

3D BORON NITRIDE FOAM REINFORCED FLEXIBLE INSULATED POLYMER WITH HIGH THERMAL CONDUCTIVITY

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ABSTRACT

In this work, a series of novel flexible polymer composites consist of boron nitride foam (BNF), and polydimethylsiloxane (PDMS) were prepared and developed by two steps of fabricating the BNF by chemical vapor decomposition (CVD) via borazane precursor, then infiltrating PDMS precursor mixtures into BN foam. Due to the interconnected network of BNF, the composites show a good thermal conductive at ultra-low loading of 0.4wt%, namely 71% enhancement compared to PDMS. Besides, these composites show excellent insulated properties and microwave transparent ability. Thus, they may be used in electronic packaging field.

1 INTRODUCTION

Heat management has become increasingly critical in modern electronic devices for better performance, longer lifetime and reliability under the trend of integrated, functional, and miniaturized development.[1] The most efficient solution to solve this challenge is to develop novel thermal interface materials (TIMs) with high thermal conductivity, insulation and softness. However, the polymeric elastomers show bad thermal conductive performance (commonly less than $0.3\text{WK}^{-1}\text{m}^{-1}$) [2]. The common strategy is to incorporate various fillers with high thermal conductivity, including metal[3, 4] (Ag, Cu powder etc.), carbon-based materials[2, 5], ceramic (aluminum nitride, boron nitride) and their hybrid mixture[6-10].

Boron nitride nanosheets (BNNS) is a kind of promising novel fillers with many unique properties, including electrical-insulating property[11], low relative permittivity (~ 3.9)[12], high thermal conductivity ($1700\sim 2000\text{WK}^{-1}\text{m}^{-1}$)[13, 14] and anti-oxidation[15]. However, the same as graphene, there are several challenges for BNNS based composites such as BNNS agglomeration and difficulty to enhance thermal conductivity of composites [16-19].

As our previous studies, forming a three dimension networks of fillers for phono transfer is an efficient strategy to improve thermal conductivity. Zhao et al.[20] reported graphene foam based composites which achieved a high enhancement of thermal conductivity by 300% with a filler loading of 0.7 wt%. At the same time, to construct the 3D networks of fillers would reduce the percolation of composites remarkably both in heat and electricity transport. However, carbon or metal based composites would change from insulators to conductors at a very low loading which limit their application in some electronic field.

In this work, we fabricated 3D boron nitride foam via template-directed CVD method, then infiltrated BNNS/PDMS precursor mixtures into the BNF to gain BNF/BNNS/PDMS composites. Due to the interconnected networks of BNF and synergistic effect of BNNS, the composites show a remarkably thermal conductive enhancement at 10%wt loading of BNNS ($0.56\text{W m}^{-1}\text{K}^{-1}$), at 10wt% loading, namely 158.5 and 55.7% higher in thermal conductivity compared to PDMS and 10wt% BNNS/PDMS respectively. Besides, due to the excellent dielectric property of BNNS, these composites show a low and stable relative permittivity (around 3), low dissipation factor (around 0.005) and highly microwave transparent ability at broadband. At the high-voltage insulation test, the breakdown strength of composites is higher than 16 kV/mm. Owing to these performances, the

BNF/BNNS/PDMS composites have a promising application in electronic packaging field, including thermal interface materials, underfill materials, molding compounds, and flexible substrates.

2 PREPARATION

2.1 GROWTH OF BN FOAM

Nickel foams of 1.5mm in thickness and $3.9 \times 10^{-2} \text{g cm}^{-2}$ in density supplied by Shanghai Zhongwei Company were first inserted into the single-zone quartz tube furnace (Lindberg/Blue M HTF55322C) to act as a catalytic template for the deposition of h-BN atomic layers. 1g of borane-ammonia complex (borazane, $\text{H}_3\text{N}-\text{BH}_3$) powder (Sigma Aldrich—Melting point: 97.61°C) was loaded into a separate quartz boat in one end of the tube and served as precursor material. Prior to the growth of h-BN, the nickel foam was annealed under H_2 gas at 20 s.c.c.m flow rates for 2 h to remove surface oxide and improve grain size, the process pressure and temperature were maintained at 100 Pa and 1000°C , respectively. After annealing of nickel, the borazane powder was sublimated to vapor by heating to 80°C precisely via another mini furnace (supplied by JGY) and the H_2 gas flow rate was increased to 25 s.c.c.m to transport the precursor. After one hour under these conditions for growth, samples were cooled down to room temperature at a slow rate [20] of $10^\circ\text{C}/\text{min}$ for larger crystal grain. To etch away the nickel template, poly (methyl methacrylate) (PMMA) (MwD996,000; 4 wt.% in ethyl lactate) was dip-coated firstly onto the samples and dried at 180°C to form a protecting layer on boron nitride. After that, the samples were undergone a selective wet etch of nickel skeleton in 3M HCl at 60°C for 6h, then immersed into acetone for 1h to remove the PMMA protecting layer. Finally, snow-white freestanding BNF was obtained after washing with deionized water several times and lyophilizing.

2.2 FABRICATION OF COMPOSITES

The liquid PDMS precursor (Sylgard184, Dow Corning) and the curing agent (base agent/curing agent = 10/1 in weight) were mixed and stirred. Then, the mixture was infiltrated into BNF in a mold, then vacuumized and cured at 80°C for 4 h to get the BNF/PDMS composite.

3 RESULTS AND DISCUSSIONS

3.1 MORPHOLOGY

The SEM image of BNF is shown in Fig.1 (a), a three dimensional boron nitride frameworks can be identified clearly, which can bring an efficient pathway for heat transfer. In Fig.1 (b), there are about sixteen layers of hexagonal boron nitride (h-BN) at the edge of one piece of BNF shown in high resolution TEM image. The SEM images of cryo-fractured surfaces of PDMS and BNF/PDMS composite were presented in Fig 1. (c, d). The cryo-fractured surface of PDMS is smooth and there are no obvious voids and cracks inside PDMS and BNF/PDMS. More importantly, the hollow arm of BNF was filled with PDMS and there are no gaps between BNF and PDMS matrix shown in Fig.1 (d).

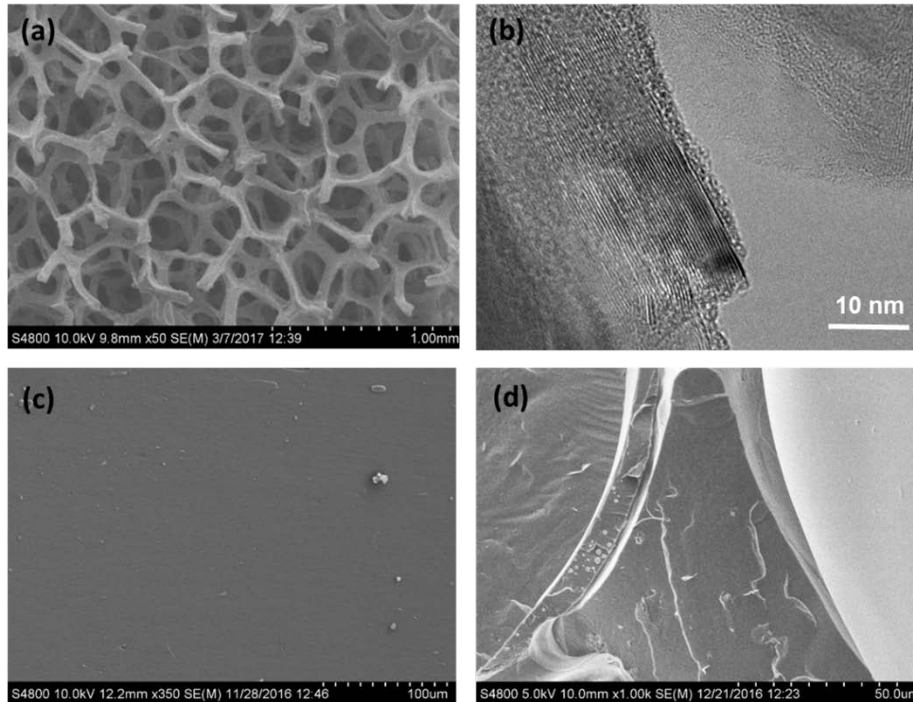


Figure 1. (a) Typical SEM images of BNF, (b) TEM images of BNF, (c, d) SEM images of cryo-fractured surfaces of PDMS and BNF/PDMS composite.

3.2 THERMAL PROPERTY

The thermal conductivity of PDMS and BNF/PDMS is given in Fig. 2(a). From the results, the thermal conductivity increases from $0.21 \text{ Wm}^{-1} \text{ K}^{-1}$ of neat PDMS to $0.36 \text{ Wm}^{-1} \text{ K}^{-1}$ of BNF/PDMS composite with 71.4% increase due to the unique three dimensional network of BNF of phonon transfer. Thermal conductivity enhancement efficiency (η) is calculated as follows.

$$\eta = \frac{TC - TC_0}{100 W TC_0} \times 100 \quad (1)$$

Where η is thermal conductivity enhancement efficiency; T_C and TC_0 are the thermal conductivity of composites and pure polymer, respectively; W is the weight loading of fillers. The enhancement efficiency of BNF/PDMS composite with only 0.4wt% of BNF loading is up to 179.

Besides, thermal stability measured by TGA is shown in Fig.2 (b). The addition of BNF can improve the thermal stability of composites. Under 350°C , the weight loss of sample is less than 5%, indicating the excellent thermal stability of composites. And there is a remarkable drop when the temperature is higher than 450°C . The weight loss can be attributed to volatile decomposition of PDMS. The heat-resistance index is calculated as follows.

$$T_{\text{Heat-resistance index}} = 0.49 * [T_5 + 0.6 * (T_{30} - T_5)] \quad (2),$$

Where T_5 and T_{30} are corresponding decomposition temperatures of 5% and 30% weight loss, respectively [21-23]. Due to interaction between BNF and macromolecular chain of PDMS, the heat-resistance index increases from 245.9 to 252.3°C . All results are given in Table 1.

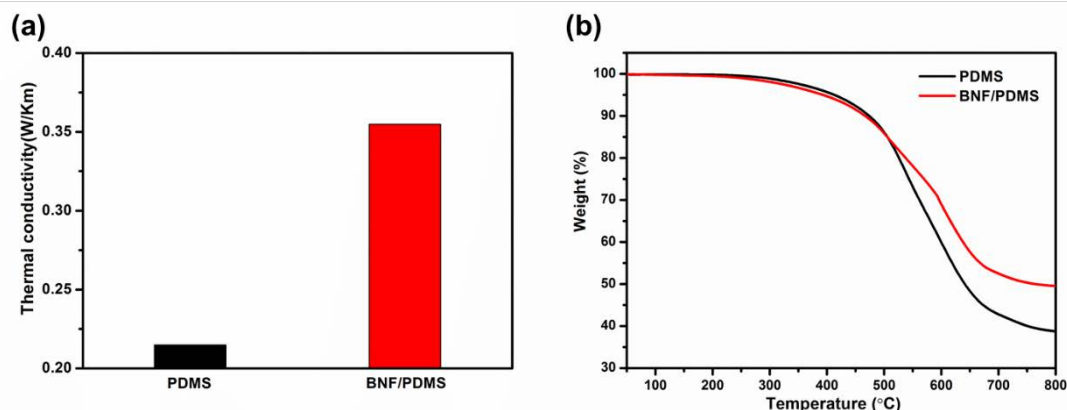


Figure 2 (a) Plots of thermal conductivity and (b) TGA curves of PDMS and BNF/PDMS composite.

Samples	Temperatures for weight loss (°C)		Heat-resistance index (°C)
	5 wt%	30 wt%	
PDMS	412.3	561.5	245.9
BNF/PDMS	392.9	596.1	252.3

Table 1. Corresponding characteristic thermal data of PDMS and the BNF /PDMS composites.

3.3 DIELECTRIC PROPERTY

Dielectric properties of materials make an important impact in high-frequency transmission substrate and microwave electronic packaging application. Owing to the low relative permittivity of BNF (~1.24 measured, 1.12 reported [12]), the relative permittivity of BNF/PDMS composite decreased about 2% compared with pure PDMS at both low frequency (1KHz to 100 KHz) and X band (8GHz to 12GHz). Moreover, variations of permittivity are less than 1%, especially at low frequency as presented in Fig.3. (a).

In order to evaluate the wave transparent ability of composites, the shielding effectiveness (SE) was measured according to IEEE standard [24]. The transmittance (T) and reflectance (R) of waves can be represented by complex scattering parameters (S-parameters): S₁₂ (or S₂₁) and S₁₁ (or S₂₂). Due to excellent dielectric property of BNF/PDMS composites, the total shielding effectiveness is less than 1.2 dB, which means nearly transparent to electromagnetic waves. And as presented in Fig.3 (d), the reflective EMI account for a major contribution to wave shielding effectiveness in BNF/PDMS composite.

For further measurement of the insulated properties, the breakdown strength of composites was tested by high-voltage withstand test. As showed in Fig. 4, breakdown strength increases from 16.8 kV/mm to 17.7 kV/mm while introducing BNF into PDMS. The reason is that BNF shows a better insulativity than pure PDMS.

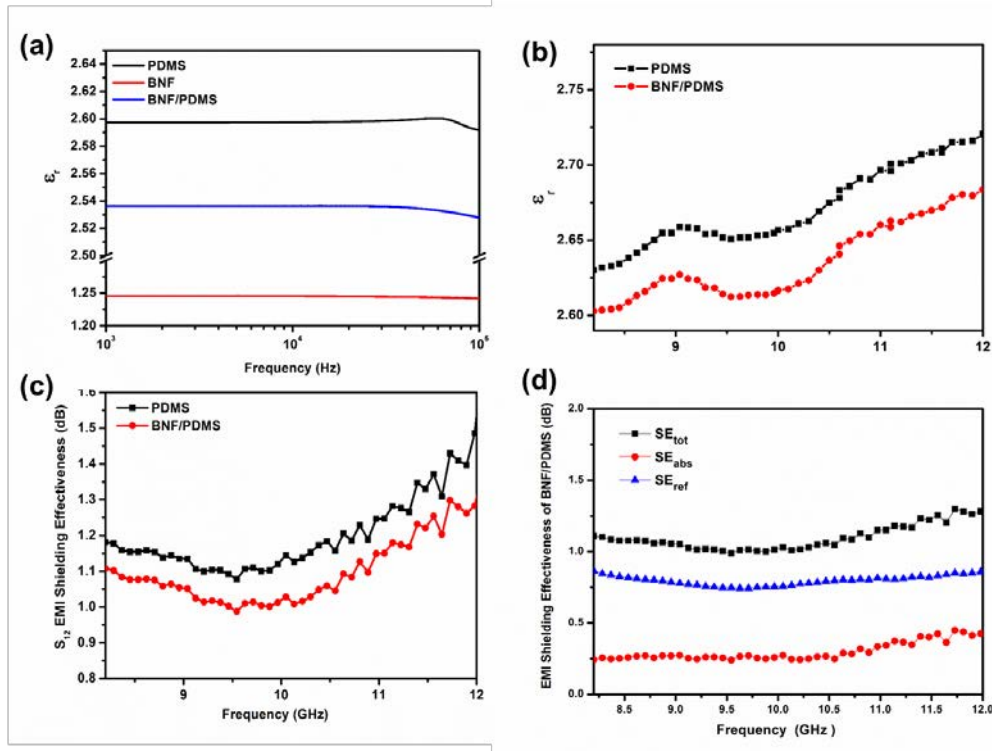


Figure 3 : (a) Relative permittivity at low frequency from 10 KHz to 100 KHz, (b) Relative permittivity at X Band, (c) S_{12} at X Band, (d) Total, absorptive and reflective EMI shielding effectiveness at X Band.

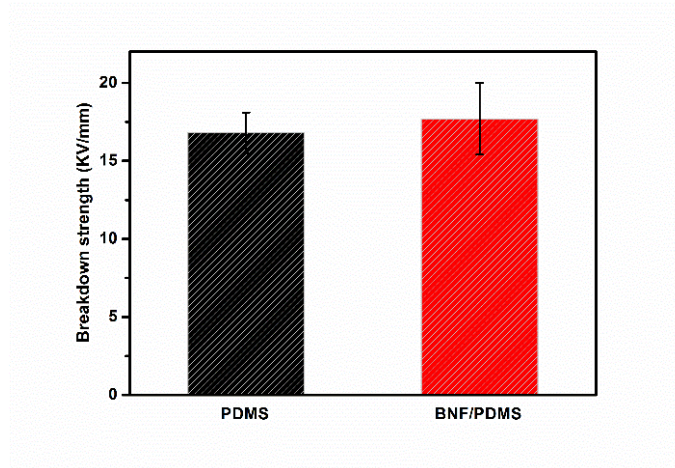


Fig. 4: Breakdown strength of PDMS and BNF/PDMS composite

4 CONCLUSIONS

A series of novel flexible polymer composites consisted of boron nitride foam (BNF), polydimethylsiloxane (PDMS) were designed and manufactured and their thermal and dielectric properties were studied. Due to the interconnected structure, adding BNF into polymer can obviously bring an important improvement of multi-performances of composites. The outstanding performance of BNF/PDMS composites will endow them with a promising application in wide electronic field.

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