

Preparation and Properties Study of Thermally Conductive Epoxy/Modified Boron Nitride/Graphene Nanosheets Composites

Hexiang Chen¹, Chunbao Zhao^{1,*}, Suichun Xu¹, Xujie Yang²

¹School of Microelectric Engineering, Nanjing College of Information Technology, Nanjing 210046, China

²School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

*Corresponding author e-mail: chenhx@njcit.cn

Abstract. A series of thermally conductive and electric-insulating epoxy composites filled with boron nitride (BN) modified by octadecyl trimethyl ammonium bromide and graphene nanosheets (GNP) were prepared. The effects of modified-BN (BNOTAB) and GNP content on thermal conductivity, electric-insulating and thermal stability properties of epoxy composite were investigated. The results indicate that the BNOTAB can homogeneously disperse into epoxy system. When the mass ratio of BNOTAB/GNP is 6:4 (total filler content is 10%), the thermal conductivity of the composites reached 0.48 W/(m·K), which is 108.7% higher than that of the neat epoxy. Meanwhile, the composite retains excellent electric-insulating property. TGA and DSC results showed that the addition of BNOTAB/GNP filler particles can improve the thermal stability of epoxy resin composites.

1. Introduction

Epoxy resin is a typical thermosetting resin that has been widely used in the electronics industry [1], due to its low cost, excellent electrical insulation properties, resistance to corrosion and good adhesion properties. Developments in the microelectronics involving integration and assembly technologies, have led to an increased demand for new materials that enable better miniaturization and higher frequency components to be incorporated into electronic devices. These demands require that materials used for the preparation of electronic devices and logic circuits exhibit good heat resistance and low coefficients of expansion. This ensures that any heat generated by electronic components can be effectively dissipated, thus enabling electronic devices to operate at higher temperatures without failure [2].

Hexagonal boron nitride, also known as “white graphene”, has a number of advantages as a material for electronic applications, including a low dielectric constant, high thermal conductivity and good electrical insulation properties. It is considered to be the optimal filling material for the preparation of thermally conducting and electrically insulating polymeric composites [3-4]. Graphene nanosheets are two dimensional materials comprised of six-membered aromatic ring structures that contain sp² hybridized carbon atoms. They demonstrate clear advantages in improving the properties of polymers for electrical applications, due to their excellent electric conductivity and thermal



conductivity profiles and their good mechanical properties [5-7]. The use of graphene nanosheets (and/or hexagonal boron nitride) as filling materials not only confer excellent thermally conducting and electrically insulating properties to a polymer, but also results in efficient dispersal of filling materials throughout the polymer matrix [8-11]. In this study, we have prepared a series of thermally conducting and electrically insulating composites using hexagonal boron nitride and graphene nanosheets as filling materials. The performance of these filling materials on the thermal conducting, electrical insulating, thermal resistance and fracture morphology of the resulting composite have been investigated. These results show that a composite containing 6%BNOTAB+4%GNP has improved thermal conductivity properties when compared to pure epoxy resin composite, indicating that it should be a better material for electronic packaging applications.

2. Experimental

2.1. Materials

WSR6101 epoxy resin was purchased from Nantong Xingchen Synthetic Material Co. Ltd. Methylhexahydrophthalic anhydride (Me HHP A) with a purity of 98% was purchased from J&K Scientific Ltd. 2,4,6-Tris(diethylaminomethyl)phenol (DMP-30, curing catalyst) was purchased from Aladdin Shanghai Biochemical Technology Co., Ltd. Hexagonal boron nitride (h-BN) with a purity of 99.9% was purchased from Zibo Jonye Ceramics Technology Co., Ltd. Analytical reagent grade Octyl trimethyl ammonium bromide (OTAB) was purchased from Shanghai Chemical Reagent Co., Ltd. Graphene nanosheets (GNP) with a purity of 99.9% and average thickness of 5-8 nm were purchased from JCNANO Tech Co., Ltd.

2.2. Sample preparation

(1) Surface modification of boron nitride powder

Modification processes were carried out using the following procedures:

Boron nitride powder was placed in a furnace box and heated at 1000 °C for 2h, before being allowed to cool naturally to room temperature. 500 mL of an OTAB solution was prepared with a concentration of 0.01mol/L and its pH adjusted to 8.0. After adding 25 g of BNO powder to the OTAB solution, the resultant dispersion was stirred for 1h before being super-sonicated for 30min. The dispersion was then stirred and heated at 80 °C for 5h. High-speed centrifugation was then used to separate the particles from the dispersion. OTAB modified boron nitride powder (BNOTA) was obtained by thoroughly rinsing the particles with distilled water (3x) and drying the resultant particles under vacuum.

(2) Preparation of epoxy resin composites

Defined amounts of BNOTAB powder and graphene nanosheets (or both additives) were added to acetone, and the resultant dispersion stirred for 20 min, followed by super-sonication for 30 min. Epoxy resin was then added to the dispersion and the mixture stirred for 1h, before being super-sonicated for a further 30min. The majority of the solvent was then evaporated by stirring the mixture for 1h at 80 °C. Curing agent (containing 75% EP by weight) and curing accelerator (containing 5% EP by weight) was then added, and the mixture stirred vigorously using a mechanical stirrer. Once this mixture became viscous, it was injected into a mould that had been preheated to 90 °C under vacuum for 45 min, which was then heated at a specific temperature for a different length of time (100 °C/1 h; 120 °C/2 h; 150 °C/4 h; 180 °C/2h; 200 °C/2 h). The mould was then cooled to room temperature to afford the desired epoxy resin thermal conducting composites to be recovered.

2.3. Tests and characterization of composite materials

Infrared spectroscopic analysis was carried out using a Bruker FTIR (SENSOR 27), with an ATR accessory used for each analysis. The wavenumber range was set from 400-4000 cm⁻¹, with data for each spectrum being collected as an average of 16-time scans. The morphology of BN powders and

cross-sections of composites were examined using a JSM-7600F JEOL SEM, after coating the surfaces of samples with thin gold films. The thermal conductivity of these composites was measured using a DRL-III thermal conductivity measuring device according to ASTM D5470-2006 standards. The volume electrical resistivity of material was measured using a Yangzhou Subo SBZC-90E electric resistance measuring device following testing procedures specified by GB1410-78 standards. Thermogravimetric analyses were carried out using a NETZSCH TG-209F3 thermogravimetric analyser to evaluate the thermal stability of each composite. Samples were analysed in a nitrogen atmosphere, with the chamber temperature raised from room temperature to 600 °C, using a heating rate of 20 °C/min. The glass transition temperature of the composites was measured using a NETZSCH DSC-214 differential scanning calorimeter. Samples were analysed under a nitrogen atmosphere, with the chamber temperature raised from 25 °C to 600 °C, using a heating rate of 20 °C/min.

3. Results and discussion

3.1. Infrared spectra of modified BN

Infrared spectra of untreated BN, BNO after heat treatment and BNOTAB modified by OTAB are shown in Figure 1.

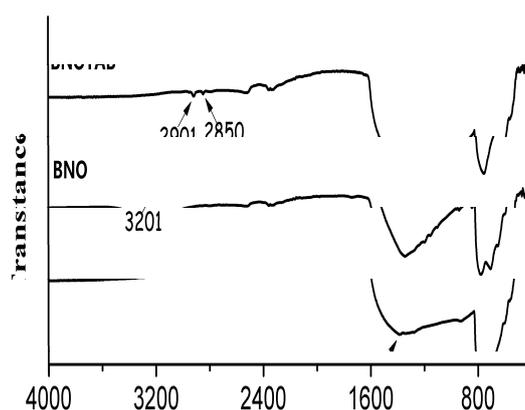


Fig. 1 FT-IR spectra of BN, BNO and BNOTAB

Absorption bands are visible at 1383 and 762 cm^{-1} corresponding to B-N stretching and bending vibrations respectively. The appearance of a strong absorption band at 3201 cm^{-1} in the BNO spectrum indicates the presence of B-OH groups on the surface of the BN particles [12-13]. C-H stretching vibration peaks for alkyl groups that appear at 2921 and 2851 cm^{-1} in the spectrum of BNOTAB demonstrate the presence of electrostatic interactions between the positive charges of OTAB molecules and the negative charges of the boron nitride lamellar. These observations clearly indicate that our derivatization process results in boron nitride particles with OTAB molecules successfully attached to their surface.

3.2. Microstructure of epoxy resin composites

Figure 2 shows SEM images of pure epoxy resin, modified boron nitride particles and epoxy resin composites. Typical fracture features for thermosetting materials are visible, including the smooth fracture surface and cracks extending in the same linear direction seen for pure epoxy resin in Figure 2 (a). Figure 2 (b) shows that lamellar structures of different sizes have been formed using surface modified BNOTAB particles, with an average thickness of their lamellar structures of around 100 nm. Figures 2 (c) and 2 (d) are SEM images of epoxy resin composites containing 10% BNOTAB and 6% BNOTAB + 4% GNP filling materials respectively. Rough fractures with blurred boundaries, cracks

extending in non-parallel directions, and dimples of different size can be observed in both images. Meanwhile, there is no evidence of any agglomeration of BNOTAB and GNP in these images, indicating that these filling materials are evenly dispersed throughout the epoxy resin matrix.

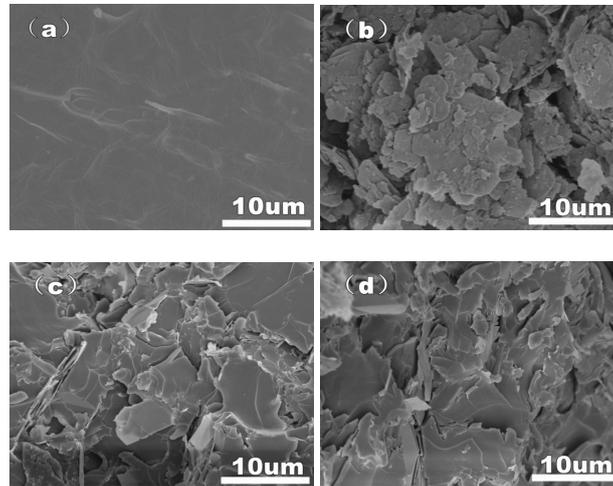


Fig. 2 SEM images of fractured surface of composites containing (a) Pure epoxy; (b) BNOTAB; (c) Modified BN; and (d) 6%BNOTAB+4%GNP

3.3. Thermal conducting properties of the epoxy resin composites

The effect of the weight ratio of BNOTAB to GNP (both used at total mass of 10%) on the thermal conducting properties of the epoxy resin composites were then investigated, by increasing the mass percentage of GNP from 0 to 40%. It was found that raising the BNOTAB content was increased from 0 to 10 % resulted in increase in the coefficient of thermal conductivity of the composites from 0.23 W/ (m·K) to 0.41 W/ (m·K) (See Figure 3). The coefficient of thermal conductivity of these composites could be raised further, by increasing the weight ratio of BNOTAB to GNP, with a maximum coefficient of thermal conductivity of 0.48 W/ (m·K) (109% higher than pure epoxy resin) achieved when the weight ratio reached 6:4. This increase in the coefficient of thermal conductivity is caused by the excellent thermal conducting properties of GNP, which counteract the negative effects that BNOTAB has on the thermal conducting properties of the composite. Therefore, it appears that the uniform dispersion of GNP and BNOTAB throughout the composite results in an increase in the number of thermal conducting paths, leading to more efficient thermal conducting networks within these resin matrices [13].

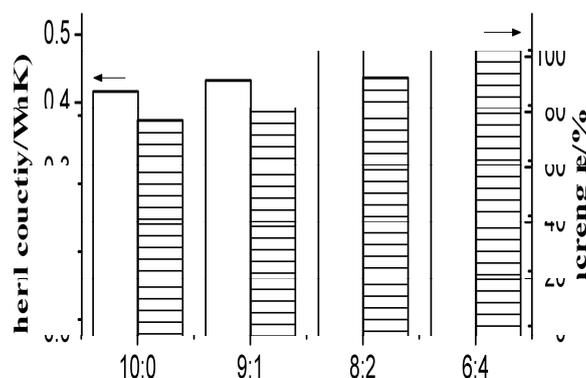


Fig. 3 Plot of thermal conductivities of composites versus the proportion of BNOTAB/GNP

3.4. Electrical insulating properties of epoxy resin composites

Only composites that display excellent electrical insulating and thermal conducting properties are suitable for electrical packaging applications. Consequently, the volume electrical resistivity (VER) of pure epoxy resin, and epoxy resin composites containing different amounts of BNOTAB/GNP, were determined (See Table 1). These data reveal that the VER of epoxy resin was increased from $7.68 \times 10^{16} \Omega \cdot \text{cm}$ to $1.14 \times 10^{17} \Omega \cdot \text{cm}$ when the content of BNOTAB was raised from 0 to 10%. This increase in VER indicates that the BN particles convey excellent electrical insulating properties to the composite. Graphene nanosheets exhibit excellent electrical conducting properties, therefore the VER was reduced when the percentage of GNP in the composites was increased. When the GNP content reached 4%, the volume electrical resistivity of the epoxy resin composite was decreased to $6.12 \times 10^{15} \Omega \cdot \text{cm}$, however this value means that this composite still has excellent electrical insulating properties that are suitable for electrical packaging applications.

Table 1. Volume electrical resistivity of epoxy composites

Content of filling material		Volume electrical resistivity ($\Omega \cdot \text{cm}$)
BNOTAB (%)	GNP (%)	
0	0	7.68×10^{16}
10	0	1.14×10^{17}
9	1	3.82×10^{16}
8	2	2.52×10^{16}
6	4	6.12×10^{15}

3.5. Thermal resistance property of epoxy resin composites

Thermogravimetric analysis of pure epoxy resin and the composite containing 6%BNOTAB+4%GNP were carried out (See Figure 4), whose thermal decomposition temperatures (at a mass loss rate of 10%) are also listed in Table 2. This data revealed that the epoxy resin and its composite both started to decompose at 200 °C, with the rate of decomposition of both samples occurring most rapidly between 350-450 °C. No significant differences between the thermogravimetric analysis graphs of pure epoxy resin and the composite were observed, indicating that their mechanism of decomposition is the same. Data from Table 2 also reveals that the overall decomposition temperature of the composite is higher than for pure epoxy resin, so it may be concluded that the presence of boron nitride and graphene nanosheets improves the thermal resistance properties of the resin. It is proposed that a “defect pathway” effect may be operating to explain improvement in thermal resistance, whereby a continuous network of boron nitride and graphene nanosheets serve to effectively block the release of volatile degradation products from the resin, thus promoted the formation of localized carbon residues [14].

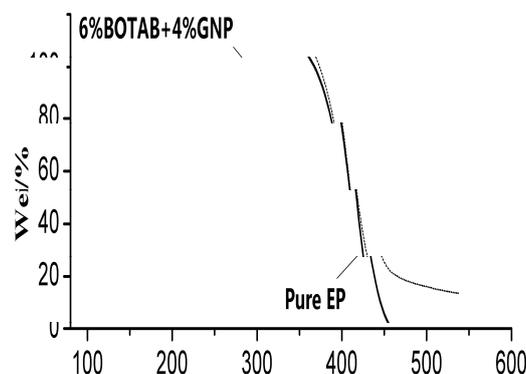


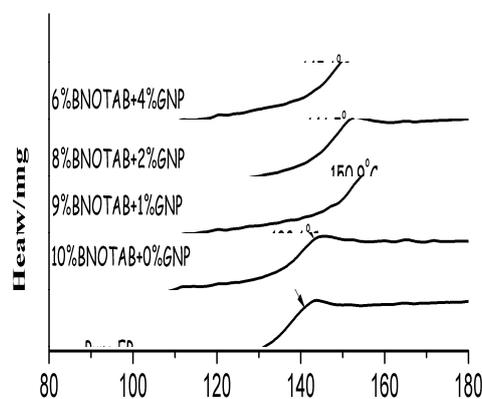
Fig. 4 TGA curves of pure epoxy and EP/BONTAB/GNP composites

Table 2. Thermal decomposition temperatures of pure epoxy and the EP/BONTAB/GNP composites

Content of filling material		Thermal decomposition temperature at T_{10} ($^{\circ}\text{C}$)
BNOTAB (%)	GNP (%)	
0	0	367.8
10	0	370.5
9	1	373.9
8	2	375.0
6	4	374.1

T_{10} corresponds to the thermal decomposition temperature at a mass loss rate of 10%

Differential Scanning Calorimetry curves revealed that the glass transition temperature (T_g) of epoxy resin composites containing increased levels of BNOTAB and/or GNP were improved when compared to pure epoxy resin. When the content of the filling material was 9%BNOTAB+1%GNP, the T_g of the composite reached 151.0 $^{\circ}\text{C}$, which is 15.0 $^{\circ}\text{C}$ higher than that for pure epoxy resin. When the content of the filling materials was 6%BNOTAB+4%GNP, the T_g of the composite was 146.0 $^{\circ}\text{C}$ which is still 10.0 $^{\circ}\text{C}$ higher than for pure epoxy resin. This means that these composite resins should be able to function at higher temperatures, with their increase in T_g likely to be caused by the presence of uniformly distributed networks within the resin. These networks may operate to hinder the movement of polymer chains, thus lowering the free volume of the composite, and increasing its overall crosslinking density. However, it was also found that very high levels of GNP content in BNOTAB and GNP composites, resulted in a decrease in their T_g values. This is potentially due to competing formation of clusters of filling material within the body of the composite resin, that result in decrease in its homogeneity that leads to an overall increase in the free volume of its polymer network [15].

**Fig. 5** DSC curves of pure epoxy and the EP/BONTAB/GNP composites

4. Conclusion

We have shown that incorporation of OTAB modified boron nitride particles and graphene nanosheets into epoxy resins affords composite resins with excellent thermal conducting and electrical insulating properties. SEM studies reveal that these boron nitride particles and graphene nanosheets are evenly dispersed throughout the epoxy resin matrix. The thermal conductivities of these composite resins were found to increase with increased GNP content, whilst their volume of electrical resistivity only decreased slightly. Their thermal resistance, decomposition temperatures and glass transition temperature properties were found to be improved when compared to pure epoxy resin, indicating that these composites are potentially useful materials for electronic packaging applications.

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References

- [1] He ZH, Yu JH, Jiang N, et al. Preparation and Thermal Property of Functionalized Boron Nitride/Epoxy Composite [J]. *Insulating Materials*, 2015, 48 (4):8-13.
- [2] Mu QW, Ren B. Preparation and properties of epoxy/ultrafine BN composite [J]. *New Chemical Materials*, 2011, 39 (4):131-133.
- [3] Hou J, Li G, Yang N, et al. Preparation and Characterization of Surface Modified Boron Nitride Epoxy Composites with Enhanced Thermal Conductivity [J]. *RSC Advances*, 2014, 4:44282-44290.
- [4] Fang H, Bai S L, Wong C P. “White Graphene”-Hexagonal Boron Nitride Based Polymeric Composites and Their Application in Thermal Management [J]. *Composites Communications*, 2016, 2:19-24.
- [5] Yu AP, Ramesh P, Sun XB, et al. Enhanced Thermal Conductivity in a Hybrid Graphite Nanoplatelet-Carbon Nanotube Filler for Epoxy Composites [J]. *Advanced Materials*, 2008, 20 (20):4740-4744.
- [6] Hu HT, Wang X, Wang JC, et al. Preparation and Properties of Graphene Nanosheets-Polystyrene Nanocomposites via in Situ Emulsion Polymerization [J]. *Chemical Physics Letters*, 2010, 484:247-253.
- [7] Yu AP, Ramesh P, Itkis ME, et al. Graphite Nanoplatelet-Epoxy Composite Thermal Interface Materials [J]. *Journal of Physical Chemistry C*, 2007, 111 (21):7565-7569.
- [8] Singh A K, Panda B P, Mohanty S, et al. Synergistic Effect of Hybrid Graphene and Boron Nitride on The Cure Kinetics and Thermal Conductivity of Epoxy Adhesives [J]. *Polymers for Advanced Technologies*, 2017, DOI: 10.1002/pat.4072.
- [9] Mosanenzadeh S G, Khalid S, Cui Y, et al. High Thermally Conductive PLA Based Composites with Tailored Hybrid Network of Hexagonal Boron Nitride and Graphene Nanoplatelets [J]. *Polymer Composites*, 2016, 37 (7): 2196-2205.
- [10] Shao L, Shi L, Li X, et al. Synergistic Effect of BN and Graphene Nanosheets in 3D Framework on The Enhancement of Thermal Conductive Properties of Polymeric Composites [J]. *Composites Science & Technology*, 2016, 135:83-91.
- [11] Deng JY, Yan D, Tang J. Preparation and properties of epoxy resin modified by graphene oxide [J]. 2016, 8 (47):8244-8247.
- [12] Cui Z, Oyer A J, Glover A J, et al. Large Scale Thermal Exfoliation and Functionalization of Boron Nitride [J]. *Small*, 2014, 10 (12):2352-2355.
- [13] Muratov DS, Kuznetsova DV, Il' Inykh IA, et al. Thermal Conductivity of Polypropylene Composites Filled with Silane-modified Hexagonal BN [J]. *Composites Science & Technology*, 2015, 111:40-43.
- [14] Huang T, Lu R, Chao S, et al. Chemically Modified Graphene/Polyimide Composite Films Based on Utilization of Covalent Bonding and Oriented Distribution [J]. *ACS Appl Mater Interfaces*, 2012, 4 (5):2699-2708.
- [15] Peng P, Yu JH, Jiang Pk. Preparation and Properties of Boron Nitride/Epoxy Composite Grafted with Hyperbranched Aromatic Polyamide [J]. *Insulating Materials*. 2012, 45 (3):1-5.