Performance of silicone rubber composites using boron nitride to replace alumina tri-hydrate

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Abstract
Boron nitride (BN) has attracted increasing attention as a filler using in insulating materials. In this work, by using an equal amount of BN to replace alumina tri-hydrate (ATH), various SR/BN/ATH composites were prepared, and for comparison, vinyl trimethoxysilane (VTMS) was added to prepare SR/BN/ATH-VTMS composites. With the increasing BN content, Shore A hardness, breakdown strength and thermal conductivity of the silicone rubber (SR) composites increased despite the tensile strength slightly reduced. By replacing all the ATH with BN, the SR composite showed a ~47% increase in breakdown strength, reaching 33.8 kV mm⁻¹. The lower dielectric constant and dielectric loss were found for the SR composites with higher BN content, while the decreased dielectric loss and increased dielectric constant were achieved by the introduction of VTMS. Owing to the improved filler-rubber interfacial interactions by adding VTMS, with the same BN content, all the SR/BN/ATH-VTMS composites exhibited better property than the SR/BN/ATH composites. The best thermal conductivity of the SR composite reached 0.448 W m⁻¹ K⁻¹, ~156% higher than that of the ATH filled SR composite.

1 | INTRODUCTION

High temperature vulcanised silicone rubber (SR) has been commonly used in producing high-voltage composite insulator, which has the advantages of light weight, easy installation and excellent anti-contamination over glass or porcelain insulators [1–5]. For high-voltage insulating SR composites, the breakdown strength is one of the most important performance. It is well known that the defects in the dielectric materials limit their breakdown strength, although it is possible to reduce the defects by exploring novel methods to synthesise alternative polymers [6]. However, the appropriate addition of inorganic filler particles to form SR composite to achieve high-performance would be more efficient and inexpensive [7–13].

So far, the most widely used filler in the high-voltage insulating SR composite is alumina tri-hydrate (ATH), which endows the composite with good flame retardance and erosion resistance [14–16]. However, the improvement of breakdown strength using ATH was not as satisfied as expected. Recently, owing to its high thermal conductivity, excellent chemical stability, low dielectric loss and outstanding electrical insulation, boron nitride (BN) has attracted increasing attention as a filler using in insulating materials [17–21]. It was reported approximately 16.5% increase in breakdown strength for the polypropylene by adding 9 wt% BN nanoparticles [22]. The increased time for surface dielectric breakdown during arcing discharge with increasing BN content was also found in the polyethylene [23]. Besides, the improvement of tracking and erosion resistance was also reported in the SR/BN composites due to the good thermal conductivity of the BN particles [24, 25]. However, the replacement of ATH by BN was rarely investigated for the application of insulating materials.

In this work, SR composites with different amount of BN and ATH were prepared, and vinyl trimethoxysilane (VTMS,
a commonly used silane coupling agent) was added to strengthen the filler-rubber interfacial interactions. The microstructure, thermal properties, mechanical performance and dielectric properties were investigated to further understand the structure-property relationship of the SR composites.

2 | EXPERIMENTAL

2.1 | Preparation

Preparation of SR composites: ATH (2~5 μm, 97.0%, Zhongke Flame-retardant New Material Co., Ltd.), BN (5~10 μm, 99.0%, Yimu Material Co., Ltd.), vinyl tri-methoxysilane (VTMS) (Chenguang Chemical Industry Co., Ltd.) and 2,5-bis (tert-butyleroxy)-2,5-dimethyl hexane (DBPMH, Meixing Chemical Industry Co., Ltd.) were mixed with pure SR (MVQ110, vinyl weight percentage: 0.23%, Mw: 680,000, Wynca Chemical Group Co., Ltd.) using a 6 in. two-roll mill to prepare SR compounds, which were then placed in a standard mould and vulcanised using a hydraulic hot press (XLB-D 350, Dongfang Machinery, Co., Ltd.) at 170°C and 15 MPa to obtain SR composites. The recipe was as follows: 100 g SR, 100 g filler, 0.5 g DBPMH, 0 or 1.0 g VTMS. The above-mentioned SR composites were abbreviated as SR/BNx/ATHy and SR/BNx/ATHy-VTMS, respectively, where x and y refer to per hundred rubber (phr) of BN and ATH in the SR composites, respectively.

2.2 | Measurement

Thermogravimetric analysis (TGA) was conducted using TG-Q500 analyzer (TA Instruments) with a heating rate of 20°C Cmin⁻¹ under the nitrogen atmosphere. The morphologies of the samples after the tensile tests was observed by SU8010 scanning electron microscopy (SEM) (Hitachi Co. Ltd.) at an accelerating voltage of 5 kV. Mechanical performance was conducted by AI-7000S1 electrical tensile tester (Goodtechwill Testing Machines, Co. Ltd.) with a tensile speed of 500 mm min⁻¹ following ASTM D412-2016 (5 samples were tested). 6500B impedance analyzer (Wayne Kerr Electronics) was used to detect the dielectric constant and dielectric loss (at least three samples were tested). Dielectric breakdown strength was tested by HCDJC-50kV dielectric strength tester (Beijing Huace Testing Instrument Co. Ltd.) with a stepping voltage of 1 kV/s (at least 12 samples were tested). Thermal diffusivity (α), specific heat (Cp) and density (ρ) of the samples were evaluated by laser flash apparatus (LFA 427, NETZSCH), differential scanning calorimetry (DSC, NETZSCH, heating rate of 10°C/min under nitrogen atmosphere), and density tester (MH-300A, MatsuHaku) respectively, and then the equation (κ = αCpρ) was used to calculate the thermal conductivity (κ) (3 samples were tested). All measurements were performed at 25°C unless mentioned otherwise.

3 | RESULTS AND DISCUSSION

3.1 | TGA analysis

The TGA curves of BN, ATH and SR composites are shown in Figure 1. BN powder shows the excellent thermal stability since there is no weight loss in the TGA curve below 700°C. As for ATH powder, due to the crystal water evaporation from ATH, there is a ~34% weight loss starting from 220°C. For the SR/BN100 composite, the one-stage weight loss of ~50% ranging from 360°C to 620°C should be attributed to the decomposition of SR, because the weight of SR in the composite is equal to that of BN and BN is thermal stable. In contrast, a two-step weight loss is observed for the SR/ATH100 composite, and only ~37% residue remains. The first step starting from ~220°C with ~15% weight loss should be ascribed to the crystal water evaporation from ATH, while the second step starting from ~360°C with ~48% weight loss is ascribed from the SR decomposition. The thermal degradation behaviour of SR/BN40/ATH60 composite is similar to that of the SR/ATH100 composites. However, as compared to the SR/BN40/ATH60 composite, the SR/ATH100 composite exhibits larger water evaporation weight loss between 220°C and 360°C because of the higher proportion of ATH in the composite. Moreover, by adding VTMS, the TGA curves of the SR composites slightly shift to the lower temperature. This could be attributed to the weaker stability of low molecule VTMS. It can be summarised that the SR composites would show better thermal stability through the replacement of ATH by BN, although it would be slightly reduced by the addition of VTMS.

To prepare SR composites with VTMS, fillers (including ATH and BN), VTMS and DBPMH were mechanically mixed with SR matrix. Meanwhile, the hydroxyl groups on the filler surface could react with the silane coupling agent (Figure 2 reaction A), leading to the immobilisation of VTMS on the surface of the fillers. When the compounds were cured at high temperature, the free radicals would generate from the
decomposition of DBPMH (Figure 2 reaction B), and then the radical addition reactions between the C=C groups on both VTMS and SR (Sketch 1, reaction C) would be initiated by these free radicals. No weight loss is shown in the TGA curves of the SR composites with VTMS below 200°C, indicating that the VTMS molecules have been chemically bonded in the composites (FTIR proof of the reaction between BN and VTMS shown in supporting information figure S1), because the boiling point of VTMS is ~123°C. Therefore, VTMS plays a role as the covalent connections between SR matrix and ATH or BN fillers to strengthen the filler-rubber interfacial interactions.

### 3.2 SEM observation

The SEM observation of surface morphologies of the tensile fractured composites with various ATH and BN contents are presented in Figure 3. It is evident to distinguish the spherical ATH from the flake-like BN even though both of them are dispersed in the SR matrix. For the SR/BN/ATH composites shown in Figure 3(a)(A)-(F), it can be observed that there exist some voids and some filler particle agglomerations exposing on the surface of the tensile fractured samples, demonstrating relatively weak filler-rubber interfacial interactions. While for the SR/BN/ATH-VTMS composites shown in Figure 3(g)(G)-1 (L), there exist fewer aggregates and voids, which should be due to the improved filler-rubber interfacial interactions. However, with the increasing of BN content in the composites, it is found that the improvement in the filler-rubber interfacial interactions by using VTMS becomes less effective. This might be ascribed to fewer hydroxyl groups on the surface and larger aspect-ratio of BN as compared to ATH. The fewer hydroxyl groups on the BN surface means the fewer active sites reacting with VTMS, leading to the poorer modification effect of the silane coupling agent. The larger aspect-ratio of BN makes the filler particles more difficult to be embedded in the SR matrix. It is worthy to mention that the SR composites with higher BN content exhibit more voids, indicating the weaker interfacial interactions between SR and BN as compared to those between SR and ATH.

### 3.3 Mechanical properties of SR composites

Figure 4 shows the stress-strain curves of SR composites. As can be observed, when the strain is lower than 50%, the SR composites with higher BN content exhibit a much faster increase in stress with the increasing strain, while such increase becomes slower with strain higher than 50%. During the stretching process, slippage and orientation of the rubber chains occur under the load of filler particles, therefore, the mechanical behaviour of the composites should be related to not only the filler-rubber interfacial interaction but also the restriction effect of filler on rubber [26]. At small deformation, filler restriction plays a dominant role in stress-strain behaviour [27], and much stronger restriction of BN than ATH is applied to the SR molecular chains because of the higher aspect-ratio of BN. Consequently, the composites with higher BN content exhibit larger stress at the same strain. However, with a further increase of the strain, the filler-rubber interfacial interaction becomes more and more important. Since the interfacial interactions between SR and BN are weaker than those between SR and ATH, BN particles would slip much easier from the surface of SR macromolecular chains than ATH particles, resulting in less increase of stress with strain for the SR composite with higher BN content at strain higher than 50%.

Figure 5 shows the Shore A hardness and tensile strength of SR composites. Generally, Shore A hardness reflects the resistance to the deformation induced by compression stress, which also belongs to the condition of small strain. Therefore, Shore A hardness increases with the increasing BN content. Moreover, with the same BN content, the SR/BN/ATH-VTMS composites exhibit higher tensile strength and Shore A hardness than the SR/BN/ATH composites, which should be due to the improvement of filler-rubber interfacial interactions. The decrease in tensile strength with the increase of BN content could be attributed to the shape difference between the two fillers. As shown in Figure 3, there are more flaws and larger cracks between the interfaces for the SR composites with more BN as compared to those for the SR composites with
more ATH. This could be due to the following factor: the larger aspect-ratio of BN as compared to that of ATH makes it more difficult to be covered by rubber macromolecules, resulting in more defects in the SR composites with high BN content. Therefore, the tensile strength of the SR composites decreases with BN content.

3.4 | Dielectric properties of SR composites

Figure 6 shows the dielectric loss and dielectric constant of SR composites as a function of BN content. Since the polarity of ATH is stronger than that of BN, reduction of the interfacial polarisation in the SR composite occurs when replacing ATH by BN. As a result, the SR composites with more BN particles show lower dielectric loss and dielectric constant. Additionally, at the same BN content, the SR/BN/ATH-VTMS composites show lower dielectric loss and higher dielectric constant than the SR/BN/ATH composites. Space charge accumulation induces the electric field distortion [28], resulting in a higher dielectric loss in dielectrics. Since the SR matrix is more compatible with the VTMS in-situ modified filler particles, the SR/BN/ATH-VTMS composites exhibit the decreased interfacial polarisation and space charge accumulation as compared
to the SR/BN/ATH composites. As a result, the addition of VTMS in the SR composites would lower the dielectric loss. However, the introduction of VTMS could also increase the composite crosslinking density, leading to a decrease in free volume and then enhancing the dielectric constant, which is also reported in the literature [11, 29]. Besides, the improved dispersion of the filler particles in the SR matrix would create more filler-rubber interfaces, which promotes the effect of high permittivity filler in increasing the dielectric constant of SR composites.

Moreover, the electrical breakdown strength of the SR composites increases with the increasing BN content as shown in Figure 7. The SR/BN100 composite reaches the breakdown strength of 33.8 kV mm⁻¹, ~47% higher than SR/ATH100 composite (23.0 kV mm⁻¹), which is mainly due to the better insulating property of BN and the lower interfacial polarisation for the BN particles filled composites. Besides, when exposing at high voltage electric field, the BN plates with large aspect-ratio would act as barriers to inhibit the electrical treeing propagation, which is also beneficial to breakdown strength. Moreover, with the same BN content, all the SR/BN/ATH-VTMS composites present higher breakdown strength than the SR/BN/ATH composites. This should be due to the fewer defects resulting from the strengthened interfacial interactions between rubber and filler by adding VTMS in the SR composites.

3.5 | Thermal conductivity of SR composites

The thermal conductivity of SR/BN/ATH and SR/BN/ATH-VTMS composites as a function of BN content is shown in Figure 8. The thermal conductivity of either SR/BN/ATH or SR/BN/ATH-VTMS composites raises gradually with the increase of BN content. Since BN has higher intrinsic thermal conductivity as compared to ATH, the replacement of ATH by BN can enhance the composite thermal conductivity. As compared to the SR/ATH100 composite (0.175 Wm⁻¹ K⁻¹), there is a ~104% increase in thermal conductivity for the SR/BN100 composite (0.357 Wm⁻¹ K⁻¹) in which all the ATH particles is replaced by BN particles. Moreover, by adding VTMS, the thermal
4 | CONCLUSIONS

In this work, SR composites with different amounts of BN and ATH were prepared, and VTMS was added to prepare SR/BN/ATH-VTMS composites for comparison to strengthen the filler-rubber interfacial interactions, which was verified by SEM observation. TGA curves demonstrated that the thermal stability of the SR composites was enhanced by using BN as a substitute filler. For the SR/BN/ATH composites, Shore A hardness increased and tensile strength slightly decreased with the increase of BN content, while both of them increased by incorporating VTMS. The dielectric loss and dielectric constant decreased with the increase of BN content, and the introduction of VTMS in the composites decreased the dielectric loss, meanwhile, increase the dielectric constant. The breakdown strength was significantly improved by using BN to replace ATH in the SR matrix. Moreover, owing to the improved filler-rubber interfacial interactions, all the SR/BN/ATH-VTMS composites exhibited better performance than the SR/BN/ATH composites with the same BN content. Our work indicated that BN would be a promising filler applied in the high-voltage insulation field.

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