

Barium Titanate-reinforced Acrylonitrile-Butadiene Rubber: Synergy Effect of Carbon-based Secondary Filler

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Abstract Acrylonitrile rubber (NBR) composites filled with barium titanate (BT) were prepared using an internal mixer and a two-roll mill. Also, a secondary filler, namely carbon nanotubes (CNT), was added in order to find a potential synergistic blend ratio of BT and CNT. The cure characteristics, tensile and dielectric properties (dielectric constant and dielectric loss) of the composites were determined. It was found that NBR/BT composites with CNT secondary filler, at a proper BT:CNT ratio, exhibited shorter scorch time (t_{s1}) and cure time (t_{c90}) together with superior tensile properties and reinforcement efficiency, relative to the one with only the primary filler. In addition, the NBR/BT-CNT composite with 80 phr BT and 1–2 phr CNT had dielectric constant of 100–500, dielectric loss of 12–100 and electrical conductivity below 10^{-4} S/m together with high thermal stability. Thus, with a proper BT:CNT mix and filler loading, we can produce mechanically superior rubber composites that are easy to process and low-cost, for flexible dielectric materials application.

Keywords Acrylonitrile-butadiene rubber; Barium titanate; Carbon nanotube; Dielectric properties; Mechanical properties

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INTRODUCTION

Highly dielectric materials have become attractive and desirable for the electrical and electronics industries. The technology trend is towards flexible and tunable devices, and ceramic/polymer composites have great potential for these applications. Flexible highly dielectric ceramic/polymer composites can be produced in any form for flexible electronic devices, such as capacitors, actuators, sensors, electrostrictive artificial muscles, gate dielectrics, memories, energy storage devices, and microwave devices. It has been found that high dielectric constant, low dissipation factor, high dielectric strength, simple processability and good mechanical properties can be achieved by combining advanced ceramic fillers with advanced rubbers.^[1,2]

Theoretically, due to the negligible contribution of the ionic component to total dielectric constant, most polymers have a low dielectric constant.^[3] The ceramic materials are fragile with poor processability and high density. Ceramic fillers in a polymer matrix can provide high dielectric constant and low dissipation factor, flexibility, excellent processability, and mechanical properties. Therefore, ceramic filling of a polymer matrix can overcome its limitations.^[4]

Barium titanate (BT, chemical formula BaTiO_3) is a typical perovskite ceramic material with excellent piezoelectric and ferroelectric properties. Due to its ferroelectric properties, BT has a very high dielectric constant, up to 1.0×10^4 .^[5] In addition, it is highly stable with excellent electrical, mechanical and chemical properties.^[6] Several studies have reported on BT filled polymer and rubber composites in recent years, using as the matrix polyaniline (PANI),^[7] epoxy resin,^[8,9] natural rubber (NR),^[10,11] polyester,^[12] butyl rubber (BR),^[13] silicone elastomers,^[14–17] poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP),^[18] poly(vinylidene fluoride) (PVDF),^[19–21] poly(methyl methacrylate) (PMMA),^[6,22] ethylene propylene diene monomer (EPDM),^[23] polyamide (PA),^[24] acrylonitrile-butadiene rubber (NBR),^[25] and polycaprolactone (PCL).^[26]

However, high ceramic filler loading is usually required for high enough permittivity. Further, these composites exhibit high density with poor physical and processing properties. An alternative approach, incorporating a conductive filler such as graphene oxide (GO),^[3,27,28] carbon nanotubes (CNT), etc., can provide percolated insulator/conductor polymer composites. When the volume fraction of the conductive filler reaches the percolation threshold, the composite can show high permittivity.^[29] The two main types of CNT are single-walled and multi-walled CNT. Using CNT in rubber composites has been

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investigated for about a decade, and when the percolation threshold is exceeded, good thermal stability, tensile strength and especially electrical conductivity due to the unique sp^2 -hybridized carbon atoms in cylindrical nanotubes with high aspect ratios can be simultaneously achieved.^[8,30] Nevertheless, due to a leak current in the polymer/CNT nanocomposite, a large dissipation factor ($\tan\delta$) has limited high-frequency applications, as in embedded capacitors, because of loss of electrical energy to heat and overheating of the devices.^[31] In order to improve the dielectric properties, BT and CNT mix filled various types of polymers, including polypropylene (PP),^[33] poly(cyclohexyl methacrylate),^[31] PA,^[33] polydimethylsiloxane (PDMS)^[34] and PVDF.^[35–39] have been reported. In cases of rubbers, Joseph *et al.*^[40] prepared BR/single-walled CNT composites as the electrostatic discharge shielding material by using solution mixing process; Kumar *et al.*^[41] studied vulcanization of silicone rubber/BT-CNT composites using room temperature for providing the elastomer slab; Bizhani *et al.*^[42] provided electromagnetic wave absorption foams from EPDM/BT-CNT through melt mixing and compression molding procedures. It was found that the CNT concentration beyond the percolation period is necessary because then there is no conductive CNT pathway and the electric charges have to remain inside the composite.^[43] However, to the best of our knowledge, no prior report has been presented on the fabrication and characterization of BT-CNT filled nitrile butadiene rubber (NBR) as the matrix using CNT below the percolation concentration.

NBR is a synthetic rubber consisting of acrylonitrile and butadiene copolymers. Due to its excellent oil resistance, low gas permeability, good processability and moderate cost, NBR has been used in many applications such as oil seals, hoses, shoe soles and tubes.^[44] NBR was chosen for this research because its irregular chain structure with strongly polar carbon-nitrogen triple bond ($C\equiv N$) groups and permanent dipole moments enables orientation polarization that is important for dielectric properties.^[45] It does have a higher dielectric constant (>10) than most non-polar polymers.^[46] Prior studies on its dielectric applications have assessed the fillers calcium copper titanate (CCTO), titanium dioxide (TiO_2),^[47] and barium titanate (BT).^[48]

In this present study, NBR composites with hybrid BT and CNT fillers were prepared by melt compounding using BT as the ferroelectric component and CNT as the electrically conductive filler component. The main goals of this work were to: (1) fabricate composites that contain BT, and CNT at 1–3 phr that is below the percolation threshold in NBR matrix; (2) determine the cure characteristics, mechanical and morphological properties and thermal stability; and (3) evaluate the dependency of electrical and dielectric properties on the filler mix and loading. These composites with BT and CNT are suitable for flexible dielectric materials.

EXPERIMENTAL

Materials

The acrylonitrile-butadiene rubber (NBR) with 33% acrylonitrile content was obtained from Nantex public Co., Ltd. (Kaohsiung

832, Taiwan). Zinc oxide (ZnO) and stearic acid used as activators were purchased from Bossoftical public Co., Ltd. (Songkla, Thailand). 2-Mercaptobenzothiazyl disulfide (MBTs) and sulfur were manufactured by Vessel chemical public Co., Ltd. (Bangkok, Thailand). Barium titanate (BT) was synthesized in-house following the process described elsewhere,^[49] and had 4.8 μm particle diameter. Furthermore, multiwall carbon nanotubes (CNT) of 9.5 nm in diameter, about 1.5 μm in length, and 90% purity were manufactured by Nanocyl S.A. (Sambreville, Belgium). The specific characterization of the CNT can be also seen in our previous work elsewhere.^[50,51] The compounding formulation is summarized in Table 1.

Table 1 Compounding formulation of NBR/BT composites with various CNT loadings.

Chemical	Content (phr)
NBR	100
BT	80 and 120
CNT	1, 2 and 3
ZnO	5
Stearic acid	2
MBTS	1.5
Sulphur	1.5

Preparation of NBR/BT Composites with and without CNT Secondary Filler

NBR composites were prepared by melt mixing in an internal mixer (Brabender VR GmbH & Co. KG, Duisburg, Germany) with 60 r/min rotor speed at 60 °C. The compounding was initiated by mastication of NBR for 2 min. Then, the sulfur was added to the chamber and mixing was continuous for another 2 min. This aims to disperse and distribute sulfur particles throughout the NBR matrix since sulfur atoms will crosslink only to the $C=C$ bonds in butadiene chain during compression. The ZnO (2 min) and stearic acid (1 min) were then added and mixed in sequence. Thereafter, the dispersed BT, CNT or BT-CNT was added and mixing continued for another 3 min before adding MBTs, and eventually dumping the compound. It is noted that the compounding had 10 min total mixing time at optimum temperature of 80 °C, and all the fillers were stirred using a mechanical stirrer at 200 r/min for 5 min before going in the internal mixer. The rubber compounds were eventually sheeted out with a two-roll mill, and kept in a desiccator for 24 h at room temperature before testing and vulcanizing. Finally, rubber composite sheets with dimensions of 150 mm $\times$ 160 mm $\times$ 2 mm were prepared at 160 °C by compression molding, using as molding time the cure time determined from rheometer test. The NBR composites with BT, CNT and BT-CNT are here labeled with “NBR/BT_x”, “NBR/CNT_x” and “NBR/BT_x-CNT_x”, respectively, where x refers to the filler content in parts per hundred rubber (phr).

Characterization

Cure characteristics of neat NBR and its compounds were determined with a moving die rheometer (MDR) (Monsanto Co., Ltd., Ohio, USA). The measurements were performed at a fixed 1.66 Hz oscillation frequency and 1 arc degree amplitude at 160 °C. Also, the storage modulus as a function of strain amplitude was measured using a rubber process

analyzer (RPA) (Alpha Technologies, Akron, USA) in order to elucidate the filler reinforcement and the Payne effect. Thus, the strain sweep mode was used over the strain range 0%–100% with a fixed oscillation frequency of 1 Hz at 100 °C. Here, the Payne effect is quantified by the difference of storage moduli at maximal and minimal strains.

The NBR vulcanizates with and without BT or CNT secondary filler were subjected to mechanical testing in a universal tensile testing machine (Tinius Olsen, model 10ST, Salfords, England) as dumbbell-shaped specimens according to ASTM D-412. The tests were carried out using 500 mm/min cross-head speed at room temperature, and tensile strength, 100% modulus and elongation at break are reported.

Thermal stabilities of the neat NBR and NBR composites with BT and BT/CNT hybrid filler were assessed from thermogravimetric analysis (TGA) using Simultaneous Thermal Analyzer (STA8000, Perkin Elmer, Waltham MA, USA) with 5–10 mg samples, in the temperature range 25–1000 °C with a 10 °C/min heating rate. In the initial stage, the samples were examined in nitrogen atmosphere, which was then changed to oxygen when temperature passed 550 °C. To determine the glass transition temperature (T_g) and tan delta ($\tan\delta$) for the composites and for the neat NBR, a Perkin Elmer DMT 8000 (Perkin Elmer, Singapore) was used for dynamic mechanical thermal analysis (DMA). The samples were tested from –100 °C to 50 °C with a heating rate of 3 °C/min in tension mode, fixing the frequency and the strain at 10 Hz and 0.1%, respectively.

In addition, the dielectric properties resistance (R_p), capacitance (C_p) and dissipation factor ($\tan\delta$) were measured for the vulcanizates at room temperature, using an impedance analyzer (E4990A, Keysight Technologies Inc., Denver, USA) over the frequency range from 20 Hz to 10 MHz and with 1 V of AC amplitude. The sample was first placed between two parallel plate electrodes with 5 mm diameter. The dielectric constant (ϵ'), dielectric loss (ϵ'') and electrical conductivity (σ) were calculated using Eqs. (1)–(3), respectively:^[52]

$$\epsilon' = \frac{C_p(d)}{A(\epsilon_0)} \quad (1)$$

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \quad (2)$$

$$\sigma = \frac{1}{\rho} = \frac{d}{(R_p)A} \quad (3)$$

where ϵ_0 is the dielectric constant of the free space, which is 8.854×10^{-12} F/m. The parameters d and A refer to sample thickness and area of an electrode, respectively. The volume resistivity ρ is the reciprocal of conductivity.

To assess the dispersion of BT and CNT secondary filler in the NBR composites, they were imaged using a scanning electron microscope (SEM) (ZeissSupra-40 VP, Carl Zeiss Microscopy GmbH, Oberkochen, Germany) and an optical microscope (OM) (Carl Zeiss Microscopy GmbH, Oberkochen, Germany). For SEM, the samples were first cryogenically fractured in liquid nitrogen to create a fresh cross-sectional surface, which was sputter-coated with a thin layer of gold under vacuum before imaging. On the other hand, for OM the samples were initially fast cut with a razor blade (Energizer® Holdings, Inc., Missouri, USA) in order to make a smooth

sample surface for imaging.

RESULTS AND DISCUSSION

Cure Characteristics

The cure curves of neat NBR and its compounds filled with BT and with CNT as secondary filler are shown in Fig. 1. It is seen that the cure-curve of neat NBR exhibited marching cure behavior, with increasing torque at over 90% cure time (t_{c90}) ($t_{c90} \sim 18$ min). This was attributed to acrylonitrile functional groups in NBR that can prevent sulfur atoms from reacting with allylic radicals in the butadiene backbone probably due to steric effect. Thus, slow vulcanization reaction is indicated by the increasing torque after cure time, as seen in Fig. 1. This marching cure behavior was also observed for the NBR composites with 80 and 120 phr of BT. However, plateau cure-curve behavior (i.e., torque is constant past the cure time) was seen with 1–3 phr of CNT secondary filler in the NBR/BT₈₀ composites. This might be due to the high thermal conductivity and stability of CNT, which activated sulfur atoms to react with butadiene in the NBR matrix and crosslinks the NBR/BT-CNT vulcanizates.^[53] On the other hand, NBR/BT-CNT composites with 120 phr BT exhibit again marching cure, as observed for neat NBR and NBR/BT₈₀ without CNT. This is due to the strong agglomeration of BT, which obstructed CNT linkages that would activate vulcanization of NBR.

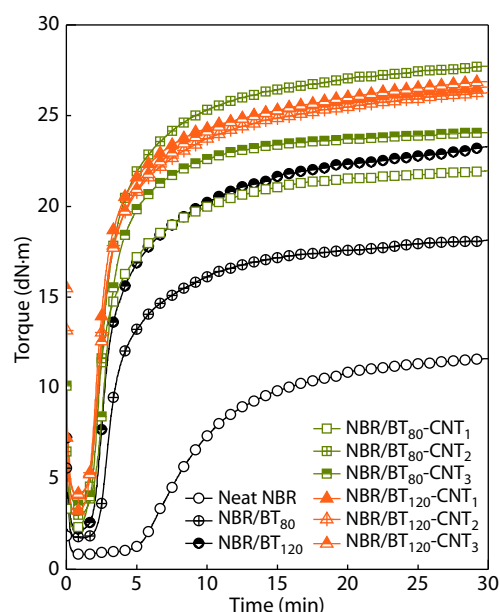


Fig. 1 Cure characteristic curves of neat NBR and NBR composites filled with BT and CNT secondary filler.

The scorch time (t_{s1}) and cure time (t_{c90}) for neat NBR and its compounds are shown in Fig. 2 and summarized in Table 2. The t_{s1} and t_{c90} for the filled NBR vulcanizates were slightly lower than those for the unfilled NBR vulcanizate, especially with CNT secondary filler. As expected, shortened t_{s1} and t_{c90} were caused by the exceptional thermal conductivity of CNT speeding up the vulcanization. For NBR compound with solely BT as filler, the decreased t_{s1} and t_{c90} were due to the high frictional heat generated by BT particles during shear in

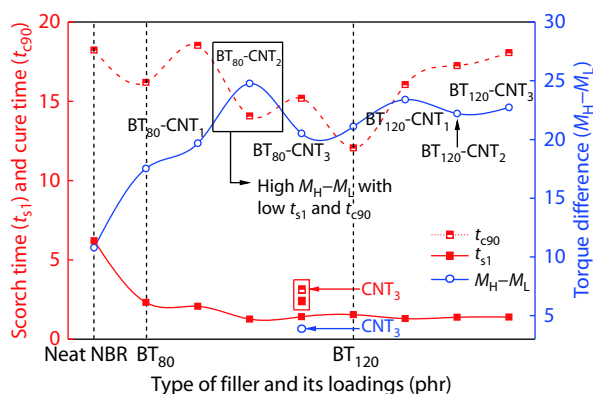


Fig. 2 Scorch time and cure time (red, left) and torque difference (blue, right) of neat NBR and NBR composites filled with BT and CNT secondary filler.

Table 2 Minimum torque (M_L) and maximum torque (M_H), torque difference ($M_H - M_L$), scorch time (t_{s1}) and cure time (t_{c90}) of neat NBR and NBR composites filled with BT and CNT secondary filler.

Case	M_L (dN-m)	M_H (dN-m)	$M_H - M_L$ (dN-m)	t_{s1} (min)	t_{c90} (min)
Neat NBR	0.81	11.61	10.80	6.21	18.23
NBR/BT80	1.73	18.14	17.53	2.32	16.19
NBR/BT120	2.19	23.29	21.10	2.07	18.53
NBR/BT ₈₀ -CNT ₁	2.26	21.97	19.68	1.26	14.07
NBR/BT ₈₀ -CNT ₂	2.97	27.73	24.76	1.42	15.19
NBR/BT ₈₀ -CNT ₃	3.55	24.07	20.52	1.55	16.06
NBR/BT ₁₂₀ -CNT ₁	3.18	26.58	23.40	1.30	16.05
NBR/BT ₁₂₀ -CNT ₂	4.08	26.28	22.20	1.38	17.25
NBR/BT ₁₂₀ -CNT ₃	4.15	26.88	22.73	1.39	18.07

the rheometer test, as heat induced vulcanization of the compound. Thus, BT with CNT secondary filler effectively decreased t_{s1} of the NBR compound synergistically. However, the t_{s1} and t_{c90} of NBR/BT and NBR/BT-CNT compounds increased with excessive BT or CNT content, possibly because then the filler might prevent the interactions of sulfur atoms with NBR, required in vulcanization reactions. This mechanism can explain the longer t_{s1} and t_{c90} with BT and CNT secondary filler, compared to only NBR.

Minimum torque (M_L) is associated with the viscosity of a compound. The BT and CNT secondary filler increased M_L consistently with filler loading due to filler-filler and rubber-filler interactions as well as by the hydrodynamic effect.^[54] The highest M_L was found for the NBR/BT₁₂₀-CNT₃ compound, indicating it had the highest viscosity. On the other hand, the extent of crosslinking and the reinforcement by filler in rubber matrix are associated with the maximum torque (M_H). A significantly increased M_H was observed for NBR filled with BT and CNT secondary filler due to the high surface to volume ratio and the physical interactions of the fillers with the NBR matrix that restricted mobility of rubber chains, increasing stiffness and hardness of the NBR composite.^[55,56]

The torque difference ($M_H - M_L$) allows estimating the crosslink density of the neat NBR and the NBR composites filled with BT and CNT secondary filler. It is seen that $M_H - M_L$ increased with BT and CNT secondary filler loadings. This relates to the activation of vulcanization reaction and the reinforcement efficiency of the fillers in NBR matrix. It was also found

that the CNT secondary filler strongly increased $M_H - M_L$ from that of to NBR/BT. This was due to high specific surface of the mixed filler allowing high content of bound rubber on the filler. The NBR/BT₈₀ composites with 2 phr CNT exhibited the highest of $M_H - M_L$ among the composites. Further increase in CNT content led to agglomeration and poor filler distribution in the NBR matrix (as seen later in SEM and OM images). As a consequence, the reinforcing effect of the fillers in the rubber matrix was reduced.^[57] Therefore, the combination of BT with CNT secondary filler in NBR matrix at a proper ratio (BT:CNT=80:2, phr:phr) can significantly retard the compound/composite degradation (showing plateau curves), shorten t_{s1} and t_{c90} , as well as enhance crosslink density and reinforcing effect (increase of $M_H - M_L$).

Filler Dispersion

The state of filler dispersion can be assessed from storage modulus as a function of strain amplitude, shown in Fig. 3. The storage modulus increased with BT and CNT secondary filler loadings, as seen in Fig. 3(a). This is due to reinforcement by BT and CNT as seen in increased $M_H - M_L$ (Fig. 2). However, when strain was applied, the storage modulus decreased drastically due to lowering of viscosity by molecular chain movements.^[53] Considering the storage moduli at maximal and minimal strain amplitudes, the Payne effect (ϕ_p) associated with filler-filler interactions in the NBR matrix can be quantified. Thus, Fig. 3(b) shows the ϕ_p response to BT and CNT secondary filler loadings. It was found that ϕ_p increased with the filler loadings to approximately 170 kPa with BT at 120 phr, whereas 80 kPa was observed for the NBR/BT₈₀ composite. This is due to the strong agglomeration of BT in the NBR matrix. However, in CNT filled composites, ϕ_p serves to indicate the formation of CNT networks in the rubber matrix.^[58–60] It is seen in Fig. 3(b) that ϕ_p of the NBR/BT composites with CNT secondary filler increased with CNT loading. This suggests synergistic BT-CNT interactions as proposed in the models of Fig. 4. Here, the BT aggregates were thoroughly dispersed in the NBR matrix, and BT agglomerated strongly at 120 phr loading level, as exhibited in Fig. 4. In addition, interactions of BT aggregates with CNT networks took place in the NBR matrix, particularly in NBR/BT₈₀ composites with 1–3 phr CNT since stronger BT and CNT agglomerates were formed after 120 phr BT. This matches well the morphologies observed by scanning electron and optical microscopy imaging (see Fig. 5). It is clearly seen that strong BT and BT-CNT agglomeration took place with BT loadings over 80 phr, i.e. in NBR/BT₁₂₀ and NBR/BT₁₂₀-CNT₁–NBR/BT₁₂₀-CNT₃ composites. Homogenous dispersion and good distributions of BT and CNT secondary filler are observed for NBR/BT₈₀-CNT₂, whereas strong agglomeration of BT/CNT (agglomerate size ~100 μ m) is seen in NBR/BT₁₂₀-CNT₂ composite (i.e. dark area in an image).^[60,61] These match the observed $M_H - M_L$ and also the storage moduli in Figs. 2 and 3, respectively.

Tensile Properties

The stress-strain curves, tensile strength and 100% modulus of neat NBR and NBR composites with BT and CNT secondary filler are shown in Fig. 6 and summarized in Table 3. Normally, NBR is a non-self-reinforcing rubber type. Its mechanical properties depend on intermolecular interactions of the strong polar group ($C \equiv N$).^[25] The stress-strain curves of composites significantly depended on the fillers. Reinforcement by BT and CNT

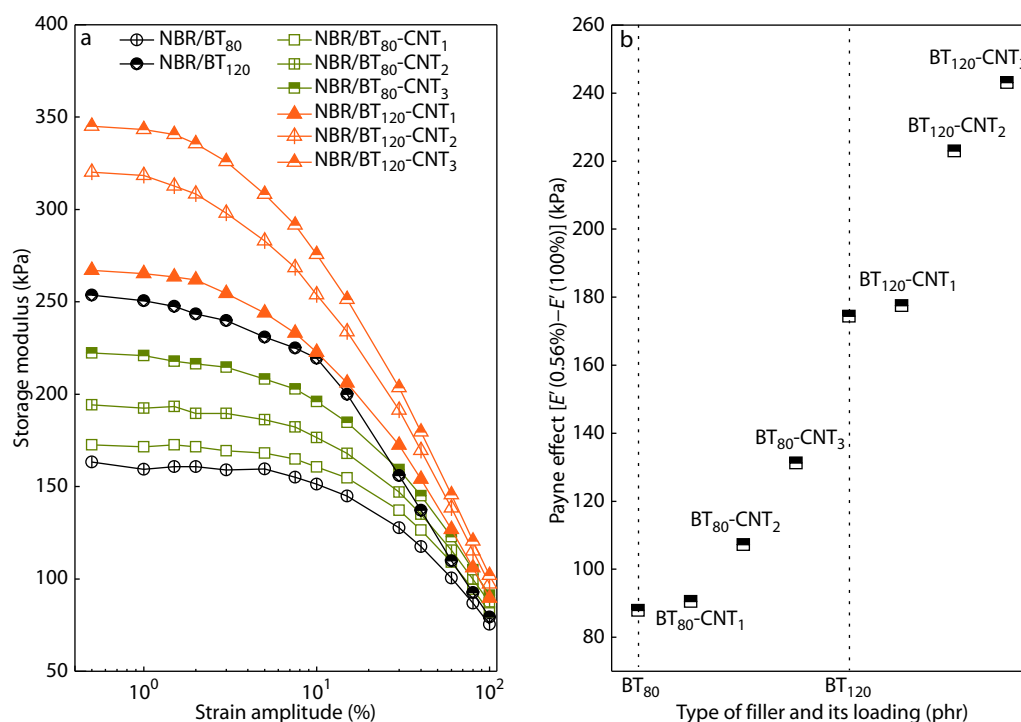


Fig. 3 Storage modulus as a function of strain amplitude (a), and Payne effect (ϕ_p) (b) of NBR composites filled with BT and CNT secondary filler.

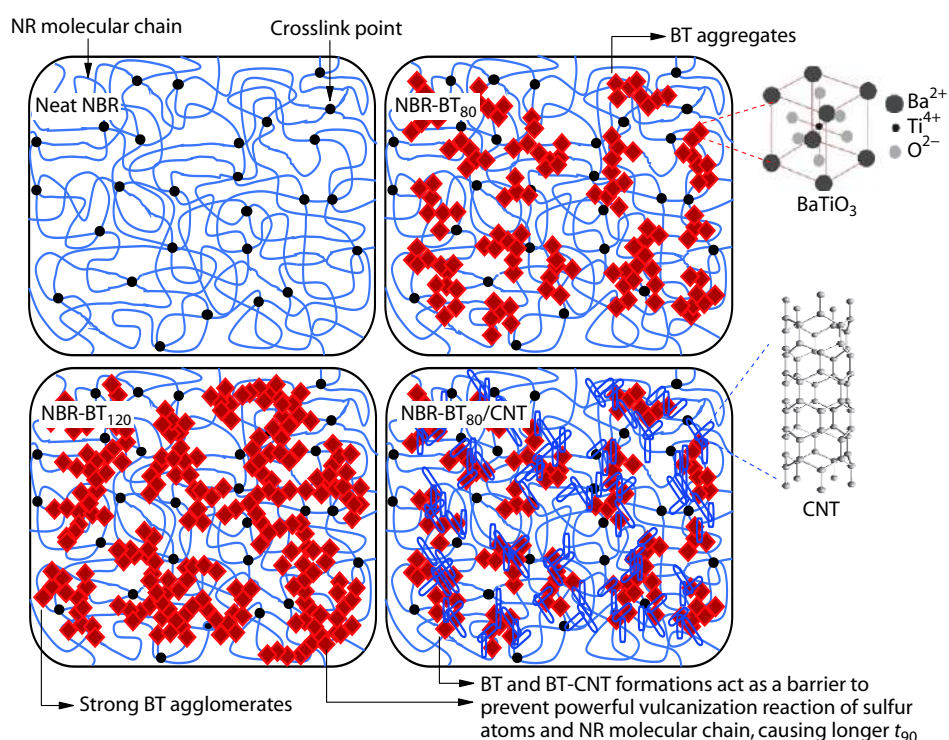


Fig. 4 Proposed models of BT and CNT secondary filler dispersed in NBR matrix.

secondary filler in the NBR matrix improved the 100% modulus and tensile strength of the NBR composites. All the filled NBR composites had tensile strengths higher than 6 MPa. This agrees well with the storage moduli in Fig. 3, which increased with filler loadings. The NBR/BT₈₀-CNT₂ composite showed the highest

tensile strength among the composites. There was synergy between the microparticle (BT) and nanoparticle (CNT) fillers, associated with the dispersion of both fillers in the NBR matrix, as seen in Fig. 5. Both BT and CNT secondary filler had homogeneous dispersions in the NBR matrix. On the other

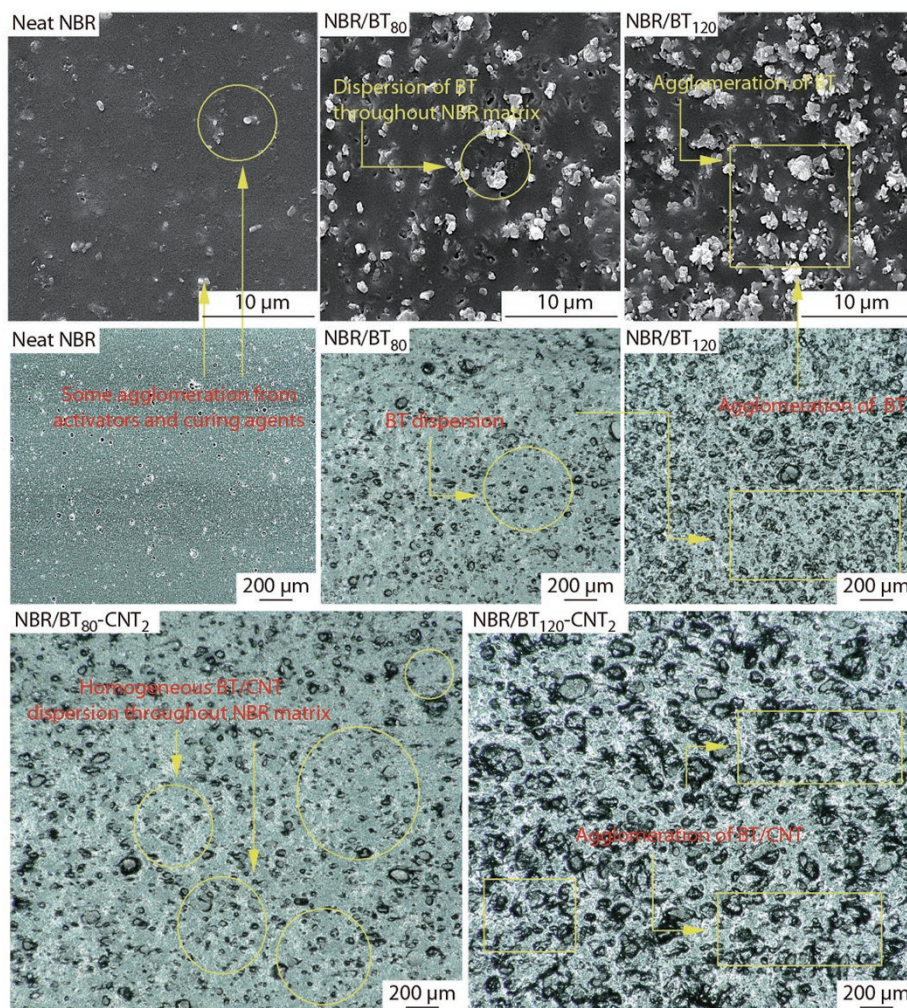


Fig. 5 Images obtained from SEM and OM of neat NBR and NBR composites filled with BT and CNT secondary filler.

hand, with over 80 phr of BT, the tensile strength of the composites drastically decreased to approximately 7 MPa. This was potentially caused by filler agglomeration.

Thermal Properties

Thermal properties in terms of thermal decomposition (T_d) and glass transition (T_g) temperatures, and also tan delta ($\tan\delta$), were assessed from TGA and DMA analyses, respectively. Fig. 7 shows the TGA thermograms of the neat NBR and the NBR-BT/CNT composites. Also, Table 4 exhibits the thermo-oxidative degradation steps of each composite *i.e.* at 5 wt%, 10 wt%, and 50 wt% degradation ($T_{5\%}$, $T_{10\%}$ and $T_{50\%}$), with T_d and residual weight (%). It is seen that the addition of BT and also of BT/CNT increased significantly the thermal stability of the composites due to effectively increased $T_{5\%}$, $T_{10\%}$, $T_{50\%}$ and T_d relative to the neat NBR. This is attributed to the superior thermal resistance of both BT and CNT fillers, which disperse throughout the NBR matrix and resist decomposition of the NBR molecules.^[10,43] It is also observed in Fig. 7 and Table 4 that BT and CNT can synergistically increase T_d of the composites, particularly of NBR-BT₈₀/CNT₂. Considering the residual weight (%) of each composite, which strongly increased with BT content, two decomposition steps are observed in temperature range

600–700 °C. Possibly some NBR was embedded in strong agglomerates of BT/CNT. Here, BT₈₀/CNT₃ and BT₁₂₀/CNT₁, BT₁₂₀/CNT₂, BT₁₂₀/CNT₃ can form wide areas of agglomeration in NBR matrix and the NBR molecules diffused to the agglomeration space of BT-CNT, and were decomposed at temperatures beyond 700 °C. However, NBR composites with BT₈₀/CNT₁ and BT₈₀/CNT₂ showed only a single decomposition step owing to the good dispersion and distribution of BT₈₀/CNT₂.

Thermodynamic behaviors of neat NBR and the NBR-BT/CNT composites are also exhibited in Fig. 8 by means of T_g and $\tan\delta$ from dynamic mechanical testing. It was found that the T_g of NBR increases significantly with the addition of BT and BT/CNT owing to restricted rubber movement at lower temperatures. Increasing BT loading also increased T_g of the composites. This relates to the reinforcement efficiency of the BT/CNT hybrid filler. It is seen in Table 5 that the T_g of NBR composites with BT₈₀/CNT₂ was moderate and close to the T_g of NBR-BT₁₂₀/CNT₁ and NBR-BT₁₂₀/CNT₂. This is due to the dispersion and distribution of BT₈₀/CNT₂ in the NBR matrix. Here, the increased T_g with increasing CNT content in NBR-BT₁₂₀ is due to the strong agglomeration of both fillers. Considering the $\tan\delta$ peak height, it relates to dissipation energy and elastomeric behavior of the polymer.^[10] It is noted that a

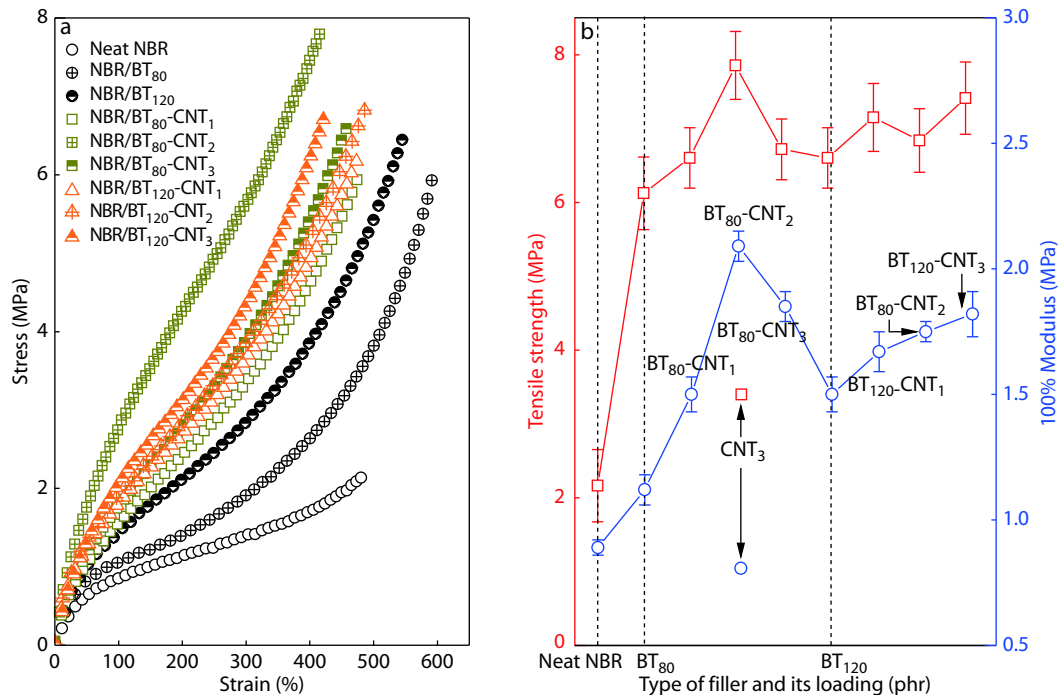


Fig. 6 Stress-strain curves (a) and tensile strength and 100% modulus (b) of neat NBR and NBR composites filled with BT and CNT secondary filler.

Table 3 Mechanical properties of NBR composites.

Case	Tensile strength (MPa)	100% Modulus (MPa)
Neat NBR	2.16±0.49	0.89±0.03
NBR/BT ₈₀	6.12±0.49	1.12±0.06
NBR/BT ₁₂₀	7.14±0.41	0.65±0.07
NBR/BT ₈₀ -CNT ₁	6.60±0.41	1.50±0.07
NBR/BT ₈₀ -CNT ₂	6.83±0.43	1.75±0.04
NBR/BT ₈₀ -CNT ₃	6.71±0.41	1.85±0.06
NBR/BT ₁₂₀ -CNT ₁	7.15±0.46	1.67±0.09
NBR/BT ₁₂₀ -CNT ₂	9.41±0.49	1.82±0.08
NBR/BT ₁₂₀ -CNT ₃	9.15±0.46	2.59±0.06

Table 4 Degradation temperatures in terms of $T_{5\%}$, $T_{10\%}$, $T_{50\%}$, T_d and residual weight (%) of neat NBR and NBR composites filled with BT and CNT secondary filler.

Case	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	T_d (°C)	Residual weight (%)
Neat NBR	345	404	465	369	1.01
NBR/BT ₈₀	393	424	495	378	42.97
NBR/BT ₁₂₀	388	415	N/A	424	53.88
NBR/BT ₈₀ -CNT ₁	381	406	493	421	43.78
NBR/BT ₈₀ -CNT ₂	382	413	499	423	44.55
NBR/BT ₈₀ -CNT ₃	422	437	603	428	44.00
NBR/BT ₁₂₀ -CNT ₁	401	436	N/A	438	52.80
NBR/BT ₁₂₀ -CNT ₂	424	444	N/A	444	54.05
NBR/BT ₁₂₀ -CNT ₃	434	453	N/A	460	54.21
NBR/CNT ₃	362	405	480	440	5.99

N/A = Not applicable.

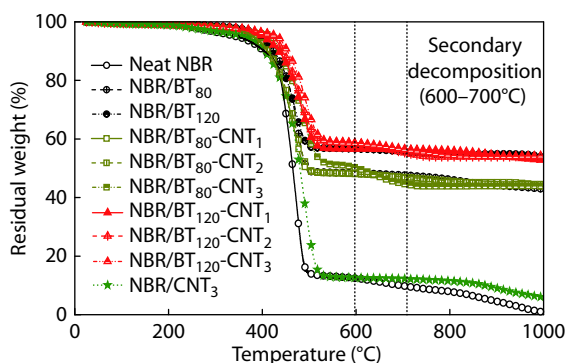


Fig. 7 Thermograms of neat NBR and NBR composites filled with BT and CNT secondary filler.

low height of $\tan\delta$ peak means high elasticity. It was found in Fig. 8 and Table 5 that incorporation of BT and BT/CNT to NBR diminished the $\tan\delta$ peak, since the fillers restrict molecular motions of the NBR chains, corresponding to bound rubber absorption on BT/CNT surfaces. It is also observed here that the NBR-BT₈₀/CNT₂ showed again a moderate $\tan\delta$

height of 1.43. However, lower $\tan\delta$ can also be seen for NBR-BT₁₂₀/CNT₂ and NBR-BT₁₂₀/CNT₃ owing to high loading of the filler hard phase, which reduces energy dissipation.

Dielectric Properties of NBR Composites

The dielectric properties and electrical conductivity of the composites were measured over a range of frequencies. Fig. 9 shows the dielectric constant (ϵ'), calculated using Eq. (1), for the NBR composites with and without CNT secondary filler. It is seen that ϵ' of neat NBR was increased significantly by BT at 80 and 120 phr. This is due to polarization of BT that contains cations barium (Ba^{2+}) and titanium (Ti^{4+}) and oxygen anions (O^{2-}). Therefore, dipole-dipole attractions and polarization effects were possible in NBR.^[62–64] Interestingly, the CNT secondary filler in NBR/BT composites effectively increased the dielectric constant, even though CNT has extremely high electrical conductivity. This relates to the concentration of CNT in the NBR

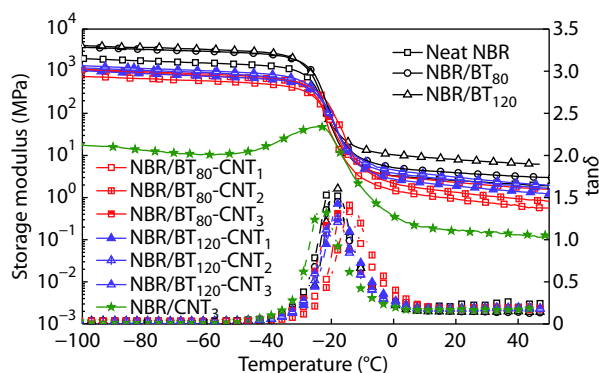


Fig. 8 Storage modulus and $\tan\delta$ as functions of temperature for neat NBR and NBR composites filled with BT and CNT secondary filler.

Table 5 The glass transition temperature T_g and loss factor $\tan\delta$ of neat NBR and NBR composites filled with BT and CNT secondary filler.

Case	T_g (°C)	$\tan\delta$
Neat NBR	-24.9	1.64
NBR/BT ₈₀	-24.4	1.54
NBR/BT ₁₂₀	-24.1	1.64
NBR/BT ₈₀ -CNT ₁	-21.8	1.39
NBR/BT ₈₀ -CNT ₂	-20.3	1.35
NBR/BT ₈₀ -CNT ₃	-22.3	1.44
NBR/BT ₁₂₀ -CNT ₁	-19.2	1.43
NBR/BT ₁₂₀ -CNT ₂	-19.8	1.31
NBR/BT ₁₂₀ -CNT ₃	-20.3	1.28
NBR/CNT ₃	-18.5	1.44

matrix. The percolation concentration of CNT in NBR is about 3 phr.^[65] Therefore, CNT at 1–3 phr will not form a conductive network spanning the whole NBR matrix, and charges could not escape, as seen in the proposed model of Fig. 10. Here, the anionic charges, particularly on CNT sidewalls and tube ends, can interact with cationic charges of BT and cause polarization effects with dipole-dipole attraction (Fig. 10a). Thus, the dielectric constant of the composites strongly increased. However, it is seen in Fig. 9 that the dielectric constant was not increased in the cases BT₈₀-CNT₃ and NBR/BT₁₂₀-CNT₁–NBR/BT₁₂₀-CNT₃. This is due to the formation of CNT network and of BT-CNT agglomerates.

In Fig. 10(b), the CNT particles begin to form a network inside the NBR matrix and therefore electrons can flow CNT-to-CNT. This can deplete the charges in the composite and therefore the dielectric constant decreased. On the other hand, considering NBR/BT₁₂₀-CNT₁–NBR/BT₁₂₀-CNT₃, the dielectric constant did not increase significantly compared to NBR/BT₈₀-CNT₁–NBR/BT₈₀-CNT₃. Possibly BT agglomeration prevented polarization with CNT secondary filler, as seen in Fig. 10(c). Here, CNT did not effectively affect polarization and dielectric constant since the BT was in the form of large agglomerates in the NBR matrix. Thus, the CNT might also strongly agglomerate, enabling electron transfer among the CNT particles, and reducing polarization in the NBR/BT₁₂₀-CNT composites. This hypothesis also matches the high Payne effect (Fig. 3) and the poor tensile properties (Fig. 6) relative to the NBR/BT₈₀-CNT composites. Fig. 11 shows the dielectric loss and electric conductivity of neat NBR and its composites.

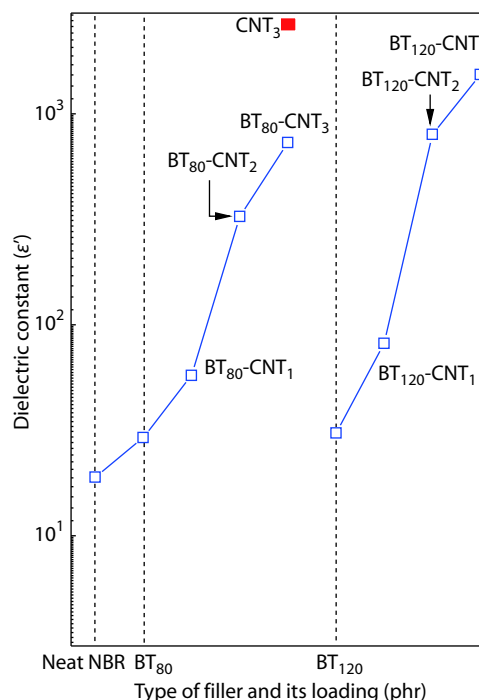


Fig. 9 Dielectric constant of neat NBR and NBR composites filled with BT and CNT secondary filler.

The ϵ'' increased with BT and CNT loadings to its maximum at 500. This is due to electron transfer throughout the NBR matrix enabled by the conductive fillers. However, as expected, at BT loading over 80 phr, agglomerates of BT and CNT formed and the dielectric loss significantly increased with filler loading. Considering the NBR/BT₈₀-CNT₂ composites, the ϵ'' was approximately 100 and ϵ' was 500, while ϵ'' and ϵ' of 12 and 100 were observed in NBR/BT₈₀-CNT₁. Therefore, in order to achieve proper dielectric properties responding to the needed product, BT:CNT ratios of about 80:1–80:2 phr are recommended.

Overall, based on Figs. 9 and 11, the addition of CNT secondary filler to NBR/BT composites can effectively increase the dielectric constant with low dielectric loss. Here, CNT concentrations were kept below the percolation threshold. This is confirmed by the electrical conductivity (σ) of the composites shown in Fig. 11, where no dramatic conductivity increase is seen relative to neat NBR and NBR/BT composites (σ in the range 10^{-8} – 10^{-6} S/m). The charges from sp^2 hybridized carbon in CNT secondary filler could not escape, and they strongly polarized BT in the NBR matrix. It was also found that the dielectric constant did not significantly increase when CNT networks were formed in NBR matrix, whereas dielectric loss effectively increased. This confirms that the CNT secondary filler concentration needs to be below the percolation session, in order to have strong polarization and dielectric response of BT. In addition, it was found that the addition of CNT secondary filler to the NBR/BT composites at a proper BT:CNT ratio not only increased dielectric properties, but also affected cure characteristics and mechanical properties. Here, the NBR/BT-CNT exhibited shorter scorch time and cure time together with higher crosslink density than the neat NBR or

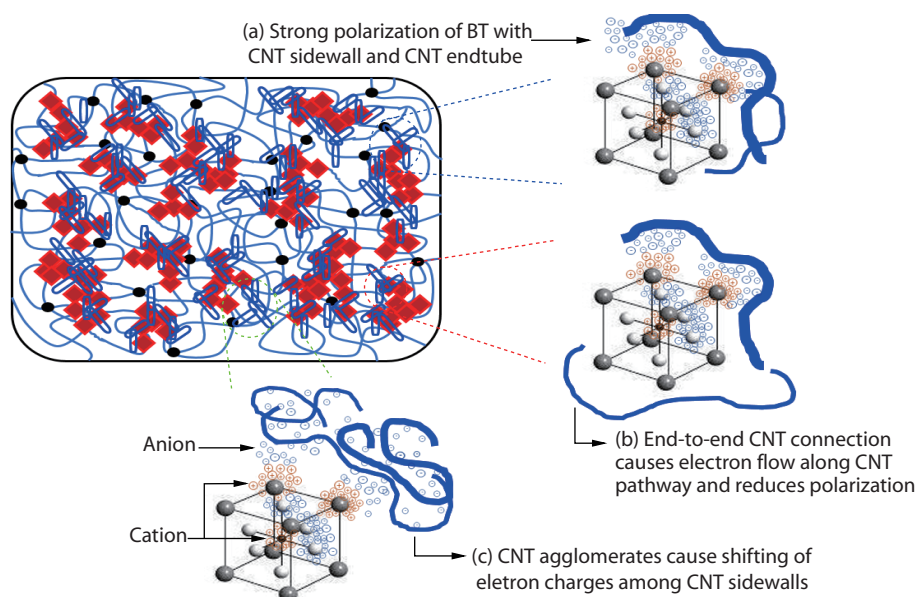


Fig. 10 Proposed models of BT and CNT formation producing polarization with different CNT loadings.

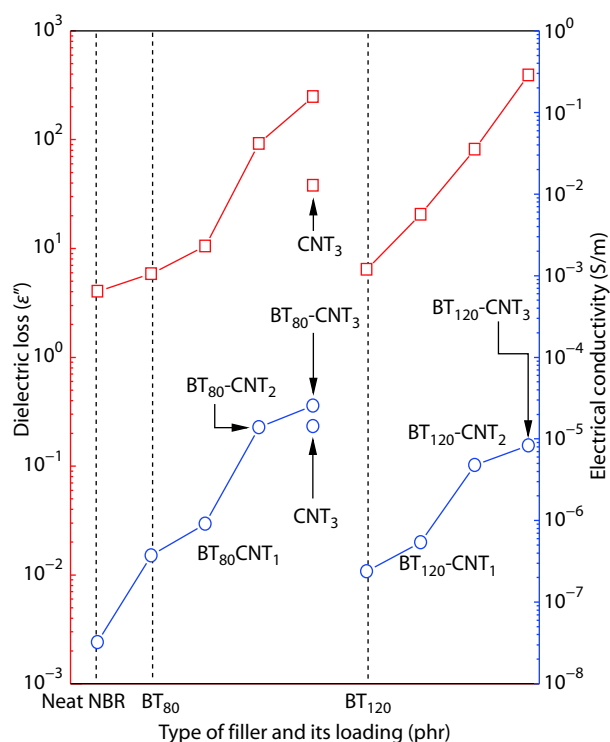


Fig. 11 Dielectric loss and electrical conductivity of neat NBR and NBR composites filled with BT and CNT secondary filler.

NBR composites with solely BT. Also, tensile strength and modulus of the composites were significantly enhanced. Thus, this might be a new way to produce flexible dielectric materials with superior mechanical and dielectric properties.

CONCLUSIONS

NBR/BT composites with and without CNT secondary filler were carefully prepared by melt blending in an internal mixer and on

a two-roll mill. CNT loading was varied keeping it below the percolation concentration, from 1 phr to 3 phr. It was found that CNT in NBR/BT composites shortened the scorch time and cure time and gave plateau cure-cure behavior. Here, the proper BT:CNT ratio was found to be 80:2, which gave superior mechanical properties in terms of storage modulus, 100% modulus, and tensile strength. In addition, the NBR/BT-CNT composites at BT:CNT ratios of 80:1–80:2 phr exhibited suitable dielectric properties (dielectric constant 100–500 and dielectric loss of 12–100) with below 10^{-4} S/m conductivity. This enables making flexible dielectric products that are easy to prepare and low-cost.

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