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Properties of thermally conductive micro and nano size boron nitride reinforced silicon rubber composites

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ABSTRACT

In the current study, the effects of loading level of micro or nano size BN particles on the thermal, mechanical, and morphological properties of silicone rubber are investigated. Three micron size and two nano size BNs with different particle sizes and shapes are used. All five types of BNs are found to be well-dispersed in silicone rubber matrix despite some local agglomerates. In general, the addition of BN particles in silicone matrix decreases the tensile strength and strain at break, coefficient of thermal expansion (CTE) values, on the other hand increases modulus, hardness and thermal conductivity. Nano size fillers have more pronounced effect on tensile properties of composites in comparison to micron size BNs at any given loading level. The aspect ratio of the filler is found to be very effective in achieving high thermal conductivity in composite systems. Dielectric constants of composites vary between dielectric constant of silicone and BN.

1. Introduction

Heat dissipation is a critical problem for the electronic devices in terms of performance and the reliability [1–3]. Heat produced during the operation of the device is generally dissipated by thermal conduction [4–6]. Traditionally, heat sinks are utilized to remove heat from the device. Heat dissipation capacity of a heat sink decreases due to interfacial thermal resistance arising from the mismatch of surface roughness of both device and heat sink in the absence of a good thermal contact. In order to improve the performance of a heat sink, the remaining air gaps are filled with suitable thermal interface materials (TIMs), whose thermal conductivity is greater than air.

An ideal TIM must possess high thermal conductivity, low coefficient of thermal expansion (CTE) and low dielectric constant as well. Additionally, the material must be soft enough to be easily deformed by contact pressure to fill all the gaps between the mating surfaces [4,7]. TIMs can be classified as elastomeric thermal pads, thermal greases, solders and phase change materials [4,8]. Elastomeric thermal pads have been recently shown increasing interest due to ease of handling and high compressibility. Elastomeric thermal pads are typically made of an elastomeric polymer, such as silicon rubber, and reinforced with highly thermally conductive but electrically insulating fillers, such as aluminum nitride (AlN), boron nitride (BN), silicon carbide (SiC), and alumina (Al_2O_3) [9–11].

Zhou et al. focused on the thermal conductivity of poly(dimethyl siloxane) (PDMS)/silicone nitride (Si_3N_4) and/or silicone carbide whisker (SiC_w) [7]. It was reported that combined use of hybrid Si_3N_4/SiC_w at a weight ratio of 9:1 provided higher thermal conductivity, improved thermal stability and reduced coefficient of thermal expansion (CTE). The effects of content and particle size of BN filler on the thermal conductivity and mechanical property of silicone rubber were studied in an other study [2]. The results showed that silicone rubber compounded with larger BN particles exhibited higher thermal conductivity compared to smaller particles at the constant filler loading level. The use of hybrid size BN particles in silicone rubber resulted in a better thermal conductivity. This behavior was attributed to the high packing density and ease of formation of conductive pathways. Sim and coworkers examined the thermal properties of silicone rubber filled with thermally conductive, but electrically insulating Al_2O_3 or ZnO fillers to be used as elastomeric thermal pads [4]. The effects of micron size Al_2O_3 or ZnO fillers on the thermal conductivity and coefficient of thermal expansion (CTE) of the silicone rubber were investigated. It was concluded that the thermal conductivity of the thermal pads increased as the increasing content of Al_2O_3 or ZnO fillers. Moreover, it was found that at fixed filler composition, ZnO filled silicone rubber exhibited better thermal performance compared to Al_2O_3 filled silicone rubber due to its higher intrinsic thermal conductivity.

The studies reported in the literature deal with the properties of micron size conductive fillers. To our knowledge, the properties of nano BN reinforced polymer composites have not been reported. In the current study, the effects of loading level of micro or nano

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sized BN particles on the thermal, mechanical, and morphological properties of silicone rubber are investigated.

2. Materials and methods

2.1. Materials

The silicone rubber was vinyl terminated poly(dimethyl siloxane) (SILASTIC® NEW GP 30) provided by DOW CORNING. Dicumylperoxide (DCP) (Peradox® BC-FF, AKZO NOBEL Company) was used as curing agent. The thermally conductive fillers were five different types of boron nitride (BN) with purity of 99%. Three types of micron size BN (VSN 1149, VSN1159, and VSN1142) were kindly provided by ESK Advanced Technical Ceramics Company, Germany. One of the nanometer size BN powders was purchased from Lower-Friction Lubricants, Canada (MK-hBNN70), and the other was purchased from Bortek Ltd. Sti., Turkey (BORTEK).

2.2. Sample preparation

The silicone rubber was compounded with five types of BN (VSN 1142, VSN 1149, VSN 1159, BORTEK, MK-hBNN70). The curing agent level was fixed at 0.5% by weight. Filler loading level varied as 0, 10, 30 and 50% by weight. The compounding was carried out in a laboratory scale co-rotating twin-screw extruder (DSM Xplore 15 ml Microcompounder) at 35 °C, 50 rpm, for 5 min. The compounds were compression molded at 180 °C, and 150 bar for 4 min into either $60 \times 40 \times 3\ \mathrm{mm}^3$ or $150 \times 150 \times 1\ \mathrm{mm}^3$ sheets.

2.3. Characterization

Morphologies of composites and the BN powders were observed by scanning electron microscopy (SEM, JEOL JSM-6335F). The composite samples for SEM studies were cryogenically fractured in liquid nitrogen. All the samples including BN powders were sputter coated with gold and palladium prior to observation.

Tensile tests were conducted on dumbbell shaped samples cut from compression molded sheets using an Instron 3341 Universal Testing Machine according to ASTM D 638. At least five measurements were performed for each composition.

Shore A hardness of composites was measured with a durometer (Zwick Shore Durometer) according to ISO 868. At least five measurements were performed for each composition.

The specific heat capacity (C_p) of the composites was measured by performing differential scanning calorimeter (DSC) (Mettler Toledo DSC1) analysis under nitrogen atmosphere. The DSC analysis was carried out between 0 °C and 200 °C at a heating rate of 10 °C/min. Thermal conductivity (k, W/mK) of composites was calculated from thermal effusivity (e). A material's thermal effusivity is a measure of its ability to exchange thermal energy with its surroundings. A TC (temperature compensation) probe is contacted with sample surface. The device emits a constant heat and the temperature rise at the surface is monitored. Materials that conduct heat produce a lower rate of temperature rise because heat is conducted away from the surface. In contrast to that the insulating materials conduct heat poorly and the temperature rises substantially at the surface. The effusivity of the samples was measured by using a Perkin Elmer Pyris TC Probe at 25 ± 3 °C. Thermal conductivity was calculated from the following equation:

$$e = (k\rho C_p)^{1/2} \tag{1}$$

where ρ is density (kg/m^3), which was measured by weighing the samples with a known volume, and C_p (J/kg K) is heat capacity obtained from DSC analysis.

Samples for dielectric measurements were prepared in the disk form with a diameter of 6 mm and thickness of 1 mm. The surface of the disks was coated with silver paste on each side. The dielectric measurements were conducted on an Agilent Impedance Analyzer 4284A LCR at 25 °C ± 3 °C.

Coefficient of thermal expansion (CTE) measurements were performed by using a thermo-mechanical analyser (Setaram Labsys TMA) under nitrogen atmosphere, between 25 °C and 100 °C, at a heating rate of 2 °C/min. CTE was determined from the slope of thermal expansion versus temperature plots.

3. Results and discussion

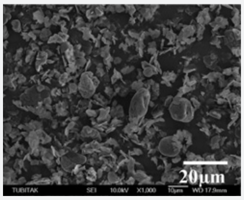
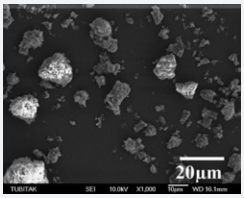
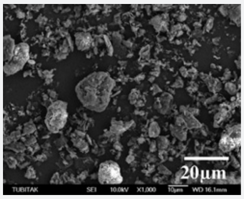
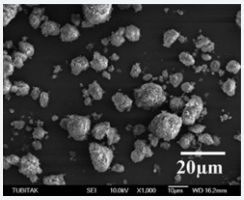
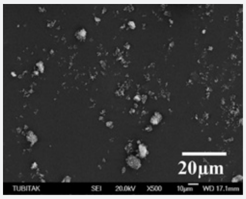
3.1. Characteristics of BN powders

Five types of BN powders are used in the study. The characteristics of BN powders used in experimental study are given in Table 1. VSN 1149 is a mixture of spherical particles with approximate diameter of 10 μm and plates with thickness of 0.1–1 μm (app. aspect ratio in the range of 1–20). VSN 1159 is composed of spherical and irregular shaped agglomerated particles with average particle size of 10 μm. VSN 1142 has the largest average particle size among the BN powders. It is formed by spherical and irregular shaped particles. BORTEK consists of nanometer sized plate-like agglomerated particles. The average agglomerate size is 8 μm, whereas the plate-like particles forming the agglomerates have an approximate size of 100 nm (see Fig. 1a). MK-hBNN70 is also a nanometer size BN powder consisting of plate-like particles with an average size of 70 nm (Fig. 1b).

3.2. Morphology of silicone/BN composites and nanocomposites

Thermal conductivity of composite materials depends on intrinsic conductivity of the filler and matrix, the concentration of the filler, shape and size of filler. Moreover, the filler/matrix interface plays an important role in thermal conductivity of the composites since the conductance of the heat in non-metallic materials occurs by the flow of lattice vibration energy, or phonons, along the temperature gradient in the material; therefore, for a two phase system, interfacial contact between phases is very important, because phonons are very sensitive to surface defects at the interface [12]. The incompatibility at the interface results in a contact resistance to the conductance of the heat. On the other hand, it is also important for the filler particles to touch one another to form a continuous heat conductive pathway in the composite [4,13]. Fig. 2 shows the SEM micrograph of fracture surface of 30% VSN 1142 filled silicone rubber. VSN 1142 particles are generally well-distributed in the matrix, although local agglomerations are visible (shown with white arrows). The apparent particle size in the composite varies between approx. ~1–10 μm indicating the dispersion of agglomerates of VSN 1142. SEM micrograph of 30 or 50% VSN 1149 filled silicone rubber composites are given in Fig. 3a–c. The state of dispersion of VSN 1149 particles is well in both loading levels (Fig. 3a and c). It can be seen from Fig. 3b that the interfacial interaction between silicone elastomer and the VSN 1149 particles are good. As the VSN 1149 content increases to 50% (Fig. 3c), particles tend to touch each other, which is desired to have a conductive path. Fig. 4a–c represents the fracture surface morphology of VSN 1159 filled silicone rubber. The local agglomerated VSN 1159 particles (shown with a white arrow in Fig. 4a) can be seen in 30% filled composites. As the loading level increases to 50%, the frequency of agglomeration increases as well. The black shadows seen inside the agglomerates indicate that the matrix cannot properly wet the agglomerates (Fig. 4a and b). The average apparent particle size is smaller than

Table 1
Properties of BN powders.

BN type	Representative SEM picture	Description
VSN 1149		Average particle size[a]: 7.5 μm Description: mixture of spherical particles with approximate diameter of 10 μm and plates with thickness of 0.1–1 μm (approx. aspect ratio of 1–20)
VSN 1142		Average particle size[a]: 23.8 μm Description: mixture of agglomerated spherical and irregular shaped particles
VSN 1159		Average particle size[a]: 10.0 μm Description: mixture of spherical and irregular shaped aggregated particles
BORTEK		Average particle size[b]: 8.0 μm Description: agglomerates of nanometer size plates
MK-hBNN70		Average particle size[a]: 70 nm Description: irregular shaped nanometer size partially aggregated particles

[a] Reported by the manufacturer.
[b] Obtained from SEM micrographs by performing image analysis (ImageJ).

10 μm. SEM micrographs of 30 and 50% BORTEK filled silicone rubber composites are exhibited in Fig. 5a and b The particles are disperses at nano level for all 30 and 50% composites. This indicates that the agglomerated structure of BORTEK is deteriorated by high shear exerted during compounding. .The particles are not touching to each other even at 50% loading level. Similarly, the dispersion state for MK-hBNN70 is also at nano level (Fig. 6a–c). Different than BORTEK, some local agglomerated MK-

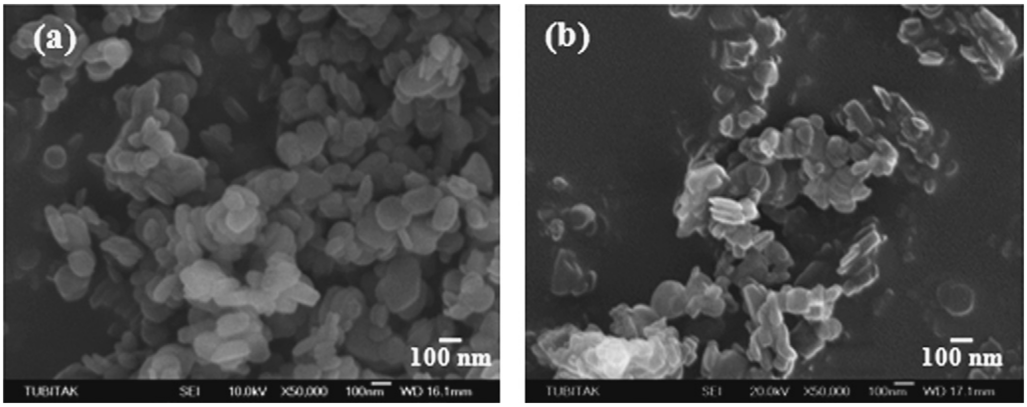


Fig. 1. Magnified SEM micrographs of nano size BN powders. (a) BORTEK and (b) MK-hBNN70.

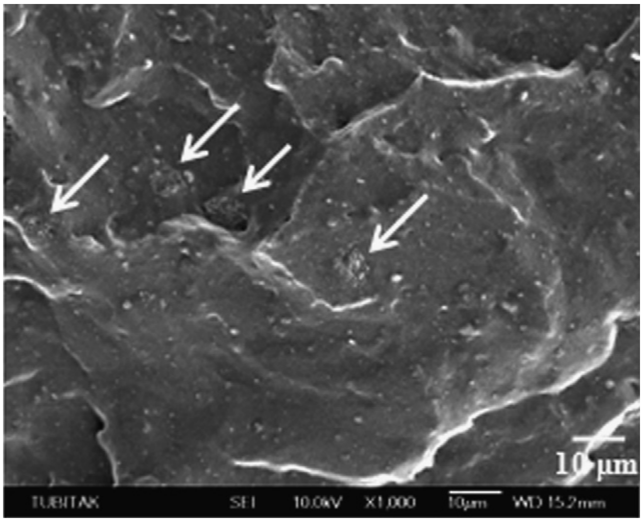


Fig. 2. SEM micrograph of 30% VSN 1142 filled silicone rubber.

hBNN70 particles are visible in the composite (shown with white arrows).

3.3. Mechanical properties of silicone/BN composites and nanocomposites

The mechanical properties of BN filled silicone rubber composites are characterized by their tensile strength, strain at break, tensile modulus and hardness.

The influence of BN type on the tensile strength of composites is compared in Fig. 7 as a function of BN type and loading level. The neat silicone rubber has higher tensile strength as compared to composites. The addition of BN to the silicone rubber decreased the tensile strength of the composites regardless of BN type. This is typical for composites with poor interfacial interaction [14–16]. The nano size BN powders (BORTEK and MK-hBNN70) fillers yield higher tensile strength at 30 and 50% loading level. When micron size BNs are compared, it can be seen that VSN 1149 filled composites has slightly higher tensile strength with respect to VSN 1159 and VSN 1142 filled composites. This can be attributed to its smaller particle size and high aspect ratio. In addition to that, as seen from the SEM photos of fracture surfaces of VSN 1149 filled silicone rubber (Fig. 3) that BN particles are uniformly dispersed in silicone rubber in contrast to other type of BN filled composites in which BN particles tended to form agglomerates in the matrix. Fig. 8shows the effect of BN type and amount on the strain at break values of silicone rubber composites. The incorporation of fillers into the silicon rubber resulted in a drastic reduction in the strain at break values regardless of BN type. This behavior is generally explained by stress-concentration phenomena [14] and commonly seen in the lack of particle/matrix adhesion. VSN 1142 and VSN 1159 filled composites have nearly the same strain at break values. VSN 1149 filled silicone has slightly higher strain at break values when compared to them at any given BN loading level. This observation can be attributed to the better dispersion of VSN 1149 in comparison to VSN 1142 and VSN 1159. Nano size fillers (BORTEK and MK-hBNN70) yield highest strain at break values at any given loading level when compared to micron size BNs. The tensile modulus of composites generally obeys 'the rule of mixtures' (see Fig. 9). Since the modulus of BN is much higher than silicone rubber, the improvement in tensile modulus with the incorporation of BN into silicone is expected. The enhancement of modulus with the use of nano size fillers is much significant than that of micron size fillers. Among the micron

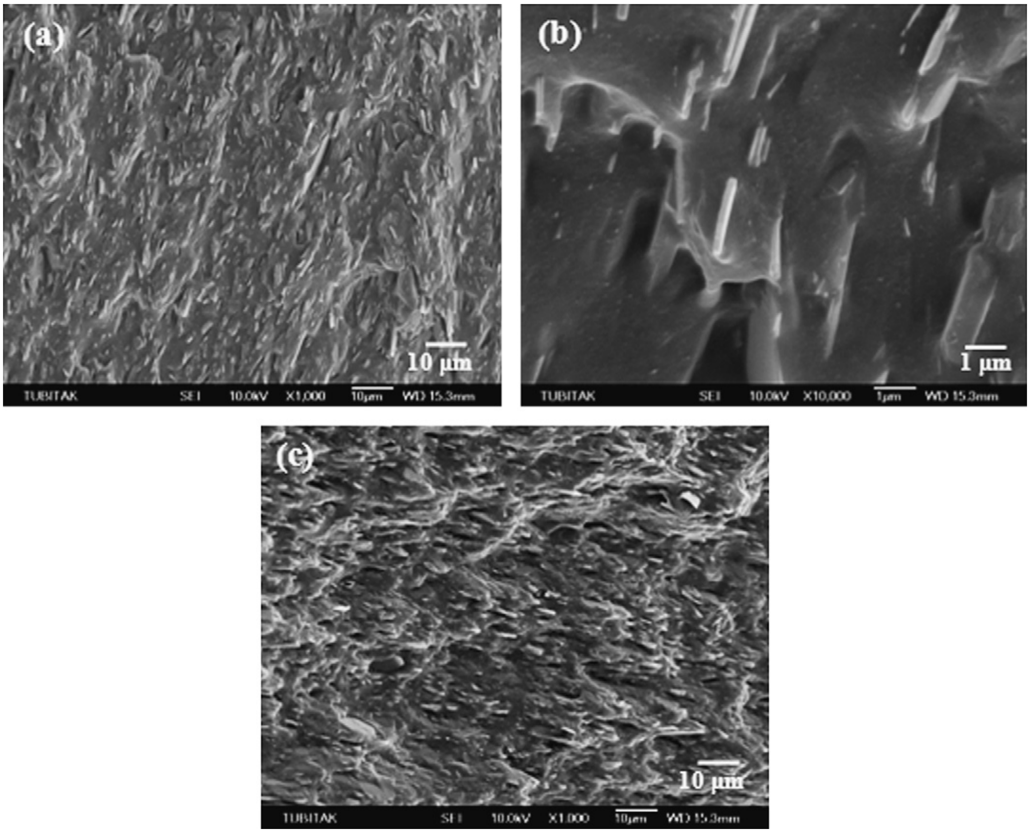


Fig. 3. SEM micrograph of (a) 30% VSN 1149 filled silicone rubber (1000×), (b) 30% VSN 1149 filled silicone rubber (10,000×), (c) 50% VSN 1149 filled silicone rubber (1000×).

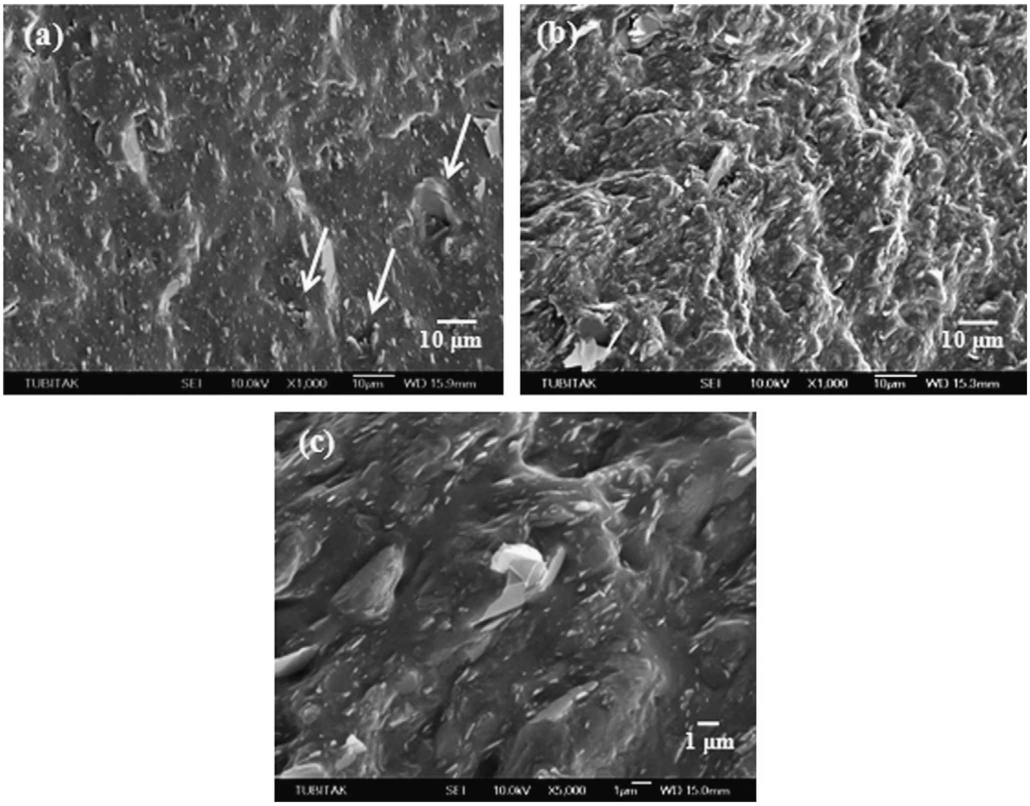


Fig. 4. SEM micrograph of (a) 30% VSN 1159 filled silicone rubber (1000×), (b) 50% VSN 1159 filled silicone rubber (1000×), (c) 50% VSN 1159 filled silicone rubber (5000×).

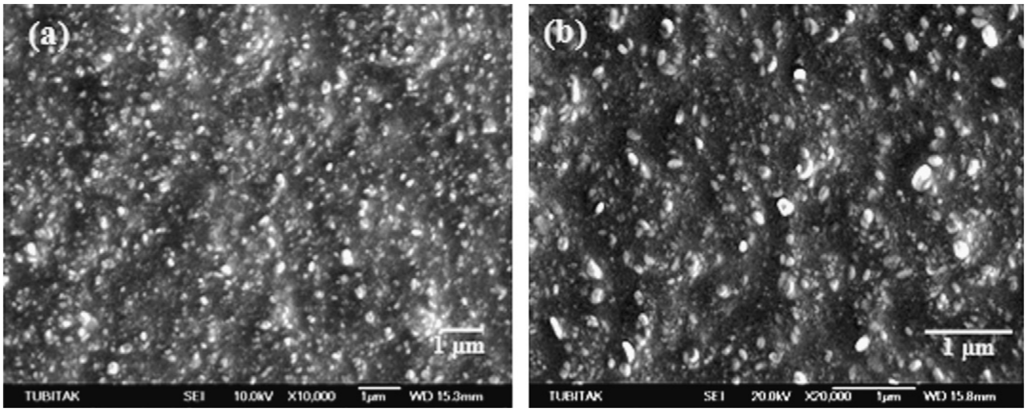


Fig. 5. SEM micrograph of (a) 50% BORTEK filled silicone rubber (10,000×) and (b) 50% BORTEK filled silicone rubber (20,000×).

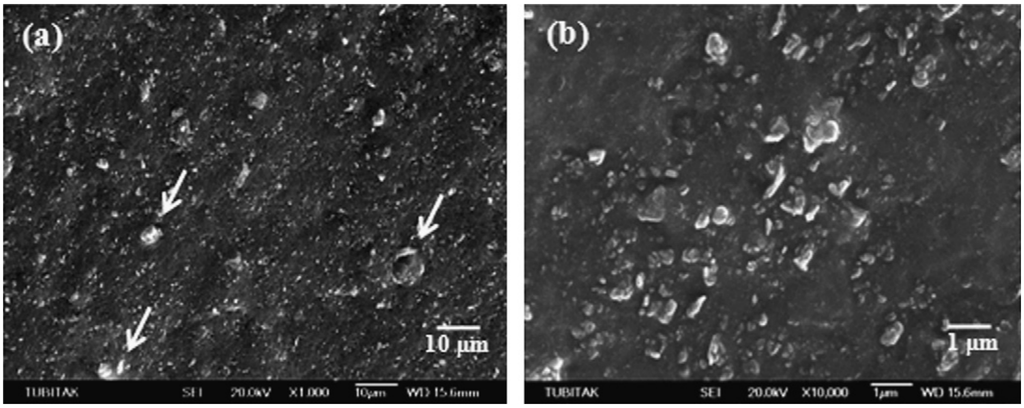


Fig. 6. SEM micrograph of (a) 30% MK-hBNN70 filled silicone rubber (1000×), (b) 50% MK-hBNN70 filled silicone rubber (10,000×).

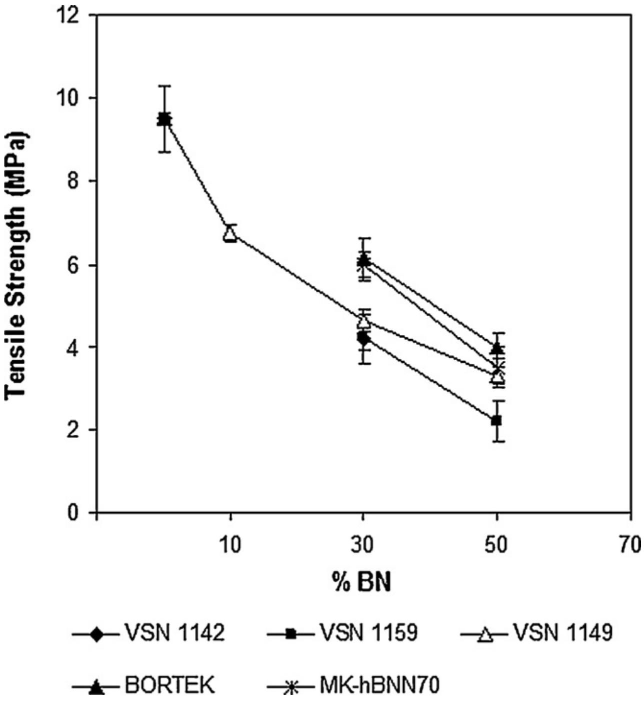


Fig. 7. Effect of BN type and amount on the tensile strength of silicone rubber composites.

size fillers, VSN 1149 results in a higher modulus with respect to others.

An ideal TIM should be soft enough to be easily compressed by applied contact pressure to fill all the gaps between the mating surfaces even at high filler loading level [4,7]. The surface hardness of composites can be an indication of compressibility. Fig. 10 shows the effect of BN type and amount on the hardness of silicone rubber composites. The hardness increases with the addition of the BN particles regardless of BN type. VSN 1149 or MK-hBNN70 reinforced composites have the lowest hardness values in comparison to other type of BN at ay given loading level.

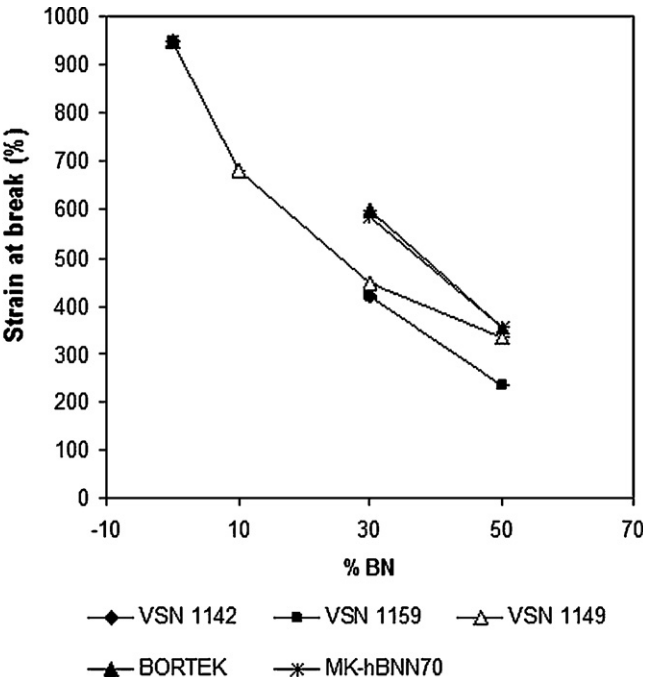


Fig. 8. Effect of BN type and amount on the strain at break values of silicone rubber composites.

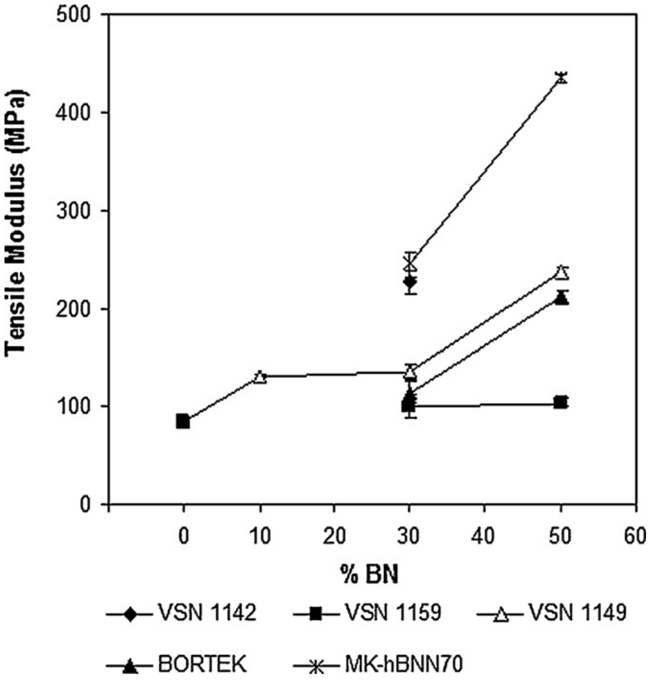


Fig. 9. Effect of BN type and amount on the tensile modulus of silicone rubber composites.

3.4. CTE and thermal conductivity of silicone/BN composites and nanocomposites

Fig. 11 shows the effect of BN type and amount on the CTE of silicone rubber composites. As expected, the incorporation of BN particle into the silicone elastomer results in a reduction in CTE

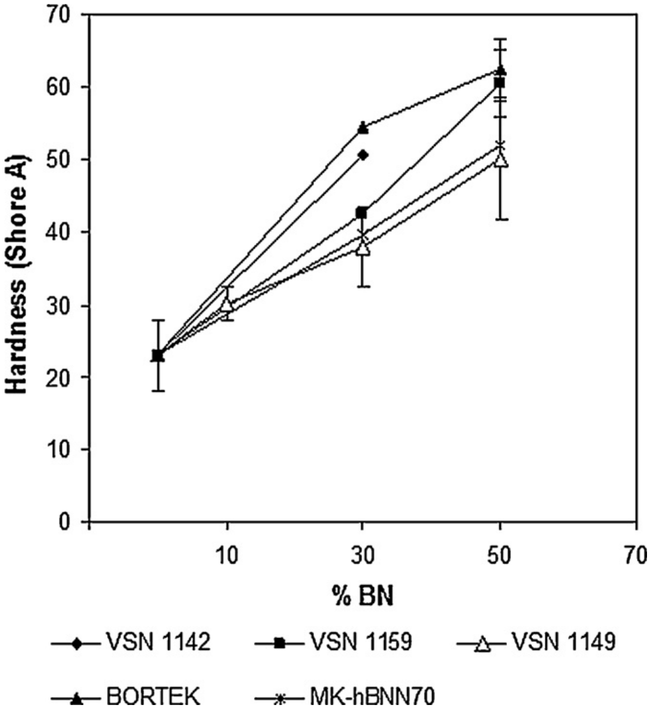


Fig. 10. Effect of BN type and amount on the hardness of silicone rubber composites.

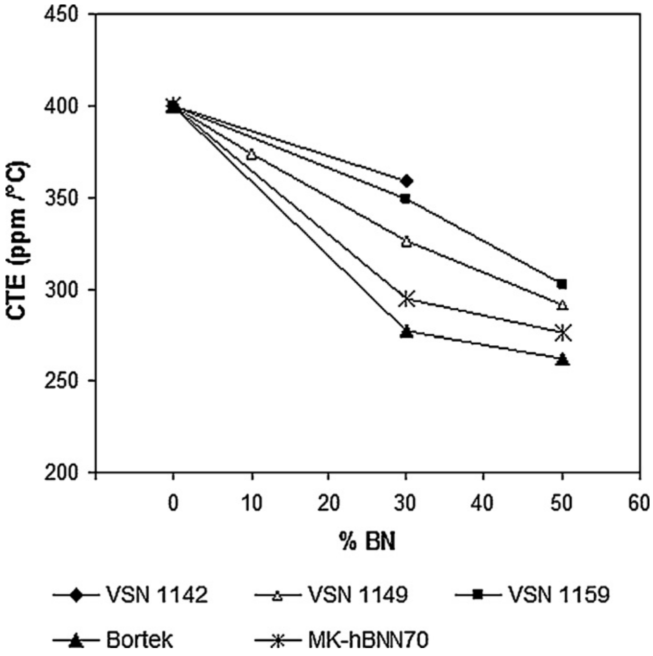


Fig. 11. Effect of BN type and amount on the CTE of silicone rubber composites.

of the composites due to the restriction of the mobility of the silicone molecules because of the adsorption on the BN surfaces [4]. As the particle size of the BN is decreased, the CTE decreased at any given loading level. The lowest values are obtained for composites of BORTEK and MK-hBNN70, which are nano size fillers. This is probably due to the high surface/volume ratio of nano size fillers which promotes a higher level of interaction at the interface when compared to micron size fillers.

The thermal conductivity of the composites is controlled by the intrinsic conductivities of filler and matrix, shape and size of the filler, and the loading level of filler [11]. The ability to form a conductive network of the filler in the matrix depends on the aspect ratio (diameter/thickness ratio) and concentration of the filler. When the concentration and the aspect ratio of the filler increase, after a critical concentration particles percolates and touch one another by forming a conductive network. This structure is essential in achieving thermal conductivity in composites [12]. Fig. 12 shows the variation of the thermal conductivity of BN/silicone composites with respect to BN type and loading level. The thermal conductivity of pure silicone rubber is about 0.2 W/mK. Regardless of BN type, the addition of thermally conductive particles to the silicone matrix enhances the thermal conductivity. The highest thermal conductivity values are obtained from VSN 1149 filled composites at any given filler loading level. This can be attributed to the high aspect ratio of VSN 1149. At 50% VSN 1149 loading level, the thermal conductivity is increased more than 10 times when compared to pure silicone. The composites of nano size fillers (i.e. BORTEK and MK-hBNN70) exhibit lower thermal conductivities at any given loading level in comparison to micron size fillers. This is probably due to their lower aspect ratio.

3.5. Dielectric constant of silicone/BN composites and nanocomposites

An ideal TIM must be not only thermally conductive and soft but also electrically insulating. In order to evaluate insulating properties of BN/silicone rubber composites, dielectric constants are measured. The dielectric permittivity of a material is usually given relative to that of vacuum (ε_0), and is known as relative permittivity (ε_r), or dielectric constant [17]. It can be calculated by Eq. (2) by

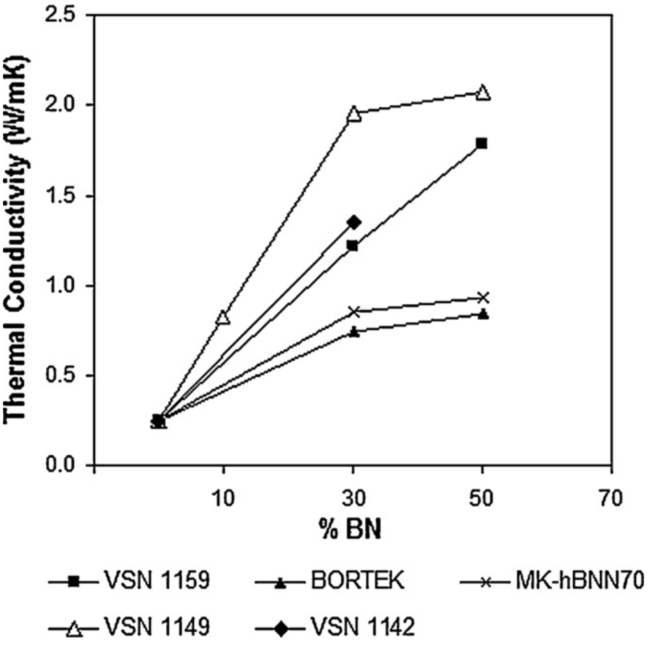


Fig. 12. Effect of BN type and amount on the thermal conductivity of silicone rubber composites.

measuring the dielectric capacitance, C:

$$\varepsilon_r = \frac{tC}{A\varepsilon_0} \tag{2}$$

where A and t are the cross-sectional area and the thickness of specimen, respectively.

The dielectric properties of the composites depend on the loading level of the filler, size and shape of filler and the interfacial properties of the composites [18–20]. The variation of dielectric constant of composites with respect to BN loading level and type are given in Fig. 13. One should note that the dielectric constant of BN is about 4.5, whereas the dielectric constant of silicon rubber is 3.3 at 25 °C. It is observed from Fig. 13 that increasing the

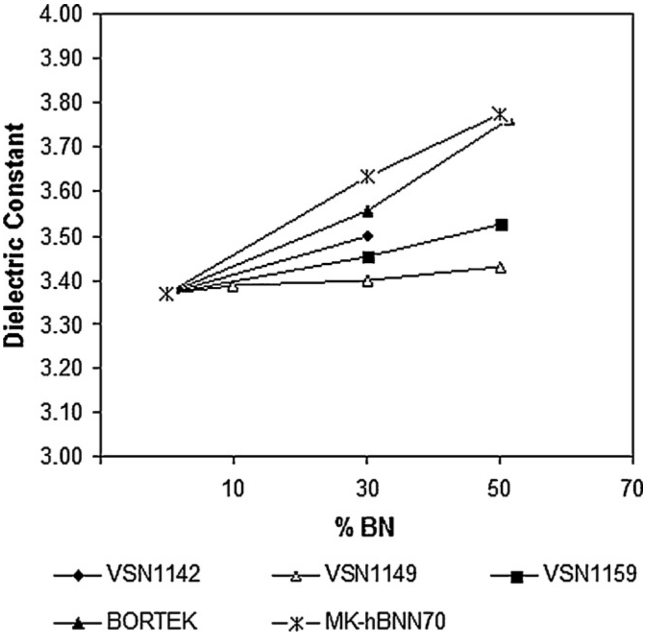


Fig. 13. Effect of BN type and amount on the dielectric constants of silicone rubber composites.

amount of BN in composites results in an increase in dielectric constant of silicon composites. It is generally observed in the literature that the dielectric constant of the resulting composite materials increases with the increasing amount of filler. Beyond a critical limit the dielectric constant increases dramatically. This phenomenon is explained by percolation theory [21–24].

As the pure silicone matrix is compared with BN/silicone composites, the amount of accumulated charge will increase due to interfacial polarization at the BN/silicone interface [25]. Therefore, the dielectric constant of the composites is higher than the neat matrix regardless of BN type. The further addition of the filler increases the dielectric constant since the amount of interface increases in the composite. The composites filled with VSN 1149 exhibits the lowest dielectric constant value, whereas the composites of BORTEK and MK-hBNN70 (nano-BNs) have the highest dielectric constant values at any given silicon rubber loading level, which can be explained by higher interfacial area in comparison to micron size BNs.

4. Conclusions

BN/Silicone thermally conductive rubber composites are investigated as a function of BN type and loading level. Three micron size and two nano size BN with different average particle size and particle shape are used. The tensile strength of composites lowers with the addition of any type of BN which implies that the interfacial interaction between silicone and BN are poor. Nano size fillers have more pronounced effect on modulus, tensile strength, and CTE in comparison to micron size BNs; however they do not promote the thermal conductivity as expected. It is found that effect of aspect ratio of the filler is very critical in achieving high thermal conductivity. VSN 1149, having a plate-like particle shape with an approximate aspect ratio of 20, gives the highest thermal conductivity among the all five types of BNs.

Acknowledgements

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