Dielectric BN nanosheet / PVDF composites with high thermal conductivity

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Abstract. With the development of electronic devices, high thermal conductivity polymer will become an ideal electronic packaging material. Therefore, Polyvinylidene fluoride (PVDF) nanocomposite was prepared doped with boron nitride nanosheet (BNNS), which has significantly improved thermal conductivity, excellent electrical insulation and outstanding flexibility. These nanocomposite films were prepared by mixing BNNS/PVDF in organic solution, drying, slicing, and then hot-pressing. Compared with the pristine polymers, the nanocomposite films have excellent thermal conduction, which indicates that new high-performance thermal conductivity materials will play an important role in high-power density electronic devices.

1. Introduction

At present, as the volume of electronic components decreases, the cooling area also decreases. And the working frequency of electronic components increases sharply, the semiconductor will produce more heat during the working process. In order to ensure the long and reliable normal operation of electronic components, the heat dissipation of electronic components has become an urgent problem to be solved in the field of electronics.

Because of its unique structure, easy modification and easy processing, polymer insulating materials have excellent properties that are incomparable and irreplaceable to other materials. Meanwhile, as the carrier material of electronic components, high thermal conductivity polymer composites play an important role in many manufacturing industries and high-tech fields such as microelectronics, aerospace, motor and electrical appliances.¹³ However, polymer materials are generally poor conductors
of heat, and their thermal conductivity is generally lower than 0.5 W/m·K. Therefore, it has become a research hotspot to develop high thermal conductivity polymer composites with excellent comprehensive performance.

Polyvinylidene fluoride (PVDF) is a nonflammable solid with a melting point of 172 °C. Its density is within the range of 1.77-1.80 g/cm³, thermal deformation temperature range is 112 °C - 145 °C, and long-term use temperature range is -40 °C - 150 °C. Moreover, PVDF has strong hydrogen bonds, and the molecular chains are closely arranged. Therefore, PVDF has great advantages as the matrix of thermal insulation polymer composites.

Hexagonal boron nitride (H-BN), similar to graphite, is a promising thermal filler. Not only does it have inherently high thermal conductivity, but it can also be stripped into ultrathin boron nitride nanosheets (BNNS). In addition, H-BN has a 5.9 eV wideband gap and has excellent electrical insulation properties such as high resistivity, low dielectric constant and low dielectric loss. Due to its superior performance, H-BN has a good prospect as a thermal conductive filler for thermal insulation polymer composites, which has been the focus of research in recent years.

In this paper, high thermal conductivity polymer-based composites BNNS/PVDF were prepared by using BNNS as thermal conductivity filler and PVDF as substrate.

2. Experimental section

2.1. Materials
BN powder was obtained from Guangzhou Xijia Chemical CO. LTD, China, and the average diameter of BN powder was 3 μm. Isopropanol (99%) is provided by Modern Oriental (Beijing) Technology Development CO. LTD, China. The PVDF (Solef 6010) used in this work was purchased from SOLVAY (Belgium). N, N-dimethylformamide (99%) was purchased from Tianjin Concord Technology CO. LTD, China. The XRD pattern shows the high-purity H-BN phase and PVDF phase in figure 1.

Figure 1. X-ray diffraction pattern of H-BN and PVDF.

2.2. Preparation of BNNS
First, H-BN powder was added to a mixed solvent with a 1:1 volume ratio of isopropyl alcohol and deionized water, and then the solution was ultrasonic. After ultrasonic treatment, the solution is centrifuged and the precipitate is taken. Finally, the precipitate is dried and BNNS are obtained. BN powder with diameter of about 3 μm was treated to obtain BNNS of nanometer length and width. The preparation method of BNNS is shown in figure 2.
2.3. Preparation of pure PVDF and BNNS/PVDF composites

PVDF composites were prepared by solution blending and hot pressing. First, PVDF powder was completely dissolved in an appropriate amount of N, N-Dimethylformamide (DMF) solution under the condition of heating in a water bath, and then BNNS was added to the solution and stirred until evenly dispersed. The solution is then put into a vacuum oven to dry the solvent. Amorphous BNNS/PVDF composites were obtained by drying. The obtained dry BNNS/PVDF mixture was cut into pieces. Finally, the fragments are then placed into a mold and hot pressed into BNNS/PVDF composites of a certain size and thickness.

Through the above experimental steps, pure PVDF and BNNS/PVDF composites with the proportion of 10wt% and 20wt% BNNS were obtained respectively. The complete preparation process of BNNS/PVDF composite material is shown in figure 3.

2.4. Characterization

The surface morphology of PVDF and BNNS/ PVDF composites was observed by scanning electron microscope (SEM) (HITACHI S-4800, HITACH Corporation, Japan). Optical photographs of the PVDF/BNNS composite were taken by a digital camera (Canon 650D, Canon Corporation, Japan). Differential scanning calorimetry (DSC) (NETZSCH 404 F3, NETZSCH Corporation, German) was
used to measure the melting point of nanocomposites at a range in nitrogen atmosphere. The shape, size and thickness of BNNS were observed by a scanning probe microscope (SPM) (Bruker Multimode 8, Bruker Corporation, German).

3. Result and discussion

3.1. Microscopic analysis of samples
Figure 4 is the AFM picture of BNNS. And figure 5 shows the thickness variation curve of BNNS along the linear direction of Section A. It can be seen the flaky BNNS with a thickness of about 20 nm. This indicates that we have successfully prepared BNNS of suitable size, shape and thickness.

![Figure 4. AFM image of BNNS.](image)

![Figure 5. Measurement curve of BNNS thickness of Section A.](image)

Figure 6 a, b and c were pure PVDF, BNNS/PVDF composites with a ratio of 10wt% BNNS, and BNNS/PVDF composites with a ratio of 20wt% BNNS, respectively. And Figure 6 e, f and g were pure PVDF, BNNS/PVDF composites with a ratio of 10wt% BNNS and BNNS/PVDF composites with a ratio of 20wt% BNNS, respectively.

In figure 6 b and c, on the surface of BNNS/PVDF composites material, we can obviously observe BNNS filled in PVDF. The size of BNNS basically matches the size of BNNS in the pictures measured by AFM, and BNNS are well dispersed in PVDF.

It can be seen from figure 6 a that there is no BNNS, while the number of BNNS gradually increases from figure 6 b to figure 6 c.

![Figure 6. SEM images and Optical images of pure PVDF and BNNS/PVDF composites materials.](image)
3.2. Measurement of thermal conductivity

In this experiment, based on the steady-state axial heat flow method, the thermal conductivity of samples was measured by the thermal property measurement device of solid materials. In the case of cartesian coordinate system with one dimension, that is, when the isothermal planes in the object are parallel to each other and perpendicular to the direction of heat flow (set as z axis), the Fourier law is simplified as follows:

\[ Q = \frac{P}{A} = -\lambda \cdot \text{grad}T = -\lambda \cdot \frac{dT}{dz} \]  

The above equation is the basic principle of steady-state axial heat flow method to measure the thermal conductivity. Where, \( Q \) is the heat flow density (W/m\(^2\)), which represents the heat flowing through a unit area in a unit time; \( P \) is the heat (W) passing through the sample section per unit time, and in the measuring system, is the heating power of the heat source; \( A \) is the cross-sectional area (m\(^2\)) of the sample perpendicular to the direction of heat flow; \( \lambda \) is the thermal conductivity (W/m/K), reflecting the heat passing through the vertical area per unit time per unit temperature gradient; \( T \) is the temperature of the sample, and \( \text{grad}T \) is the temperature gradient (K/m).

When the sample is isotropic and the temperature difference between the two ends of the sample is small, the thermal conductivity can be treated as a constant. Therefore, equation (1) can be simplified as:

\[ \lambda = -\frac{P \cdot \Delta z}{A \cdot \Delta T} \]  

\( \Delta T \) after reaching steady state heat conduction for the inside of a sample, the temperature difference between the hot end and cold end; \( \Delta z \) to sample the distance between the measurement point, the unit is m.

The sample is placed in an adiabatic container. Then, the cold source maintains a good thermal contact with one end of the sample, and the other end of the sample is heated by a heat source, so that a stable heat flow only along the axial direction of the sample (assuming the positive direction of z-axis) is passed through the sample. When the heat transfer process reaches a steady state, the thermal conductivity of the sample can be calculated.  

Figure 7 shows the curve of thermal conductivity of BNNS/PVDF composites material changing with the amount of BNNS filling. It is obvious that the thermal conductivity of BNNS/PVDF composites increases with the increase of BNNS mass ratio. The axial thermal conductivity of pure PVDF was measured as 0.1940 W/m/K, the axial thermal conductivity of BNNS/PVDF composites with 10wt% BNNS was 0.4450 W/m/K, and that of 20wt% BNNS/PVDF composites was 0.5050 W/m/K. Compared with pure PVDF, the axial thermal conductivity of BNNS/PVDF composites with 20wt% BNNS increased by about 260%.

![Figure 7](image)

**Figure 7.** The curve of thermal conductivity of BNNS/PVDF composites material changing with the amount of BNNS filling.
4. Conclusions
In short, BNNS/PVDF composites were successfully prepared. And as the mass proportion of BNNS increases, the thermal conductivity of BNNS/PVDF composites also increases. Compared with pure PVDF, the axial thermal conductivity of BNNS/PVDF composites with a BNNS ratio of 20wt% is increased by about 260%.

Further research is needed to construct effective thermal conduction pathways to obtain greater thermal conductivity with less BNNS filling. At the same time, it is necessary to further study the thermal conduction mechanism of inorganic particles doped with high thermal conductivity in polymer.

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