Synergistic construction of thermally conductive network in polybenzoxazine with boron nitride hybrid fillers

Wang Yi, Wei Wu, Dietmar Drummer, Wanting Shen, Liu Chao and Wang Ning
1 Sino-German Joint Research Centre of Advanced Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai, 200237, People’s Republic of China
2 Institute of Polymer Technology, Friedrich Alexander University Erlangen-Nuremberg, 91058 Erlangen, Germany
E-mail: wuwei@ecust.edu.cn

Keywords: nanocomposites, thermosets, thermal properties, high performance polymers, networks

Abstract
Synergistic effect between micrometer boron nitride/nanometer boron nitride (mBN/nBN) at different mass ratio was investigated. Hybrid fillers of mBN/nBN at certain ratio (mBN:nBN = 1:1) performed best synergistic improvement of thermal conductivities of mBN/nBN/polybenzoxazine (mBN/nBN/PBz) composites fabricated via ball-milling followed by a hot-compression method. The effect of hybrid mBN/nBN fillers on thermally conductive coefficient (λ), curing behavior and thermal stability was also studied. The λ value was improved from 0.2276 W · m⁻¹ · K⁻¹ for pristine PBz to 0.9196 W · m⁻¹ · K⁻¹ for (m/n)BN/PBz composites with 25 wt% hybrid filler. Agari model fitting revealed that mBN/nBN hybrid fillers constructed thermally conductive networks much easier than mBN did. The curing behavior and thermal stability of (m/n)BN/PBz composites were dampened with the addition of m/n hybrid fillers. Also, the addition amount of (m/n)BN hybrid filler had great influence on filler alignment in the matrix.

1. Introduction

After more than 50 years’ exponential development, semiconductor integrated circuits has almost reached its physical limit on device integration [1]. Such a complex network generates a large amount of heat during operation while most widely applied encapsulating materials like phenolic resin, epoxy resin, are poor conductors of heat (∼0.2 W · m⁻¹ · K⁻¹) [2], which hinder the dissipation of heat, resulting in the rising of working temperature of electronic devices [3]. Then operating energy consumption of the devices increases correspondingly, which forms a negative feedback loop. Consequently, the practical component stability and service life are much lower than the theoretical value [4]. An effective way to break this loop is to thermally modify the encapsulating material in order to accelerate the dissipation of heat.

A commonly used method to improve thermal conductivity of polymer materials is introducing highly thermally conductive fillers [5] including metal material (Ag [6], Cu [7], etc), carbon-based materials (CNT [8], GNP [9], etc) or ceramic materials (BN [10], AlN [11], etc) into the polymer matrix. Among them, metal materials and carbon materials have high thermal conductivity, but they are forbidden from packaging materials due to their conductivity. Therefore, ceramic modified polymer materials have attracted the attention of researchers and become a research hotspot. The thermal conductivity of hexagonal boron nitride (h-BN) is 33 W · m⁻¹ · K⁻¹, while nanometer BN is theoretical of 300 W · m⁻¹ · K⁻¹, in addition with electrical insulation and similar thermal expansion coefficient to silicon makes it the most promising thermally conductive filler for encapsulating materials. In most cases, an extremely high loading, normally 50 vol% or even higher, is needed to satisfy percolation thresholds and to obtain a high thermal conductivity to form continuous thermally conductive network in the matrix [12–14]. For the thermally conductive polymer composites, the construction of effective thermally conductive pathways can affect the enhancement in thermal conductivity, which is mainly related to filler contents, filler dispersion state and filler geometric parameters [15]. Previous
studies revealed that hybrid thermally conductive fillers can perfect the formation of thermally conductive pathways in the matrix, resulting in higher thermal conductivity [16].

Ren et al fabricated cyanate ester nanocomposites with high thermal conductivity (4.13 W · m⁻¹ · K⁻¹) with addition of 5 wt% graphene nanosheets (GNSs) and 15 wt% magnetic carbonyl iron-nickel alloy powder (CINAP). The synergistic enhancement is significantly affected by the formation of efficient thermally conductive pathways [17].

Thermally conductive mechanism of polymeric composites reveals that thermally conductive percolation behavior plays a major role in the improvement of λ value. Agari [18] reported that for given filler loading, the corresponding λ value of polymeric composites ranked as followings: ‘Melted blending’ < ‘Twin-rolling blending’ < ‘Powdering blending’. In addition, those molded through powdering mixing cooperating with hot-compression could obtain segregated structure [19], which reduced the conductive percolation threshold by forcing fillers distributing on the interface of matrix particles.

Wang et al [20] mechanically wrapped BN and AlN upon ultrahigh-molecular-weight polyethylene (UHMWPE) granules followed with high-pressure consolidation. At the total filler content of 50 wt%, the BN/AlN/UHMWPE composite with a filler ratio of 6:1 showed the thermal conductivity of 7.1 W · m⁻¹ · K⁻¹, outperforming BN/UHMWPE and AlN/UHMWPE composites by 35.1% and 61.3%, respectively.

Gu et al [21] employed BN with different diameter to fabricate thermally conductive insulating polyphenylene sulfide composites via mechanical ball-milling followed by hot-compression method. The thermal conductivity value was improved from 0.286 W · m⁻¹ · K⁻¹ for pristine PPS matrix to 2.638 W · m⁻¹ · K⁻¹ for the BN/PPS composite with 60 wt% hybrid fillers.

Since most of thermostet resin intermediate is liquid at room temperature, forming segregated structure via powdering blending has seldom been discussed. Therefore, BOZ, intermediate of thermostet resin, which is amber solid at room temperature and melts around 100 °C, is a proper candidate for such study.

Benzoxazine [22] (BOZ) is an intermediate containing a heterocyclic structure which undergoes ring-opening polymerization with heating and/or a catalyst and forms a network of nitrogen-containing and phenolic resin-like network., namely Polybenzoxazine (PBz) [23], a new type of phenolic resin [24]. Since the curing process of BOZ requires no curing agents and releases no small-molecule along with zero volume shrinkage [25], PBz has become an emerging electronic packaging material.

In this study, mBN and nBN are used as hybrid thermally conductive fillers. The different mass ratio between them were employed and the synergistic effect was observed at the ratio of 1:1. mBN/nBN/PBz composites were then fabricated via ball-milling followed by a hot-compression method. The results showed that (m/n)BN hybrid fillers formed more complete thermally conductive networks than mBN did.

2. Methods

2.1. Main materials

Benzoxazine (BOZ), AIBZ682, 1.20 g cm⁻³, was supplied by Shanghai Ruiyi Chemical Technology Co., Ltd; Micrometer boron nitride (mBN, mean diameter of 50 μm, 2.25 g cm⁻³) was purchased from Zibo Jingyi Ceramic Technology Co., Ltd; nanometer boron nitride (nBN, mean diameter of 50 nm) was received from Shanghai Aladdin Biochemical Technology Co., Ltd.

2.2. Preparation of mBN/nBN/PBz composites

mBN and nBN were firstly dried in oven at 120 °C for 12 h. And the mBN/nBN/PBz composites were prepared according to the following procedures: (a) Blending BOZ particles and mBN/nBN hybrid fillers with ball-milling machine for 6h at room temperature; (b) Hot-compression moulding (140 °C/1 h + 160 °C/1 h + 180 °C/1 h + 200 °C/1 h) with the pressure of 12 MPa to fabricate thermally conductive mBN/nBN/PBz composites.

2.3. Analysis and characterization

Thermally conductive coefficient (λ) of the samples were measured with thermal conductivity instrument TC3000E (Xi’an Xianxi Electronic Technology Co., Ltd, China), the corresponding dimension of specimen was 60 mm × 40 mm × 2 mm.

The dielectric constant (ε) and dielectric loss factor (tanδ) values of composites were measured on a broadband dielectric spectrometer (Novocontrol Technology Company, Germany). The testing frequency range is from 10–1 to 107 Hz. Samples were cylindrical shaped of 21.0 mm in diameter and 1 mm in thickness. The volume resistivity (R) was measured with high resistivity meter model LK2679A at 250V, the corresponding dimension of specimen was 80 mm × 80 mm × 1 mm; Differential scanning calorimetry (DSC)
analyses of the samples were carried out at 10 °C min\(^{-1}\) (nitrogen atmosphere), over the whole range of temperature (25 °C–300 °C) by Pyri 1 (PerkinElmer, Inc., USA);

Thermogravimetric analysis (TGA) of the samples were carried out by WRT-2P (Shanghai Shangping Instrument Co., Ltd, China) at 10 °C min\(^{-1}\) (nitrogen atmosphere), over the range of temperature (50 °C–750 °C).

Transmission electron microscopy (TEM) was employed to observe morphology of nBN with JEM-1400 (Hitachi, Ltd, Japan).

Morphology of the hybrid filler particles and fabricated composites were characterized by scanning electron microscope (SEM, S-3400, Hitachi Ltd, Japan). Specimens were fractured in liquid nitrogen and coated with a thin layer of gold before observation.

X-ray diffraction (XRD) measurements were carried out at x-ray Diffractometer (D8 Advance, Bruker Co., USA) with Cu-K\(\alpha\) radiation (40 kV, 40 mA, \(\lambda = 0.154\) nm, 5°–80°).

3. Discussion

3.1. Synergistic effect between mBN/nBN on thermal conductivity of mBN/nBN/PBz composites

Mass ratio of mBN to nBN affecting on the \(\lambda\) values of PBz composites was shown in figure 1. To fully figure out the relationship between them, filler loading over and below the percolation threshold were both investigated. It can be observed that with different filler loading, mBN and nBN showed different abilities in enhancing \(\lambda\) values of PBz composites. At 10 wt% filler loading, nBN/PBz composites displayed higher \(\lambda\) values (0.4414 W m\(^{-1}\) K\(^{-1}\)) than that of mBN/PBz (0.3504 W m\(^{-1}\) K\(^{-1}\)). The reason was probably attributed that nBN attached closely to the matrix particles because of the static electricity generated while blending and the segregated structure can be formed in a more even way than mBN did. However, when 25 wt% filler were loaded, the \(\lambda\) value of mBN/PBz composites reached 0.7620 W m\(^{-1}\) K\(^{-1}\) while that of nBN/PBz composites was only 0.6667 W m\(^{-1}\) K\(^{-1}\). The reason was attributed that, serious agglomeration of nBN hindered the formation of thermal conductive network and the poor affinity between nBN and PBz matrix resulted in serious phonon scattering between the nBN-PBz interfaces. While 10 wt% mBN/nBN hybrid fillers were employed, the \(\lambda\) values of mBN/nBN/PBz composites ranked between that of mBN/PBz and nBN/PBz composites in most cases. However, when filler loading reached 25 wt%, mBN/nBN hybrid fillers exhibited better abilities in improving \(\lambda\) values of PBz composites compared to that of single mBN or nBN. The main reason was that when the filler loading was not enough to form complete thermal conductive network, the synergistic effect between mBN/nBN hybrid fillers can only be observed at certain mass ratio. With increasing filler loading, the hybrid fillers started to contact with each other and form complete thermal conductive network. In this case, nBN fill the interstitial space of the mBN so that the packing density of the fillers can be increased, resulting in the enhancement in thermal conductivity. It can be observed that when the mass ratio of mBN to nBN was 1:1, the \(\lambda\)
value of the PBz composites achieved 0.4763 W m⁻¹ K⁻¹ and 0.9196 W m⁻¹ K⁻¹ respectively, at 10 wt% and 25 wt% filler loading, which was higher than that of PBz composites filled with other mBN/nBN hybrid fillers. The reason was attributed that when nBN was less than mBN, gaps between mBN-mBN and mBN-BOZ could not be filled and the obtained thermally conductive network was not complete enough. With the increase of nBN, more gaps were filled and the thermally conductive network was formed completely. Therefore, mBN/nBN hybrid fillers composed with equal amount of nBN and mBN, labeled as (n/m)BN, were used for following studies.

3.2. Thermal conductivities of (n/m)BN/PBz composites

Figure 2 presented the effects of fillers contents on the \( \lambda \) values of mBN/PBz composites, nBN/PBz composites and (n/m)BN/PBz composites. A nonlinear increase in \( \lambda \) value of PBz composites was observed with the increasing addition of mBN, nBN and (n/m)BN hybrid fillers. The corresponding \( \lambda \) value of mBN/PBz composites nBN/PBz composites and (n/m)BN/PBz composites was improved from 0.2277 W m⁻¹ K⁻¹ to 0.7620 W m⁻¹ K⁻¹, 0.6667 W m⁻¹ K⁻¹ and 0.9196 W m⁻¹ K⁻¹, respectively, with 25 wt% fillers. The enhancement reached 235%, 193% and 304%.

When the filler loading was less than 20 wt% (thermally conductive percolation threshold [26]), the \( \lambda \) values of mBN/PBz and (n/m)BN/PBz composites increased slightly while they exhibited rapid improvements with higher filler loading. The main reason of this phenomenon was that fillers were less likely to contact or overlap each other at lower filling loading, resulting in the failure to constructing thermally conductive networks. Therefore, \( \lambda \) values of composites increased slightly. With further addition of fillers, PBz particle were mostly covered with fillers, which could form effective thermally conductive networks after curing, leading to the dramatically increase in \( \lambda \) values. However, in nBN/PBz composites, the \( \lambda \) values didn’t show the same pattern. It can be observed that the enhancement in \( \lambda \) values decreased with the increasing filler loading, resulted by the agglomeration of nanoparticles. With increasing loading of nBN, the agglomeration became more serious, which hindered the construction of thermal conductive paths. In the meanwhile, the interfaces between the agglomerations would also cause phonon scattering.

In addition, a pronounced increase in the thermal conductivity for the PBz composites loaded with hybrid fillers compared to the counterparts loaded with either nBN or mBN, It is speculated that the interfacial thermal resistance between mBN flakes is reduced by the insertion of nBN, which is profitable to perfect the conductive paths.

3.3. Effect of (n/m)BN hybrid fillers on dielectric properties (n/m)BN/PBz composites

Figure 3 presented the \( \varepsilon \) and tan\( \delta \) values of the (n/m)BN/PBz composites at different testing frequency with different filler loading. It can be observed that \( \varepsilon \) values increased gradually with the increase of filler loading
while the tanδ values decreased with the addition of BN. For a given filler loading, the ε values decreased slightly with the increase in frequency. In the meanwhile, the tanδ values first increased and then decreased.

The interfacial polarization between (n/m)BN hybrid filler and PBz matrix could be produced with the addition of BN, which resulted to the increase in ε values. Moreover, with increasing testing frequency, the dipole functional groups of the PBz matrix could hardly keep up with the change of testing frequency, leading to the decrease in ε values with increasing testing frequency.

The dielectric loss of the (n/m)BN/PBz composites was mainly resulted from intrinsic loss and interfacial loss from interfacial polarization. With the addition of BN, the charge accumulation was dampened, resulting in the decreased tanδ values. However, the tanδ values of the (n/m)BN/PBz composites showed little dependence on the filler loading of (n/m)BN hybrid filler. Moreover, the loss peak indicated the existence of relaxation polarization, resulting in the maximum tanδ value neat 10^5 Hz.

3.4. Effect of (n/m)BN hybrid fillers on curing behavior of BOZ
The volume resistivity reflecting the electrical insulation of the PBz composites is presented in figure 4. It can be observed that volume resistivity of the pristine PBz was 2.8E15 Ω, which is electrically insulating. With further
addition of \((n/m)\)BN hybrid filler, the volume resistivity of \((n/m)\)BN/PBz composites increased gradually due to the insulating property of BN itself.

3.5. Effect of \((n/m)\)BN hybrid fillers on curing behavior of BOZ

DSC was used to study the curing behavior of \((n/m)\)BN/BOZ blends (Figure 5 and Table 1). The reaction heat of samples decreased with the increase of \((n/m)\)BN hybrid fillers. The onset of polymerization exotherm \((T_0)\), the peak temperature \((T_p)\) both increased sharply with the introduction of hybrid fillers while \(T_0\) and \(T_p\) grew slightly with the increase of filler loading.

In the curing process, oxazine ring-opening polymerization occurred after being heated, the formed intermediate was supposed to catalyze oxazine ring-opening polymerization [27]. However, due to the polarity of BN, the intermediate was captured by the fillers, which hindered the curing process [28]. Therefore, \(T_0\) and \(T_p\) grew dramatically when \((n/m)\)BN hybrid fillers were added into the matrix. With higher filler loading, nBN

Figure 4. Volume resistivity of \((n/m)\)BN/PBz composites.

Figure 5. DSC curves of \((n/m)\)BN/BOZ blends.
caused the increasing viscosity of surrounding matrix and restrained the movement of molecular chains, resulting in the slight increment of $T_0$ and $T_p$. In the meanwhile, with the addition of fillers, the flake-like BN segregate the attachment of BOZ particles leading to the reduction of crosslink density, which could explain the decrease of reaction heat. Curing process of BOZ is shown in figure 6.

### 3.6. Effect of ($n$/m)BN hybrid fillers on thermal stability of ($n$/m)BN/PBz composites

Figure 7 presented the TGA curves of the pristine PBz matrix and ($n$/m)BN/PBz composites, and the corresponding characteristic thermal data were listed in table 2. It can be observed that with the introduction of hybrid fillers, the $T_{\text{Heat resistance index}}$ ($T_{\text{HR}}$) decreased dramatically. However, with further addition of hybrid fillers,
fillers, the $T_{\text{heat resistance index}}$ increased gradually and finally reached $216.45 \, ^{\circ}C$ (25 wt%), higher than that of pristine PBz matrix ($213.04 \, ^{\circ}C$).

This phenomenon could be attributed that the addition of hybrid fillers reduced crosslink density of matrix, undermining the thermal stability of composites, which confirmed to the conclusion to DSC data. With further addition of hybrid fillers, higher specific heat capacity and $\lambda$ value of hybrid fillers compared to that of PBz matrix enabled fillers to absorb heat, resulting in PBz molecular chains degraded at higher temperatures [29, 30].

### 3.7. Morphology of the (n/m)BN/BOZ blends and the (n/m)BN hybrid filler network

To fully understand how (n/m)BN hybrid filler attributed to the formation of thermally conductive network, TEM was adopted to observe the morphology of nBN and SEM was used to characterize the (n/m)BN/BOZ blends and corresponding composites. Figure 8(a) is the TEM image of pristine nBN. Figure 8(b) is the SEM image of 10 wt%(n/m)BN/BOZ blends. It can be observed that BOZ particles were wrapped with fillers and most of them were nBN. The main reason is that with continuous friction during blending, static electricity was generated which enables the nBN to be absorbed to the BOZ particles.

SEM morphologies of fractures for 10 wt%(n/m)BN/PBz composites were shown in figure 9. In figure 9(a), segregated structure formed with hybrid fillers can be observed. The smooth parts were PBz matrix and the surrounding fillers contacted and overlapped with each other, forming effective thermally conductive network. In figure 9(b), it can be observed that PBz matrix was surrounded by mBN and nBN dispersed in the interspace between them, which matched with the SEM image of 10 wt%(n/m)BN/BOZ blends.

### 3.8. Characterization of the composite with hybrid fillers in alignment

As 2D filler, BN showed anisotropy in thermal conductivity property. The out-of-plane and in-plane [31] $\lambda$ values are $33 \, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $200 \, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively. Under the assistance of gravitational force, pressure during hot-compression and interactivity between the fillers, the fillers would stack alignment along the horizontal direction. In this case, the obtained composites would show great difference in thermal conductivity in different directions.

---

Table 2. Characteristic thermal data of the pristine PBz matrix and (n/m)BN/PBz composites from TGA curves.

| Sample name | $T_5$ (°C) | $T_{30}$ (°C) | Heat-resistance index (°C) |
|-------------|------------|---------------|---------------------------|
| PBZ         | 397.67     | 459.50        | 213.04                    |
| 5 wt%(n/m)BN/PBZ | 365.39     | 456.05        | 205.70                    |
| 10 wt%(n/m)BN/PBZ | 367.44     | 462.28        | 207.93                    |
| 15 wt%(n/m)BN/PBZ | 373.44     | 467.59        | 212.84                    |
| 20 wt%(n/m)BN/PBZ | 374.53     | 474.27        | 216.45                    |
| 25 wt%(n/m)BN/PBZ | 378.61     | 483.80        |                           |

$T_{\text{heat resistance index}} = 0.49 \times [T_5 + 0.6 \times (T_{30} - T_5)]$.

$T_5$ and $T_{30}$ is corresponding decomposition temperature of 5 wt% and 30 wt% weight loss, respectively.

---

Figure 8. Morphology of the (n/m)BN/BOZ blends: (a) TEM image of pristine nBN; (b) SEM image of 10 wt%(n/m)BN/BOZ blends.
To investigate the effect of \((n/m)\) BN hybrid fillers on alignment in the matrix, the value of orientation function \((f)\), which can be calculated by equation (1) \[32\], was used to estimate the degree of horizontal (or in-plane) orientation degree.

\[
f = \frac{1 - K}{1 + 2K}
\]

\[
K = k \cdot I_{(002)} / I_{(100)}
\]

where, \(k\) is the normalization coefficient determined to be 6.25 by the ratio intensity of \((002)\) and \((100)\) peak. The XRD patterns of \((n/m)\)BN/PBz composites and mBN/PBz composites are shown in figure 10. The horizontally and vertically oriented h-BN are responsible for the \((002)\) and \((100)\) peaks, respectively. The value of \(f\) describes the degree of the orientation of h-BN platelets in the composite. Complete orientation of h-BN platelets along in-plane direction in the composite has \(f = -0.5\). The obtained \(f\) values were shown in figure 11. As we can see in figure 11, with the increasing addition of fillers, the value of \(f\) became closer to \(-0.5\), indicating a high degree of in-plane orientation of the filler due to the much more mutual contact between the fillers. In the meanwhile, when the filler loading was lower than percolation threshold, the \(f\) value of mBN/PBz composites was much closer to \(-0.5\) than that of \((n/m)\)BN/PBz composites. However, the \(f\) values of both composites reached the same point when the filler loading is 25 wt%. The reason was that in the hot pressing process, the mBN flakes wrapped on the BOZ particles were compressed into localizing in the direction vertical to the pressing force. In the meanwhile, since the nBN particles were much smaller than the BOZ particles, they can still distribute on the edge of BOZ particles and the pressure had little effect on the distribution of them. Moreover, due to the tiny dimension of nBN, the interact between nBN and mBN was not strong enough to affect alignment of mBN at lower filler loading. With further addition of hybrid fillers, large amount of mBN formed mutual contact with each other and nBN was forced to stack between mBN during this process.

3.9. Mechanism study of synergistic effect of \((n/m)\)BN hybrid fillers on thermal conductivity of composites

To fully understand the role \((n/m)\)BN hybrid fillers played in the construction of thermally conductive network, experimental \(\lambda\) values were fitted into Agari semi-experimial model. The logarithmic equation of Agari was given in equation (3) \[18\]:

![Figure 9. SEM morphologies of fractures for 15 wt%(n/m)BN/PBz composites on different scales (a) × 150 (b) × 500.](image-url)
\[ \log \lambda = V_f \cdot C_2 \cdot \log \lambda_2 + (1 - V_f) \cdot \log (C_1 \cdot \lambda_1) \] (3)

where \( C_1 \) represents the effect of thermally conductive particles on the polymer structure; \( C_2 \) stands for the ability of thermally conductive fillers to form continuous channels, the larger in value represents easier formation of thermally conductive network; \( \lambda, \lambda_1, \lambda_2 \) represents thermally conductivity coefficient of composites, matrix and fillers respectively; \( V_f \) stands for the volume fraction of fillers.

The Agari model fitting curves of \( \lambda \) values for mBN/PBz composites, nBN/PBz composites and \((n/m)BN/PBz\) composites were given in figure 12. The fitted results and corresponding value of \( C_1 \) and \( C_2 \) were listed in table 3. It could be seen that the value of \( C_2 \) of \((n/m)BN/PBz\) composites was 0.9643 while that of mBN/PBz composites and nBN/PBz composites was 0.9755 and 0.7066, respectively, revealing that \((n/m)BN\) hybrid filler showed similar efficient in forming thermally conductive pathways comparing with mBN though nBN itself was not favorable to forming thermally conductive pathways. This improvement could be ascribed to the fact that when mBN was blended with BOZ particles, small voids would be formed between mBN and matrix which were too small for mBN to fill in. The cooperation of nBN would fill into those voids and form complete thermally conductive network. In the meanwhile, nBN itself tends to agglomerate and the introduction of mBN flakes can connect the agglomerations to form thermally conductive pathways. This process is schematically depicted in figure 13.
In the meanwhile, it can be observed that the value of $C_1$ of $\left(\frac{n}{m}\right)$BN/PBz and nBN/PBz composites was 1.4070 and 1.3954, respectively, much higher than that of mBN/PBz composites, 0.9944. This indicated that the introduction of nBN had much effect on polymer structure, including crosslink density and crystallinity, than mBN did. Therefore, the synergistic effect on improving thermal conductivity exhibited by $\left(\frac{n}{m}\right)$BN hybrid.

![Figure 11. Orientation function (f) of the composites.](image1)

![Figure 12. Fitting curves of $\lambda$ values for mBN/PBz composites, nBN/PBz composites and $\left(\frac{n}{m}\right)$BN/PBz composites.](image2)

|        | Intercept  | Slope    | $C_1$  | $C_2$ |
|--------|------------|----------|--------|--------|
| mBN/PBz | -0.70804   | 3.12449  | 0.9944 | 0.9755 |
| nBN/PBz | -0.49795   | 2.24818  | 1.3954 | 0.7066 |
| (n/m)BN/PBz | -0.49127   | 2.87984  | 1.4070 | 0.9643 |

In the meanwhile, it can be observed that the the value of $C_1$ of $(n/m)$BN/PBz and nBN/PBz composites was 1.4070 and 1.3954, respectively, much higher than that of mBN/PBz composites, 0.9944. This indicated that the introduction of nBN had much effect on polymer structure, including crosslink density and crystallinity, than mBN did. Therefore, the synergistic effect on improving thermal conductivity exhibited by $(n/m)$BN hybrid...
filler resulted from the combination of efficient construction of thermally conductive pathways and effect on polymer structure.

4. Conclusion

(n/m)BN hybrid filler composing of equal proportion of nBN and mBN exhibited synergistic effect on improving thermal conductivity of PBz composites. With 25 wt% of (n/m)BN hybrid filler, λ values of the composite material increases from 0.2276 W · m⁻¹ · K⁻¹ to 0.9196 W · m⁻¹ · K⁻¹, the rate of enhancement reached 304%. The existence of BN filler hindered the curing process of BOZ and lowered crosslink density of the matrix, which resulted in the reduction of thermal stability of composites. However, with further addition of hybrid filler, the thermal stability of the composite was improved gradually. With lower filler loading, (n/m)BN hybrid filler was less likely to form orientation than mBN while there was no difference at higher filler loading.

Acknowledgments

The joint research project was funded by the Chinese German Centre for the Promotion of Science via the NSFC and DFG (No. GZ1448).

ORCID iDs

Wei Wu @ https://orcid.org/0000-0002-5381-6201

References

[1] Huang X, Jiang P and Tanaka T 2011 A review of dielectric polymer composites with high thermal conductivity IEEE Electr. Insul. Mag. 27 8–16
[2] Zeng M, Wang J, Li R, Liu J, Chen W, Xu Q and Gu Y 2013 The curing behavior and thermal property of graphene oxide/benzoxazine nanocomposites Polymer 54 3107–16
[3] Yang X, Liang C, Ma T, Guo Y, Kong J, Gu J, Chen M and Zhu J 2018 A review on thermally conductive polymeric composites: classification, measurement, model and equations, mechanism and fabrication methods Adv. Compos. Hybrid Mater. 1 207–30
[4] Zhou C, Lin J, Lu X and Xin Z 2016 Enhanced corrosion resistance of polybenzoxazine coatings by epoxy incorporation RSC Adv. 6 28428–34
[5] Tanimoto M, Yamagata T, Miyata K and Ando S 2013 Anisotropic thermal diffusivity of hexagonal boron nitride-filled polyimide films: effects of filler particle size, aggregation, orientation, and polymer chain rigidity ACS Appl. Mater. Interfaces 5 4374–82
[6] Luo J, Cheng Z, Li C, Wang L, Yu C, Zhao Y, Chen M, Li Q and Yao Y 2016 Electrically conductive adhesives based on thermoplastic polyurethane filled with silver flakes and carbon nanotubes Compos. Sci. Technol. 129 191–7
[7] Zare Y and Shabani I 2016 Polymer/metal nanocomposites for biomedical applications Mater. Sci. Eng. C60 195–203
[8] Ahmed S and Masud A K M 2014 Evaluation of effective thermal conductivity of multilayered carbon nanotube reinforced polymer composites using finite element method and continuum model Procedia Eng. 90 129–35
[9] Gu J, Yang X, Lv Z, Li N, Liang C and Zhang Q 2016 Functionalized graphite nanoplatelets/epoxy resin nanocomposites with high thermal conductivity Int. J. Heat Mass Transf. 92 15–22
[10] Kelly A G et al 2017 All-printed thin-film transistors from networks of liquid-exfoliated nanosheets Science 356 69–73
[11] Bai Y, Cheng Z-Y, Bhardwaj V, Xu H S and Zhang Q M 2000 High-dielectric-constant ceramic-polymer composite applications Appl. Phys. Lett. 76 3834–6
[12] Wang G, Wang L, Mark I H, Shaheeg V, Wang G, Li H, Zhao G and Park C B 2018 Ultralow-threshold and lightweight biodegradable porous PLA/MWCNT with segregated conductive networks for high-performance thermal insulation and electromagnetic interference shielding applications ACS Appl. Mater. Interfaces 10 1193–203
[13] Zhu N, Yuan L, Liang G and Gu A 2019 Mechanism of greatly increasing dielectric constant at lower percolation thresholds for epoxy resin composites through building three-dimensional framework from polyvinylidene fluoride and carbon nanotubes Compos. Part B-Eng. 171 146–53
[14] Im H and Kim I 2012 Thermal conductivity of a graphene oxide–carbon nanotube hybrid/epoxy composite Carbon 50 5429–40
[15] Xue Y, Li X, Wang H, Zhang D and Chen Y 2019 Thermal conductivity improvement in electrically insulating silicone rubber composites by the construction of hybrid three-dimensional filler networks with boron nitride and carbon nanotubes J. Appl. Polym. Sci. 136 46929
[16] Ren F-G, Hou S-Y, Ren F, Zhang Z-P, Sun Z-F and Xu L 2016 The influence of compression moulding techniques on thermal conductivity of UHMWPE/BN and UHMWPE/(BN + MWCNT) hybrid composites with segregated structure Compos. Part A-App. Sci. Manuf. 90 13–21
[17] Ren F, Song D, Li Z, Jia L, Zhao Y, Yan D and Ren P 2018 Synergistic effect of graphene nanosheets and carbonyl iron–nickel alloy hybrid filler on electromagnetic interference shielding and thermal conductivity of cyanoate ester composites J. Mater. Chem. C 6 1476–86
[18] Agari Y, Ueda A and Nagai S 1991 Thermal conductivities of composites in several types of dispersion systems J. Appl. Polym. Sci. 42 1665–9
[19] Zhai W, Zhao S, Wang Y, Zheng G, Dai K, Liu C and Shen C 2018 Segregated conductive polymer composite with synergistically electrical and mechanical properties Compos. Part A-App. Sci. Manuf. 105 68–77
[20] Wang Z-G, Gong F, Yu W-C, Huang Y-F, Zhu I, Lei J, Xu J-Z and Li Z-M 2018 Synergetic enhancement of thermal conductivity by constructing hybrid conductive network in the segregated polymer composites Compos. Sci. Technol. 162 7–13
[21] Gu J, Guo Y, Yang X, Liang C, Geng W, Tang L, Li N and Zhang Q 2017 Synergistic improvement of thermal conductivities of polyethylene sulfide composites filled with boron nitride hybrid fillers Compos. Part A-App. Sci. Manuf. 95 267–73
[22] Ishida H and Rimduitis S 1998 Very high thermal conductivity obtained by boron nitride-filled polybenzoxazine Thermochim. Acta 320 177–86
[23] Wang X, Wang J, Liu C and Jian X 2017 An investigation of the relationship between the performance of polybenzoxazine and backbone structure of hyperbranched epoxy modifiers Polym. Int. 67 100–10
[24] Wang X, Zong L, Han J, Wang J, Liu C and Jian X 2017 Toughening and reinforcing of benzoxazine resins using a new hyperbranched polyether epoxy as a non-phase-separation modifier Polym. 121 217–27
[25] Nazeran N and Moghadasan J 2017 Synthesis and characterization of silica aerogel reinforced rigid polyurethane foam for thermal insulation application J. Non-Cryst. Solids 461 1–11
[26] Chen H, Ginzburb V V, Yang J, Yang Y, Liu W, Huang Y, Du L and Chen B 2016 Thermal conductivity of polymer-based composites: fundamentals and applications Prog. Polym. Sci. 59 41–85
[27] Kim H S, Kim J H, Kim W Y, Lee H S, Kim S Y and Khil M S 2017 Volume control of expanded graphite based on inductively coupled plasma and enhanced thermal conductivity of epoxy composite by formation of the filler network Carbon 119 40–6
[28] Agag T 2000 Polybenzoxazine–montmorillonite hybrid nanocomposites: synthesis and characterization Polymer 41 7083–90
[29] Chen Q, Xu R and Yu D 2006 Multiwalled carbon nanotube/polybenzoxazine nanocomposites: Preparation, characterization and properties Polymer 47 7711–9
[30] Cui Y, Chen Y, Wang X, Tian G and Tang X 2003 Synthesis and characterization of polyurethane/polybenzoxazine-based interpenetrating polymer networks (IPNs) Polym. Int. 52 1246–8
[31] Yu C, Zhang J, Li Z, Tian W, Wang L, Luo J, Li Q, Fan X and Yao Y 2017 Enhanced through-plane thermal conductivity of boron nitride/epoxy composites Compos. Part A-App. Sci. Manuf. 98 25–31
[32] Su Z, Wang H, Ye X, Tian K, Huang W, He J, Guo Y and Tian X 2018 Anisotropic thermally conductive flexible polymer composites filled with hexagonal boron nitride (h-BN) platelets and amine carbon nanotubes (CNT-NH2): effects of the filler distribution and orientation Compos. PART-Appl. Sci. Manuf. 109 402–12