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Preparation and Properties of Epoxy Composites with Multi-Scale BN Sheets

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Abstract: Epoxy resin is one of the most widely used thermosetting polymers and commonly applied in power electronics field. The intrinsic properties of epoxy can be improved by the introduction of inorganic filler, thus fabricating a composite material. In this paper, different scales of modified boron nitride (BN, 1 μm, 10 μm) were used to improve the thermal conductivity of epoxy resin. The surfaces BN were modification by a silane coupling agent to improve the compatibility between BN and epoxy resin. The effects of micro-and nano-BN sheets on the microstructure, breakdown strength, thermal and mechanical properties of epoxy resin composite were studied. The characterization of its morphology by scanning electron microscopy shows that nano-BN distribution is in the middle of micro-BN, forming a better bridging effect. The data of the breakdown strength and thermal conductivity indicated that when the content of micro-BN is 30 wt% and nano-BN is 20 wt%, the thermal conductivity of BN/epoxy composite was 1.52 W/m·K. In addition, the breakdown strength is 77.1 kV/mm. Thus, this type of BN-filled BN/EP composites with remarkable insulation and thermal conductivity properties would have potential for power engineering materials.

Keywords: boron nitride; epoxy resin composites; thermal conductivity; insulation properties

1. Introduction

As the electronics industry has grown towards miniaturization, multifunction, and high energy density, the generation of waste heat has become an inevitable risk leading lower performance and shortened product lifetimes [1,2]. To ensure the normal operation of the electronic equipment, the heat dissipation problem facing more and more challenges [3–5]. Due to the excellent insulation, corrosion resistance, low raw material cost and good process of Epoxy resin (EP), which always used in electronic devices as an ideal thermal interface material. In recent years, many scholars pay attention to the heat dissipation performance of epoxy resin [6,7]. However, epoxy resin has low thermal conductivity (about 0.2 $Wm^{-1} \cdot K^{-1}$) [8,9]. The intrinsic modification of epoxy has little effect on improving the thermal conductivity [10,11]. Most researchers use the addition of inorganic particles to improve the thermal conductivity of epoxy composite [12–14].

Boron nitride (BN) is an essential inorganic filler for the preparation of high thermal conductivity and insulation polymers with its unique layered structure, high surface thermal conductivity, and other comprehensive properties [15,16]. F H Yang [17] noticed that a polyethylene glycol (PEG) is introduced through a mild Diels-Alder reaction to improve its dispersibility and compatibility with epoxy resin matrix. The thermal conductivity of epoxy composites with different filler content show that the *h*-BN covalently modified by PEG with the content of 50 wt% can increase the thermal conductivity to 1.14 W/(m·K).

Yiran Zhang [18] reported that the dopamine with catechol groups and coupling agent to modify boron nitride (the dopamine-modified BN (DBN) and k-DBN (DBN modified

by coupling agent KH-560). The results showed that surface modification improved the dispersibility of BN in the Epoxy resin matrix and compatibility with the resin. Among BN/EP, DBN/EP, k-DBN/EP composites, k-DBN/EP composites had the highest thermal conductivity at the same number of additions. When the k-DBN/EP content was 30 wt%, the thermal conductivity of the composite was 0.892 W/(m·K), which was an increase of 25.5% compared with the BN/EP composite.

Through these studies found that high thermal conductivity of epoxy composite with high content of BN, it will bring problems such as reduced insulation performance. The second filler to build a thermally conductive bridge inside the material to reduce the amount of filler used to solve this problem [19–21].

M Donnay [22] prepared epoxy-matrix composites using the micro- and nano-sized boron nitride (BN) as filler for thermal management in electrical applications. The thermal conductivity of the Epoxy resin shows up to a fourfold increase for the composite containing 20 wt% of BN. The addition of BN results in an increase of the breakdown strength of the host matrix (about 10%) accompanied by improved robustness (less scattering of the measured values), both very important factors for any electrical application. S G Osanenzadeh [23] used 33.3% volume fraction of micron BN and graphene microplates (GNPs) hybrid co-filled polylactic acid (PLA). When, BN particles form effective connection points between GNPs and matrix. The formation of heat conduction network strengthens the phonon transfer effect at the interface. With the increase of GNPs/BN ratio, the thermal conductivity of PLA increases and the mixing changes. The thermal conductivity of PLA changed with the highest relative proportion of hybrid particles. It was 2.28~2.77 W/(m·K), more than 12 times that of pure PLA. T B Zhao [24] found that the mixed mass ratio of BN, AlN and Al_2O_3 was 20/5/5, the thermal conductivity of PE with mixed filling reaches the maximum (1.12 W/(m·K)), which is higher than the same content particle filled polystyrene (PS). The results show that Al_2O_3 and BN is more likely to form particle networks, and the polymer crystallizes between thermal particles play a bridge role, further improve the thermal conductivity.

Based these reports, the different particles with multi-scale play a vital role in determining and improving thermal conductivity. Here, we report the preparation and properties of highly thermally conductive composite materials, containing different proportions of micro size and nanosized BN particles dispersed in the epoxy matrix. The combination of micro size and nanosized BN particles with an appropriate ratio gives the highest thermal conductivity.

2. Materials and Methods

2.1. Materials

The epoxy resin (EP), curing agent and the accelerator formulation used in this experiment were purchased from Huntsman Corporation (Shanghai, China).

The parameters of EP are as follows: epoxy group content: 4.95–5.10 eqiv/kg, density: 1.10–1.20 g/cm³, viscosity (25 °C): 1500–3000 mpa·s, Flash point: >165 °C, vapor pressure: <0.03 mbar.

The curing agent is Aradur 3275 (density: 1.15–1.25 g/cm³, viscosity (25 °C): 150–200 mpa·s, Flash point: >150 °C, vapor pressure: <0.3 mbar)

The accelerator formulation (density: 0.92–1.04 g/cm³, viscosity: 20–100 mpa·s, Flash point: >65 °C, vapor pressure: <0.5 mbar) were purchased from Huntsman Corporation (China).

Micron boron nitride (M-BN, particle size of 10 μm, purity > 99.5%) and nano boron nitride (N-BN, particle size nearly 1 μm, purity > 99.5%) were purchased from Liaoning Dandong Chemical Research Institute Co., Ltd. (Dandong, China).

In order to increase the interaction force between BN and matrix, KH-550 (γ-Aminopropyl triethoxysilane, $NH_2CH_2CH_2CH_2Si(OC_2H_5)_3$) was used to modify M-BN and N-BN sheet. The specific steps were as follows [25,26]: (a) BN particles were immersed in 5 mol/L NaOH solution. The reaction was carried out at 110 °C for 10 h, followed by filtration and repeated washing with deionized water dried at 70 °C for 10 h for further use; (b) making an ethanol

aqueous solution (1:10); (c) adding the silane coupling agent with a set concentration to the solution and stirring for 15 min in a flask with reflux setting, adjusting the ethanol aqueous solution pH to 3–5 using diluted oxalic acid and stirring for 20 min; (d) Add a certain proportion of BN into the grinder, pour KH550 solution into BN power, grind at high speed for 24 h, and take out the modified BN when it returns to room temperature; (e) rinsing with ethanol by filtration at least four times; and (f) drying the mixture at 110 °C for 10 h.

2.2. Preparation of Epoxy Resin Composite

A certain proportion of epoxy resin matrix, curing agent and accelerator were added to the flask, stirred for 30 min at 40 °C. Then 30 wt% M-BN and different mass fractions N-BN sheets entered to the matrix, respectively. Stirred for 1 h to make it completely mixed uniformly, collected the mixture, poured it into the abrasive tool, and transferred it to a vacuum oven. Heated up to 40 °C and kept it for 10 min. Until no bubbles in the mold, transferred the matrix to a hot press. First pressurize to 5 MPa pressure at 80 °C. Then depressurize and vent, and then continue to increase the pressure to 5 MPa. Keep the pressure at 80 °C for 4 h, then the temperature raised to 130 °C and maintain it for 8 h. Last cooling the samples to the room temperature, collect them for testing.

In order to distinguish various samples, the composite with 10 wt% N-BN and 30 wt% N-BN is named as 10%N-BN/EP, and for other concentrations, they are 20%N-BN/EP, 30%N-BN/EP, and 40%N-BN/EP, respectively. The only 30 wt% M-BN added composite is called by M-BN/EP.

2.3. Performance Characterization

1. Thermal conductivity test

The samples adopt the NETSCHL FA467 laser flash diffusion thermal analyzer to test the diffusion coefficient (α). The diameter of sample is 1 cm, and the thickness of them is about 2 ± 0.1 mm. The sides of samples spraying a thin layer of graphite powder. Then calculate the thermal conductivity according to Formula (1) [27,28], where c is the heat capacity, ρ is the density, and T is the temperature. This experiment uses a fixed temperature of 30 °C. The average value of the three sample was made.

$$\lambda(\mathrm{T}) = \alpha(\mathrm{T})^*\rho(\mathrm{T})^*c(\mathrm{T}) \tag{1}$$

2. Breakdown performance test

Place a disc with a thickness of 1 ± 0.1 mm and a diameter of 3 cm on a breakdown tester (the test instrument is Huayang Instrument and Equipment Factory, Jilin Province, with a boosted rate of 1200 V/s).

The dielectric breakdown strength of the EP nanocomposites is analyzed within the framework of Weibull statistics. Weibull statistical distribution is the most important method for processing data breakdown strength, which reflects the probability of the material at certain field strength (E) or the probability of failure or breakdown at a certain time (t). Weibull cumulative distribution breakdown field strength can be described as follows.

$$p = 1 - \exp[-(\frac{E}{\alpha})^{\beta}] \tag{2}$$

where p is the cumulative probability of the dielectric breakdown E is the breakdown strength for testing; β is the shape parameter that reflects the scatter of the breakdown strength E; and α is the characteristic breakdown strength during the cumulative probability of the dielectric breakdown is 63.2%. After twice taking the logarithm, Equation (2) can be deformed as follows.

$$\log[-\ln(1 - p)] = \beta \log(E) - \beta \log(\alpha) \tag{3}$$

This point log $[-\ln (1 - p)]$ and log (E) form a linear relationship in the Cartesian coordinate system. According to IEEE Standard 930-2004, when the number of samples is less than 25, p should be computed by the formula as follows.

$$p_i = \frac{i - 0.44}{n + 0.25} \times 100\% \qquad (4)$$

where n is the breakdown times or voltages in order from smallest to largest and assign them a rank from $i = 1$ to $i = n$, and n is 12.

3.　SEM characterization

The scanning electron microscope (S-4700) of Hitachi Company was used to study the microscopic morphology of the samples. Firstly, the samples were sprayed with gold, and then the surface of the particles and the fracture morphology of the samples were observed. In the preparation of the material cross-section, the sample needs to be cooled in liquid nitrogen for 2 h, and then the brittle fracture is made using a clamp.

4.　FT-IR test

The structures of modified BN sheets were analyzed by the Fourier transform infrared spectral (FT-IR, Nexus 670).

5.　Mechanical properties

Static uniaxial in-plane tensile tests were conducted through a dynamic mechanical analyzer (DMA Q800, TA Instruments). The maximum tensile force is 18 N, which is sufficient to do the in-plane tensile tests of samples with rectangle stripe shape (length: 20 mm, width: 10 mm, thickness: 2 mm). The tensile strength was extracted from the curve before failure.

6.　DC conductivity properties

DC conductivity measurements were conducted in the room temperature (25 °C). DC conduction path testing system including the high voltage DC power with continuously adjustable output voltage within 0–10 kV, pA ammeter (measuring range of 10^{-2}–10^{-14} A), oven temperature (shielding box, the maximum operating temperature, 25 °C) and multi-branching switch was used to investigate electrical properties of the insulating materials. The samples with equal thickness each time were put into the oven. The output voltage was increased progressively. When the current is not change for 20 min, the data was read every 30 s. The mean data of 40 point were seen as the experiment data.

3. Results and Discussion

3.1. Microstructure Characterization

The grafting of KH-550 modified BN was analyzed by FT-IR. As shown in the Figure 1, it can be seen that there is an obvious H-N absorption peak at 3350 cm^{-1} in the infrared curve of the modified BN. The reaction as shown in the diagram of grafting KH550 onto BN surface. After surface hydroxylation, it is dehydrated and condensed with KH550 amino group, and KH550 amino group is combined with BN surface. After BN is surrounded by modifier, the interaction between BN and parent is increased and the repulsion between BN sheets and parent molecular chain is reduced.
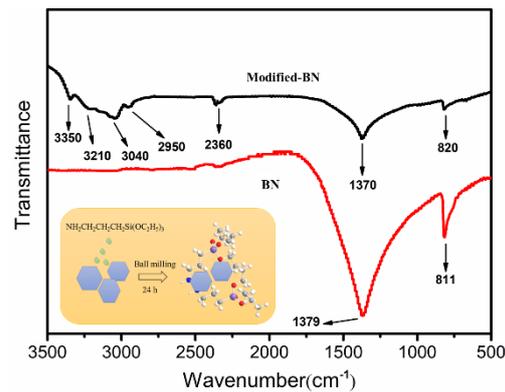
Figure 1. FT-IR spectrum of the modified-BN By KH550.

Figure 2 is the SEM diagram of the cross-section of the BN/EP composite material, in which the content of nano-BN is 10% and 20%, respectively. As shown from the figure, the small-scale BN is distributed in the middle of micro-BN, which plays a bridging role in the heat conduction process. It is the reason why the thermal conductivity increasing.

(**a**)   (**b**)
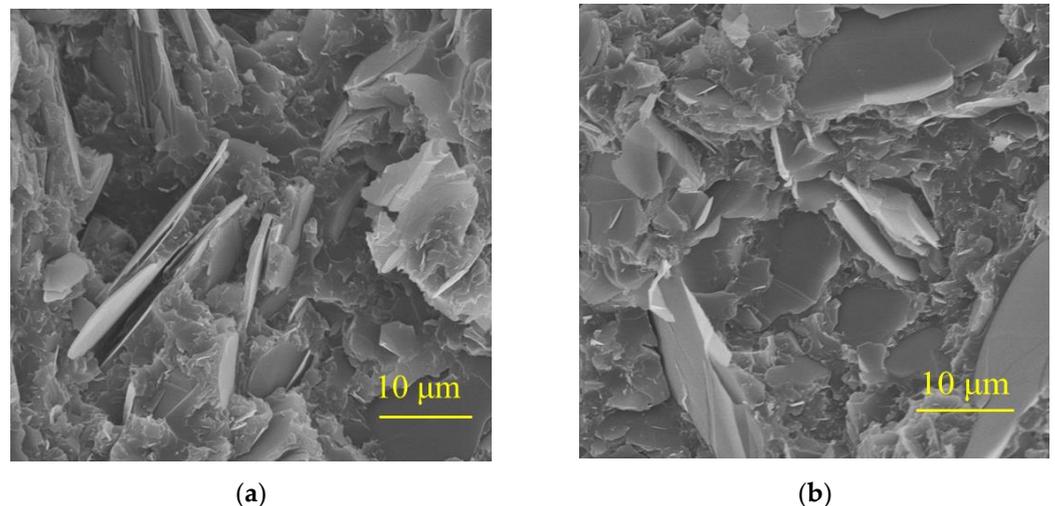
Figure 2. The SEM diagram of the cross-section of the N-BN/EP composite material. (**a**) 10% N-BN/EP; (**b**) 20% N-BN/EP.

3.2. Thermal Conductivity

BN is a softer filler, which can attain a higher packing density at a low filler content and provide a larger surface contact between micro and nano particles than other ceramic thermally conductive fillers. Figure 3 shows the thermal conductivity of the BN/EP composite. It can be seen that the addition of N-BN platelets firstly elevates the thermal conductivity of BN/EP composites, and then a tendency of declining happens. The thermal conductivity of the composites increases with the increase in the proportion of boron nitride. The thermal conductivity of N-BN/EP composites increased from 0.9 W/m·K to 1.52 W/m·K, as the N-BN added. Compared with M-BN/EP composite, the thermal conductivity of 20% N-BN/EP is increased to 1.6 times than that of it. Nanoparticles filled the gap between micron BN particles. Nano-sized BN particles played a connecting role between micron-sized BN particles, increased thermal conductivity channels, and improved thermal conductivity.
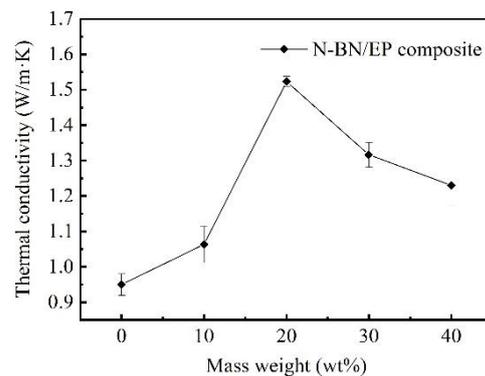
Figure 3. Thermal conductivity curve of BN/EP composite.

As the content of nano-BN increased to 30%, the thermal conductivity of 30% N-BN/EP decreases significantly. This may be caused by the agglomeration of nano BN. Aggregated BN reduces the formation of thermal conduction pathways to some extent. Local heat accumulation can also cause other performance degradation.

3.3. Breakdown Performance

Figure 4 shows the relationship of log [−ln (1 − *p*)] and log (*E*) of EP composites. The Weibull parameters *α* and *β* are shown in Table 1. The *α* is found to be strongly affected by the filler of nano-BN in the EP composites and the voltage ramping rate. The electrical breakdown strength of the material is 77.1 kV/mm when the additional amount of nano-BN is 20%, which is higher than that of M-BN/EP composite. The barrier forms by small-scale BN, and hinders the formation of conduction pathway. Thus, the breakdown strength of the 10%N-BN/EP and 20% N-BN/EP composites improve remarkably.
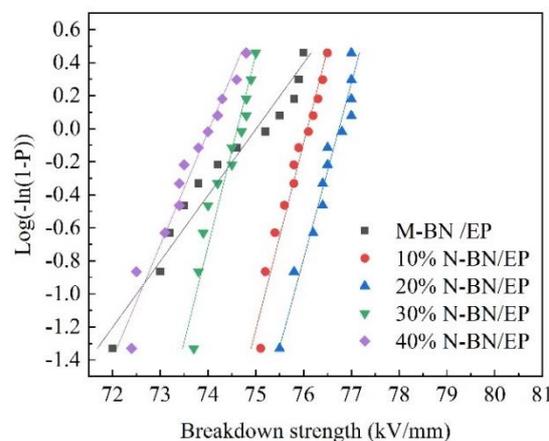
Figure 4. Breakdown strength data of BN/EP composite.

Table 1. Breakdown strength data of EP composite.

EP Composite	*α*	*β*
M-BN/EP	74.2	2.5
10% N-BN/EP	76.5	0.5
20% N-BN/EP	77.1	1.0
30% N-BN/EP	73.6	0.81
40% N-BN/EP	73.2	1.5

In the theory of electrical strength, usually referred to as free-volume theory [29], breakdown is initiated by free electrons accelerated by electric field in the largest of the holes present in the amorphous phase of all polymers. Breakdown starts when the energy gained by free electrons in field *E* on free path of length l_e attains with probability $P = 1$

the barrier energy E_μ. Then all electrons with this energy hop over E_μ, separating the traps in the compact structure [30]. The relationship is shown in Equation (5). The l_e becomes shorter after N-BN added, which result to the E_b higher. So, the breakdown strength data of N-BN/EP composites is higher than that of M-BN/EP composites.

$$E_b = \frac{E_\mu}{el_e} \tag{5}$$

when the concentration increases to 30%, the nanoparticles are likely to have agglomeration effect. The charge accumulated around the agglomeration BN will form the charge package, which resulting in the increase of local electric field and the formation of conduction channels [31,32].

3.4. DC Conductivity

It is well known that the conductivity is greatly related to the charge in the materials. In this work, the DC conductivities of BN/EP were discussed to explore the mechanisms for improving insulating properties of the BN/EP composites. Figure 5 shows the conductivities of the EP composite depended on electrical fields at room temperatures. The current changes of the materials are very little, when the electric field is less than 20 kV/mm. When the electric field reaches 25 kV/mm, the conductivity of 40% N-BN/EP and M-BN/EP composite increases rapidly. The conductivity of 20% N-BN/EP composite is relatively stable.
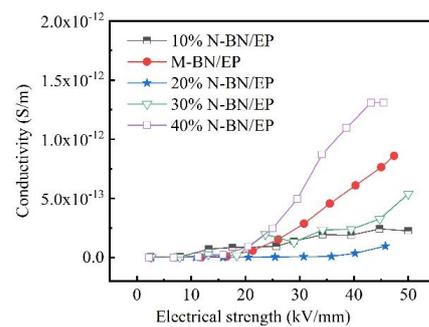
Figure 5. Conductivity of BN/EP composites depended on electrical strength at room temperature.

The current densities of BN/EP composite depended on electrical strength were shown in Figure 6. As shown in Figure 6, electric field thresholds which linked the Ohmic region and non-Ohmic region are increasing as the content of BN increased. Based on the Space Limited Current (SCLC) theory [33,34], the injecting charge nearly has been trapped in the Ohmic region. The injecting charge would not contribute to the current increasing. For the non-Ohmic region, the trapping charge in the composite will be detrapping, and the injecting charges will increase the current density. The N-BN is benefit to inhabit the charge.
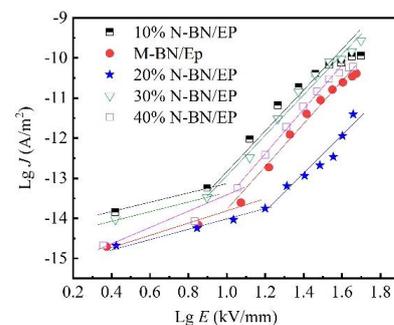
Figure 6. Current densities of sandwich-structured nanocomposites depended on electrical strength at different temperature.

3.5. Mechanical Property

Figure 7 shows the stress–strain curves of EP composite, and the corresponding strength values for the curves are summarized in Figure 7b. The addition of nano-BN platelets firstly elevate the tensile strength of N-BN/EP composites, and then a tendency of declining happens. The maximum values of tensile strength are 60 MPa at 20% nano-BN loading which are 1.25 times than that of M-BN/EP composite. Even if the composite were filled nano-BN content of ≥20%, their stress would reach 40 Mpa and 36 Mpa, respectively, still maintaining a well intact robustness in mechanical. In addition, these performances were much better than that of the 3D-BNNSs/EP composites [35] with BN of 19.7 vol % (35 Mpa), and higher than that of BNNs/EP composites [36] filled with BNNs of 75 wt % (40 Mpa).

(**a**)   (**b**)
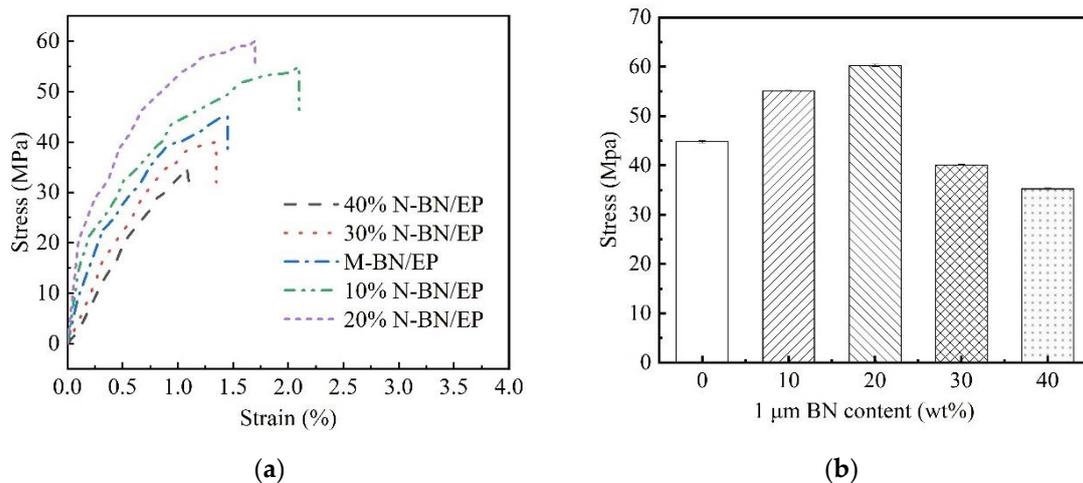
Figure 7. (**a**) Stress–strain curves of BN/EP composite and (**b**) Toughness of BN/EP composites.

There may be several reasons why the composites with micro and nano BN filling exhibited such outstanding mechanical property. First, nano-BN and EP, homogeneous coating consisting of the thinner EP layers between nano-BN could form a strong EP linking network, making them form a closely interconnected structure with EP molecules within the cured composites. Furthermore, as reported in the literature [37,38], the mechanical strength of nano-BN themselves has been proved to have higher mechanical strength than that of the micro-BN. Last, the addition of nano BN reduces the stress defects caused by the introduction of micron BN. Therefore, there existed some nano-BN in the composites, which increased the filling density of BN/EP and improved the strength of composite.

4. Conclusions

In summary, the thermal conductivity, breakdown strength, mechanical properties and electrical conductivity of BN/EP composite prepared by BN modification with different scale were investigated.

After modifying the particle surface with KH550, a good dispersion of the BN sheet in the composite was obtained. The significant results are that the yield strength of EP composite adding 20% nano-BN are increased by 37.7%. The breakdown strength of BN/EP composite reaches 77.1 kV/mm and the thermal conductivity of the material is 1.52 W/m·K. Based on the coordination of micro-nano particles, the thermal conductivity and breakdown strength can thus be enhanced simultaneously. This study will contribute to the development of advanced dielectric polymer nanocomposites with high thermal conductivity for energy storage application.

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