less appropriate geometry of SCC and PCS (as evident from the TEM images) compared with CNT resulted in comparatively poor polymer-filler interaction in NBCC and NBCS and hence lower CD and tensile strength.

Thermodynamic parameters like the free energy change (ΔG) and the entropy change (ΔS) were estimated for the nanocomposites using (1) and (2), respectively [61], and the values are given in Table 3. Consider the following:

$$\Delta G = RT \left[\ln(1 - V_r) + V_r + \chi V_r^2 \right], \quad (1)$$

$$\Delta S = \frac{\Delta G}{T}, \quad (2)$$

where χ is the interaction parameter, V_r is the volume fraction of rubber, and T is temperature in Kelvin.

The CNT-filled vulcanizates showed larger negative values of free energy change (Table 3) compared with SCC- and PCS-filled vulcanizates, which indicates better compatibility between the filler and polymer matrix in CNT-filled mixes. The negative value of change in free energy increased with the dosage of CNT indicating increased filler-polymer interaction and increased NBR/NR miscibility. Similarly, the CNT-filled mixes possessed more entropy change (Table 3). Also, the change in entropy increased with the increase in dosage of CNT. These results also support the increased compatibility between the filler and the polymer. This is a further proof of the intercalation of the polymer into the tube space of CNTs.

3.3. Oil Resistance. The effect of addition of fillers on the oil resistance of the vulcanizates was analyzed using oil swelling coefficients (σ) of circular samples (2 cm in diameter) immersed in 2 T oil for 5 days. The swelling coefficients were calculated using the following [34]:

$$\sigma = \frac{(W_s - W_i)}{W_i \times \rho}, \quad (3)$$

where W_s is the weight of swollen sample, W_i is the initial weight of the sample, and ρ is the density of rubber. Swelling coefficients decreased with increase in dosage of CNT as shown in Figure 7, due to the improved barrier property of the nanocomposites containing higher dosage of the nanofiller.

4. Summary and Conclusions

The carboxylated CNT-filled NBR/NR blend mixes showed better cure properties when cured with nanomodified BIAT and micro-CBS binary system. Cure time decreased with the increase in concentration of CNT. The delta torque values of the CNT-filled mixes increased with the increase in concentration of CNT. These improved cure properties were due to the better dispersion of CNT by increasing the filler-polymer interaction leading to intercalation of polymer matrix, as compared with silicate-coated calcium carbonate and PEO-coated calcium silicate. The polar groups on CNT could increase the NBR/NR compatibilization. The XRD curves and microscopic images provide support for the better mixing of CNT compared with silicate-coated calcium carbonate and PEO-coated calcium silicate. The improved mixing has led to the enhancement of the technological properties like tensile strength, modulus, elongation at break % values, tear strength, abrasion resistance, bound rubber content, and hardness. The enhanced crosslink density values are in agreement with other technological properties. The elongation at break % values increased with the increase in the dosage of CNT because of the sliding effect. The CNT-filled vulcanizates exhibited improved oil resistance, compared with the vulcanizates containing inorganic fillers. This is due to the improved barrier property imparted by the better dispersed CNT. Tortuous paths were created in presence of CNTs.

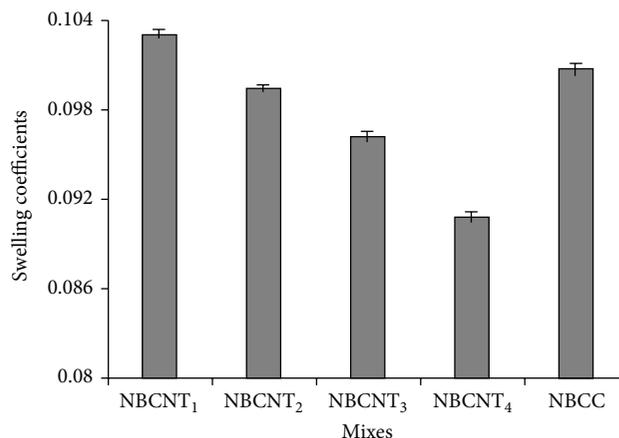


FIGURE 7: Oil swelling coefficients of NBR/NR nanocomposites.

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