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 ($t_s$) and cure time ($t_{90}$) 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

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.

Theoretically, due to the negligible contribution of the ionic component to total dielectric constant, most polymers have a low dielectric constant. 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.

Barium titanate (BT, chemical formula $\text{BaTiO}_3$) 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 $1.0 \times 10^5$.[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] silicone elastomers,[12] butyl rubber (BR),[13] polyester,[14] butyl rubber (BR),[15] poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP),[16] poly(vinylidene fluoride) (PVDF)[17,18] poly(methyl methacrylate) (PMMA),[19] ethylene propylene diene monomer (EPDM),[20] polyamide (PA),[21] acrylonitrile-butadiene rubber (NBR),[22] and polyacrylonitrile (PCL).[23]

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),[24,25,26] 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.[27] The two main types of CNT are single-walled and multi-walled CNT. Using CNT in rubber composites has been
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 sp²-hybridized carbon atoms in cylindrical nanotubes with high aspect ratios can be simultaneously achieved.\textsuperscript{[8,30]} Nevertheless, due to a leak current in the polymer/CNT nanocomposite, a large dissipation factor (tanδ) has limited high-frequency applications, as in embedded capacitors, because of loss of electrical energy to heat and overheating of the devices.\textsuperscript{[31]} In order to improve the dielectric properties, BT and CNT mix filled various types of polymers, including polypropylene (PP),\textsuperscript{[33]} poly(cyclohexyl methacrylate),\textsuperscript{[31]} PA,\textsuperscript{[33]} polydimethylsiloxane (PDMS)\textsuperscript{[34]} and PVDF,\textsuperscript{[35−37]} have been reported. In cases of rubbers, Joseph et al.\textsuperscript{[38]} prepared BR/single-walled CNT composites as the electrostatic discharge shielding material by using solution mixing process; Kumar et al.\textsuperscript{[39]} studied vulcanization of silicone rubber/BT-CNT composites using room temperature for providing the elastomer slab; Bizzani et al.\textsuperscript{[40]} 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.\textsuperscript{[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.\textsuperscript{[43]} NBR was chosen for this research because its irregular chain structure with strongly polar carbon-nitrogen triple bond (C≡N) groups and permanent dipole moments enables orientation polarization that is important for dielectric properties.\textsuperscript{[43]} It does have a higher dielectric constant (>10) than most non-polar polymers.\textsuperscript{[43]} Prior studies on its dielectric applications have assessed the fillers calcium copper titanate (CCTO), titanium dioxide (TiO₂),\textsuperscript{[47]} and barium titanate (BT).\textsuperscript{[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,\textsuperscript{[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.\textsuperscript{[50,51]} The compounding formulation is summarized in Table 1.

| 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 vulcanization. Finally, rubber composite sheets with dimensions of 150 mm × 160 mm × 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”, “NBR/CNT,” and “NBR/BT-CNT,” 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
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 ($t_{c90}$) ($t_{c90} \approx 18$ 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. 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](https://doi.org/10.1007/s10118-021-2528-9)
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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 (\(M_1\)) and maximum torque (\(M_2\)), torque difference (\(M_2-M_1\)), scorch time (\(t_{s1}\)) and cure time (\(t_{c90}\)) of neat NBR and NBR composites filled with BT and CNT secondary filler.

| Case                  | \(M_1\) (dN·m) | \(M_2\) (dN·m) | \(M_2-M_1\) (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          | 17.43             | 2.32             | 16.19            |
| NBR/BT120             | 2.19           | 23.29          | 21.10             | 2.07             | 18.53            |
| NBR/BT120-CNT1        | 2.26           | 21.97          | 19.71             | 1.26             | 14.07            |
| NBR/BT120-CNT2        | 2.97           | 27.73          | 24.76             | 1.42             | 15.19            |
| NBR/BT120-CNT3        | 3.55           | 24.07          | 20.52             | 1.55             | 16.06            |
| NBR/BT120-CNT4        | 3.18           | 26.58          | 23.40             | 1.30             | 16.05            |
| NBR/BT120-CNT5        | 4.08           | 26.28          | 22.20             | 1.38             | 17.25            |
| NBR/BT120-CNT6        | 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 BT and CNT were increased when BT or BT-CNT compounds were used as fillers, possibly because 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 (\(M_1\)) is associated with the viscosity of a compound. The BT and CNT secondary filler increased \(M_1\) consistently with filler loading due to filler-filler and rubber-filler interactions as well as by the hydrodynamic effect. The highest \(M_1\) 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 (\(M_2\)). A significantly increased \(M_2\) 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.

The torque difference (\(M_2-M_1\)) allows estimating the crosslink density of the neat NBR and the NBR composites filled with BT and CNT secondary filler. It is seen that \(M_2-M_1\) increased with BT and CNT secondary filler loadings. This relates to the activation of vulcanization reaction and the reinforce-

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=N).[58] The stress-strain curves of composites significantly

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depended on the fillers. Reinforcement by BT and CNT 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/BT\textsubscript{80}-CNT\textsubscript{2} 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 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 (Td) and glass transition (Tg) temperatures, and also tan delta (tanδ), 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 (Td5%, Td10%, and Td50%), with Td 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 Td5%, Td10%, Td50%, and Td 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 Td of the composites, particularly of NBR-BT/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/CNT1 and BT120/CNT2, BT120/CNT3, BT120/CNT3, 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 Tg and tanδ from dynamic mechanical testing. It was found that the Tg 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 Tg of the composites. This relates to the reinforcement efficiency of the BT/CNT hybrid filler. It is seen in Table 5 that the Tg of NBR composites with BT80/CNT1 and BT80/CNT2 is moderate and close to the Tg of NBR-BT120/CNT1 and NBR-BT120/CNT3. This is due to the dispersion and distribution of BT80/CNT2 in the NBR matrix. Here, the increased Tg with increasing CNT content in NBR-BT120 is due to the strong agglomeration of both fillers. Considering the tanδ peak height, it relates to dissipation energy and
elastomeric behavior of the polymer.\textsuperscript{[10]} It is noted that a low height of tanδ peak means high elasticity. It was found in Fig. 8 and Table 5 that incorporation of BT and BT/CNT to NBR diminished the tanδ 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-BT\textsubscript{80}/CNT\textsubscript{1} showed again a moderate tanδ height of 1.43. However, lower tanδ can also be seen for NBR-BT\textsubscript{120}/CNT\textsubscript{2} and NBR-BT\textsubscript{120}/CNT\textsubscript{3} 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 ($\epsilon'$), calculated using Eq. (1), for the NBR composites with and without CNT secondary filler. It is seen that $\epsilon'$ 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\textsuperscript{2+}) and titanium (Ti\textsuperscript{4+}) and oxygen anions (O\textsuperscript{2-}). Therefore, dipole-dipole attractions and polarization effects were possible in NBR.\textsuperscript{[46–48]} Interestingly, the CNT secondary filler in NBR/BT composites effectively increased the dielectric

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**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\textsubscript{80} | 6.12±0.49              | 1.12±0.06         |
| NBR/BT\textsubscript{120} | 7.14±0.41              | 0.65±0.07         |
| NBR/BT\textsubscript{80}/CNT\textsubscript{1} | 6.60±0.41              | 1.50±0.07         |
| NBR/BT\textsubscript{80}/CNT\textsubscript{2} | 6.83±0.43              | 1.75±0.04         |
| NBR/BT\textsubscript{80}/CNT\textsubscript{3} | 6.71±0.41              | 1.85±0.06         |
| NBR/BT\textsubscript{120}/CNT\textsubscript{1} | 7.15±0.46              | 1.67±0.09         |
| NBR/BT\textsubscript{120}/CNT\textsubscript{2} | 9.41±0.49              | 1.82±0.08         |
| NBR/BT\textsubscript{120}/CNT\textsubscript{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\textsubscript{80} | 393            | 424            | 495             | 378       | 42.97               |
| NBR/BT\textsubscript{120} | 388            | 415            | N/A             | 424       | 53.88               |
| NBR/BT\textsubscript{80}/CNT\textsubscript{1} | 381            | 406            | 493             | 421       | 43.78               |
| NBR/BT\textsubscript{80}/CNT\textsubscript{2} | 382            | 413            | 499             | 423       | 44.55               |
| NBR/BT\textsubscript{80}/CNT\textsubscript{3} | 422            | 437            | 603             | 428       | 44.00               |
| NBR/BT\textsubscript{120}/CNT\textsubscript{1} | 401            | 436            | N/A             | 438       | 52.80               |
| NBR/BT\textsubscript{120}/CNT\textsubscript{2} | 424            | 444            | N/A             | 444       | 54.05               |
| NBR/BT\textsubscript{120}/CNT\textsubscript{3} | 434            | 453            | N/A             | 460       | 54.21               |
| NBR/CNT\textsubscript{3} | 362            | 405            | 480             | 440       | 5.99                |

N/A = Not applicable.
constant, even though CNT has extremely high electrical conductivity. This relates to the concentration of CNT in the NBR matrix. The percolation concentration of CNT in NBR is about 3 phr. 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-CNT1 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-CNT5, 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. The $\varepsilon'$ 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 $\varepsilon''$ was approximately 100 and $\varepsilon'$ was 500, while $\varepsilon''$ and $\varepsilon'$ 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 ($\sigma$) of the composites shown in Fig. 11, where no dramatic conductivity increase is seen relative to neat NBR and NBR/BT composites ($\sigma$ 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 threshold. As a result, CNT concentrations were kept below the percolation threshold.

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/BT80      | −24.4      | 1.54        |
| NBR/BT120     | −24.1      | 1.64        |
| NBR/BT80-CNT1 | −21.8      | 1.39        |
| NBR/BT80-CNT2 | −20.3      | 1.35        |
| NBR/BT80-CNT3 | −22.3      | 1.44        |
| NBR/BT120-CNT1| −19.2      | 1.43        |
| NBR/BT120-CNT2| −19.8      | 1.31        |
| NBR/BT120-CNT3| −20.3      | 1.28        |
| NBR/CNT1      | −18.5      | 1.44        |

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

Fig. 8 Storage modulus and tan$\delta$ as functions of temperature for neat NBR and NBR composites filled with BT and CNT secondary filler.
the NBR/BT-CNT exhibited shorter scorch time and cure time with higher crosslink density than the neat NBR or 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-curve 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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