Original article

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Boron nitride nanoplatelets as two-dimensional thermal fillers in epoxy composites: new scenarios at very low filler loadings

<https://doi.org/10.1515/polyeng-2020-0046>

Received March 3, 2020; accepted August 6, 2020; published online September 7, 2020

Abstract: Hexagonal boron nitride (h-BN) nanoplatelets (0.6 μm in diameter and 100 nm in thickness) are introduced into epoxy resin to improve the polymer's thermal conducting ability. As expected, the thermal conductivities (TCs) of the composites, especially the in-plane TCs, are significantly increased. The in-plane TC of the epoxy composites can reach 1.67 W/mK at only 0.53 wt% loading, indicating h-BN nanoplatelets are very effective thermal fillers. However, after carefully studied the correlation of the TC improvement and filler content, a sudden drop of the TC around 0.53 wt% filler loading is observed. Such an unexpected decrease in TC has never been reported and is also found to be consistent with the T_g changes versus filler content. Similar trend is also observed in other 2-D nanofillers, such as graphene oxide, reduced graphene oxide, which may indicate it is a general phenomenon for 2-D nanofillers. SEM results suggest that such sudden drop in TC might be coming from the enrichment of these 2-D

nanofillers in localized areas due to their tendency to form more ordered phase above certain concentrations.

Keywords: boron nitride; polymeric composites; thermal conductivity; two-dimensional thermal fillers.

1 Introduction

With the continuous pursuing of microelectronic device miniaturization, more heat is generated in smaller volume inside the devices, which heavily affects their performances, especially the reliability [1–4]. Heat management has already become one of the key technologies in current microelectronics development. Polymers possess many advantages, such as low dielectric constant, easy of processing ability, excellent reliability, good adhesive ability, low cost and more [5–7]. They are widely used in modern electronic industry as base material, packaging material, adhesion material, thermal interfacial material etc. However, polymers are often considered and applied as thermal insulators, whose thermal conductivities are usually between 0.1 and 0.5 W/mK [8]. In many cases, polymeric components of the electronic devices are the bottleneck parts for heat dissipation. Enhancement of the thermal conducting abilities of polymeric materials used is one of the major solutions to effectively dissipate the excessive heat, thus to ensure the long-time performances of those devices.

Introducing highly thermally conductive inorganic fillers is the most common and effective way to enhance polymer's thermal conducting abilities. Various fillers, such as metals, ceramics and carbon materials in the forms of particulates, nanotubes, fibers, whiskers and platelets have all been applied to increase the thermal conductivities of polymers [9–17]. But very high filler loadings (more than 30 vol%) are often required to achieve desired thermal conductivity of the composites [9, 18, 19], which arouses many unwanted issues such as high cost, brittleness, challenges in processing and weight increase etc.

For the past decade, one-dimensional nanofillers, such as carbon nanotubes (CNT), have been favored as high

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potential thermal conductive fillers due to their extremely low percolation threshold observed in electron conductivity measurements [16]. Unfortunately, their abilities to enhance thermal conductivity are rather disappointing because of the high filler-matrix interfacial thermal resistance and high filler-filler contact resistance [9].

More recently, two-dimensional nanofillers, such as graphene, hexagonal boron nitride (h-BN) nanoplatelets or nanosheets are receiving special attention as potential thermal conductive fillers not only owing to their ultrahigh theoretical in-plane thermal conductivity (2000–4000 W/mK for graphene, 2000 W/mK for h-BN) and ultralow percolation threshold [20–32], but also the possibility of reducing the filler–filler thermal resistance via large area contact due to their unique 2D morphology [5, 33, 34]. For example, Zhu et al. prepared highly thermal conductive papers with one-dimensional nanofibrillated cellulose using h-BN nanosheets as fillers. The in-plane thermal conductivity of the composite paper at 5 wt% h-BN loading can reach 26.2 W/mK [34]. We also prepared graphene oxide/polyvinyl alcohols composite with an in-plane thermal conductivity of 17.61 W/mK at only 0.1 wt% graphene oxide (GO) loading [35].

Among all electronic insulators, h-BN possesses the highest thermal conductivity, which makes it an ideal filler candidate to be applied in electronic related applications. In this current work, h-BN nanoplatelets are introduced into epoxy resin, one of the mostly used polymers in micro-electronic devices. The thermal conductivities of the composites at various filler loadings, especially at low loadings, are carefully examined. As expected, h-BN can enhance the thermal conducting ability of epoxy resin significantly. The in-plane thermal conductivity of h-BN/epoxy composite can reach 1.67 W/mK at only 0.53 wt% filler loading. But more interestingly and surprisingly, the thermal conductivity of the h-BN/epoxy composite first increases with h-BN loadings, then suddenly it decreases notably, and continues to increase afterwards. To the best of our knowledge, such phenomenon has never been reported. Such transition is also observed in the glass transition temperatures (T_g) of the polymer composites. Similar changes are further observed in epoxy systems when using graphene oxide (GO) and reduced graphene oxide (rGO) as fillers, suggesting this may be a general phenomenon for two-dimensional fillers.

2 Materials and methods

2.1 Materials

Epoxy resin (E51) was obtained from Wuhan Loongtop New Material Technology Co. Hexagonal boron nitride (h-BN) platelets (purity >99.5%,

~0.6 μm in diameter, ~100 nm in thickness) was provided by SICCAS Co. Methyl hexahydrophthalic anhydride (AR grade, curing agent), 2,4,6-tris(dimethylaminomethyl) phenol (AR grade, catalyst), graphite platelet (purity >99.5%), sulfuric acid (95–98%), sodium nitrate (AR grade), potassium permanganate (AR grade), 30% hydrogen peroxide (AR grade), potassium hydroxide (AR grade) and hydrazine (85%, AR grade) were all from Sinopharm Chemical Reagent Co. All chemicals were used as received.

GO and rGO were prepared according to the reported method [36].

2.2 Fabrication of polymer composites

Surface modification was first performed on h-BN particles according to the literature [37].

A certain amount of surface modified h-BN was homogeneously dispersed in acetone (0.5 g/g) after 30 min ultrasonication. The h-BN/acetone dispersions were then mixed with the epoxy resin under stir. The mixture was further heated in an oil bath (~75 °C) to remove acetone. Then, the curing reagent (0.857 of resin weight) and catalyst (0.02 of resin weight) were added consequently.

The whole mixture was poured into preheated Teflon molds (75 °C) and degassed for 10 min before being cured in the oven. A two-step curing procedure was employed: 100 °C for 2 h, then 150 °C for 5 h.

GO/epoxy resin and rGO/epoxy resin composites were prepared similarly.

2.3 Instrumentation

X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer (D/Max-2250 V) with $\text{CuK}\alpha$ radiation at a generator voltage of 40 kV and a generator current of 40 mA. Scanning electron microscope (SEM) images were taken by a Hitachi S-4800 scanning electron microscope. Fourier-transform infrared spectra (FT-IR) were collected using a Thermo Nicolet 7000°C spectrometer over the range of 4000–400 cm^{-1} . Differential scanning calorimetry (DSC) was conducted on a Netzsch DSC 200 PC thermal analyzer. Photographs were taken by a Canon EOS 650DSLR digital camera. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific, ESCALAB 250 equipped with monochromatic Al $\text{K}\alpha$ as radiation source.

The thermal conductivity, k , was acquired based upon Eq. (1):

$$\kappa = \alpha \rho C_p. \quad (1)$$

in which, α is the thermal diffusivity, C_p is the specific heat capacity and ρ is the bulk density of the material. C_p is determined by employing a comparative method and the calibration standard is Pyroceram 9606, while ρ is measured by the water displacement method. The cross-plane and in-plane thermal diffusivities α of the samples (cross-plane: 10 × 10 mm, thickness 1.5 ± 0.2 mm; in-plane: diameter 25.4 mm, thickness 0.5 ± 0.1 mm) are measured on a laser-flash diffusivity instrument (Nano-Flash-Apparatus, LFA 447, NETZSCH).

3 Results and discussion

3.1 Surface modification on h-BN

Surface modification on the filler particles is the most common technique to improve the interfacial behavior in

polymeric composites. Similar to previous work [18], h-BN was treated with H_2O_2 in an autoclave. The reaction will introduce more hydroxyl groups on the particle surface [18]. XPS peak resolving results (Figure 1a) show a strong B-N peak (190.7 eV) and weak B-O peak (191.9 eV). After surface modification, the obvious increase of B-O binding is an evidence of more hydroxyl groups on the particle surface. Zeta potential of the particles changes from -39.45 mV to -51.50 mV after reaction, which will benefit particle dispersion stability [38].

SEM images in Figures 1b, c shows that surface modified h-BN still possesses nice two-dimensional morphology as pristine h-BN. But after surface modification, the platelets become thinner. Their thicknesses decrease from about 100 nm to 10–20 nm. It appears that the original stacked platelets are cleaved after the reaction. And the larger zeta potential can prevent the platelets from restacking.

3.2 H-BN/epoxy composites

A photograph of h-BN/epoxy composite at 1.73 wt% loading is shown in Figure 2a, which indicates a nice distribution of h-BN particles in the polymer matrix. The X-ray diffraction patterns for the h-BN/epoxy composites with various loadings are shown in Figure 2b. The presence of

h-BN is very clear even at very low filler loadings. The broad peak around 18° is due to amorphous epoxy resin [39].

SEM images of the fracture surfaces of epoxy composites at various h-BN loadings are shown in Figure 3. Fairly good dispersion of h-BN platelets in epoxy matrix can be observed at all filler loadings. It appears that h-BN platelets are perpendicular to the fracture surface, indicating the platelets are well aligned along the composite film plane. Such alignment happened during sample preparation due to the unique two-dimensional morphology of the filler. Moreover, SEM images also reveal the fracture model of the composites is the platelet pull-out mode, which indicates the interfacial interactions between the filler and epoxy is not very strong [40].

The thermal conductivities of h-BN/epoxy composite films at various filler loadings are summarized in Figure 4a. The thermal conductivity of the pure epoxy resin is 0.22 W/mK which is close to reported values in literature [13]. The thermal conductivities along the film plane increase significantly and are much higher than those of cross-plane values. The in-plane thermal conductivity of the composite can reach as high as 1.67 W/mK at only 0.53 wt% filler loading, which is about 800% increase of that of the pristine resin. Table 1 summarizes the TC values achieved in our work and other published works where 2D fillers were also used. It appears the h-BN nanoplatelets are quite

Figure 1: (a) XPS B1s spectra of pristine and surface modified h-BN; SEM images of (b) pristine and (c) surface modified h-BN platelets.

Figure 2: (a) A photograph of h-BN/epoxy composite with 1.73 wt% loading; (b) XRD patterns of h-BN/epoxy composites at 0.53 wt%, 1.73 wt%, 8.9 wt% and 11.71 wt% filler loadings.

Figure 3: SEM images of the fracture surfaces of h-BN/epoxy composites at 0.53 wt% (a, b), 2.56 wt% (c, d) and 11.71 wt% (e, f) filler loadings respectively at different magnifications; (g) higher magnification view of one of circled areas in (e).

efficient thermal filler. Because of the plate-like shape, h-BN nanoplatelets can be easily aligned during sample preparation and the aligned direction happens to be the same direction, along which the h-BN platelets have much larger thermal conductivity [44]. Meanwhile, the thermal conductive pathway can be formed along the aligned direction at lower filler loading due to the filler alignment. All

these contribute to the phenomenal increase of the thermal conductivity at such low filler loading.

But very surprisingly, when further increasing the filler loading, the in-plane thermal conductivity of the composites suddenly decreases. It decreased to 0.94 W/mK at 2.56 wt% loading and then grew gradually. Many theoretical models have been developed to predict the thermal conductivity of

Figure 4: (a) Plots of thermal conductivity and T_g of the composites versus filler loading; (b) DSC profiles of h-BN/epoxy composites at different filler contents.

Table 1: Summary of TC values achieved in this work and in some literature.

Filler	Loading	Matrix	K (W/mK)	References
h-BN	0.53 wt%	Epoxy	1.67	This work
Graphene-MLG	10 vol%	Epoxy	5.10	[32]
Graphene	43 vol%	Epoxy	11.22	[41]
h-BN	45 vol%	Epoxy	5.28	[41]
Graphene	6 wt%	Commercial TIM	0.77	[42]
h-BN	43.6 vol%	Epoxy	3.46	[43]
Graphene/h-BN	21.8/21.8 vol%	Epoxy	6.50	[43]
Graphite	21.2 vol%	PP	5.40	[1]
C-BNNS	9.6 vol%	Epoxy	3.13	[5]
h-BN	70 wt%	PMMA	3.73	[13]
h-BN	30 wt%	PI	1.20	[24]
BNNT	25 wt%	CNF	21.39	[27]
h-BN	44 vol%	Epoxy	9.00	[30]
BNNS	15.6 vol%	PDMS/PVA	1.94	[33]
Graphene/Cu	40/35 wt%	Epoxy	13.50	[50]
Graphene	55 wt%	Epoxy	8.00	[51]

multi-component composites. Those models differ a lot but they all predict that the thermal conductivity increases with filler loadings. It is known that in solids like polymer composites, phonons are the major thermal energy carrier. There should not be any changes in the thermal conducting mechanism. The sudden drop in thermal conductivity is more likely due to some phase behavior of the two-dimensional fillers at higher contents.

As the h-BN loading increases, some particle enriched area can be observed in the SEM images. Figure 3g is a

higher magnification view of one of the particle enriched areas in Figure 3e. It appears that the nanoscale platelets are still well dispersed in those enriched area. No particle aggregation is observed. But the localized enrichment of thermal fillers hinders the formation of the heat conduction path, leading to the decreasing of the in-plane thermal conductivity, which is illustrated in Figure 5. Currently, it still remains unknown to us the driving force for such a localized enrichment. But it might be due to the tendency of those particles to form more ordered phase. And the tendency is not strong enough to form ordered phase observed in many reported cases [45, 46]. At even higher filler loadings, the in-plane thermal conductivity starts to increase with filler loading again, which is quite straightforward to understand.

As shown in Figure 4a, the cross-plane thermal conductivities are much lower than the in-plane thermal conductivities and continue to increase with h-BN loading. The lower values are due to the orientation of h-BN nanoscale platelets and the fact that the in-plane thermal conductivity of h-BN is more than 20 times larger than the cross-plane value. Its continuous increase is also expected.

Figure 4b presents the DSC profiles of the h-BN/epoxy composites. It can be seen that the trend of T_g s of the composites exhibit a similar behavior as that of the in-plane thermal conductivity. Figure 4a indicates the transition of both T_g and the thermal conductivity occurs at similar h-BN content, around 0.53 wt%. Below 0.53 wt%, the introduction of h-BN into epoxy resin will enhance the thermal conductivity and increase the T_g s of the composite resins. The h-BN fillers can interact with epoxy molecules via H-bonding or other forces, functioning as extra cross-linking points, further immobilizing the movement of

Figure 5: Illustration of the h-BN and epoxy matrix. (Upper) Low h-BN loading; (lower) high h-BN loading. Red lines are imaginary heat transfer pathways.

polymer chains, resulting in higher T_g values. Such phenomena have been observed in many polymer composites [47, 48].

When the h-BN loading further increases, the extra crosslinking points provided by h-BN fillers become less due to the localized enrichment of h-BN particles, leading to the decrease of T_g (still higher than pristine epoxy resin). Meanwhile, possible sliding between closely packed h-BN platelets, which is beneficial to the movement of the epoxy chains, may also contribute to the decrease of T_g .

3.3 Epoxy composites with GO or rGO fillers

Based on the illustration on Figure 5, it arouses our curiosity whether such phenomenon can be observed in other 2-D filler system.

The X-ray diffraction patterns of the original graphite (Gt), GO and rGO are illustrated in Figure 6. The very sharp and strong diffraction peak around 26° is a characteristic of graphite. This peak shifts to around 12° and becomes much broader after oxidation, which is an indication of success conversion from graphite to graphene oxide. The increasing d -spacing is due to water molecule intercalation [49]. The strength of the diffraction peak of graphene becomes much weaker and this peak is much broader than that of graphene oxide, which shows the characteristics of the amorphous phase.

Figure 7 shows the thermal conductivity of epoxy composites filled with GO and rGO. The thermal conductivities fluctuate with the filler content increased, which is similar to that of h-BN/epoxy composite. We speculate that this is the common phenomenon of two-dimensional filler. Meanwhile, the thermal conductivities of rGO/epoxy composites are smaller than those of GO/epoxy composites at the same filler loadings. This may be ascribed to the fact that the

Figure 6: XRD patterns of graphite, GO and rGO.

Figure 7: Thermal conductivities of the epoxy resin composites versus GO and rGO loadings.

functional groups on the surface of rGO decreased a lot after chemical reduction with hydrazine hydrate and the interfacial interactions between GO and epoxy resin may be much stronger than the interactions between rGO and the resin.

4 Conclusions

In this work, a series of epoxy composites with h-BN sheets are prepared. The surface modified h-BN sheets were treated with hydrogen peroxide and characterized by the XRD, FT-IR, XPS and SEM analyses. The thermal conductivities of the epoxy composites filled with various h-BN loading are carefully studied. Due to the layered structure, the anisotropic fillers result in different cross-plane and in-plane thermal conductivities of the composites. The in-plane thermal conductivity is much higher than the cross-plane as expected.

A sharp increase of in-plane thermal conductivity of h-BN/epoxy composites is observed at very low filler loading. A maximum value of 1.67 W/mK is reached at 0.53 wt% loading. But surprisingly, with further increasing of h-BN loading, the in-plane thermal conductivity of the composites first decreases then increases again at a much slower rate. Tgs of the composites follow a similar trend. Such transition is probably due to the localized enrichment of h-BN sheets at higher loadings. Similar phenomena are also observed in other 2-D fillers, such as graphene oxide and rGO, which indicates this might be a common phenomenon for 2-D fillers. The localized enrichment of these 2-D fillers might be due to the tendency of them to form

more ordered phase. On the other hand, our results also implicate that the ability of 2D thermal fillers may be underestimated in many reported literatures.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The authors are grateful for the financial support from the Key Program of National Natural Science Foundation of China (no. 51732008), National Key Research and Development Program of China (2016YFB0701004), the Innovation Project of Instrument and Equipment Function Development of the Chinese Academy of Sciences (no. 2060499) and the Natural Science Foundation of Shanghai (18ZR1414000).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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