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Enhanced thermal conductivity for traditional epoxy packaging composites by constructing hybrid conductive network

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Abstract

A cost-efficient and practical strategy was developed for preparing high thermal conductive epoxy packaging composites. The effective conductive network was constructed by the bridging effect between boron nitride (BN) and spherical silica (SiO2). Compared to the epoxy (EP) composites with randomly dispersed BN and SiO2, the EP/SiO2@BN showed a great enhancement in thermal conduction. The thermal conductivity of EP/SiO2@BN reached to 0.86 W m⁻¹ K⁻¹ with 60 wt% content of hybrid filler, which was 91% higher than that of EP/SiO2 samples and was around 12% higher than that of epoxy composites with unmodified BN and SiO2. In addition, the EP/SiO2@BN exhibited lower thermal interface resistance in comparison with EP/SiO2&BN composites according to the effective medium theory (EMT). The encapsulation of BN on the surface of SiO2 greatly enhanced the thermal transfer efficiency of the epoxy matrix and showed great potential in the epoxy packaging practical application.

1. Introduction

The rapid development of electronic technology and the emergence of emerging industries have put higher requirement on the thermal performance of the traditional packaging materials [1–4]. Most polymers have the advantages of good processability, low cost and excellent insulation, etc, but the lower thermal conductivity of polymers (around 0.1–0.3 W m⁻¹ K⁻¹) limits the application in the field of thermally conductive packaging [5–7]. In order to ensure the great stability and lifetime in practical application of materials, thermally conductive fillers are widely used to improve the thermal conductivity of the composites [8–12]. In this case, to obtain the high thermal conductivity of composites, the increase of filler content will lead to a decrease in the mechanical and processing performance of materials [13]. In order to solve the above problem, one method is to enhance the interaction between the filler and the polymer through modification of fillers [14, 15]. However, the high thermal interface resistance between randomly distributed fillers limits the further improvement of thermal conductivity of composites. Other approaches are to construct the efficient thermally conductive filler structure in the composites by using special processing methods, such as segregated structure [16, 17], thermal template [18–20] and single or double continuous structure [21, 22], etc. Nevertheless, the complicated processes of these methods are not conducive to the applications in large-scale fabrication. The more attention should be paid on the other approaches to achieve the high thermal conductivity of packaging materials.

The addition of hybrid fillers is considered as a cost-efficient and practical strategy to achieve the high conductivity of materials by the bridging effect between the fillers [23–26]. For example, Owais et al reported that the addition of short carbon fibers and hybrid fillers of graphene nanoplatelets (GNPs) and boron nitride (BN) can significantly enhance the thermal conductivity and stability of epoxy resin and also simultaneously maintain the high electrical resistivity of the composites [27]. Gu et al found that the size of hybrid fillers showed a great influence on the thermal conductivity of the polyphenylene (PPS) composites [28]. However, the randomly distributed fillers inside the composites still limit the construction of the continues thermal...
The BN and SiO2 power were dried at 80 °C for 12 h before the surface modification. After that, the BN powder was calcined in a muffle furnace at 1000 °C for 2 h to obtain hydroxylated boron nitride (BNO). The BNO and KH-560 (BNO : KH-560 = 20 : 1, wt/wt) were mixed in ethanol/water solution (50 : 50, wt/wt) and stirred at 70 °C for 6 h. The mixture was centrifugally washed with ethanol for 3–4 times to remove residual siloxane moieties. Finally, the product was dried at 80 °C for 24 h to obtain modified BN (f-BN).

The SiO2 powder and APS (SiO2 : APS = 15 : 1, wt/wt) were added into ethanol/water solution (98 : 2, vol/vol) and stirred at 60 °C for 10 h. After centrifugally washed for several times, the powder was dried at 80 °C for 24 h. Finally, the APS grafting SiO2 was obtained and named m-SiO2.

A certain proportion of m-SiO2 and f-BN powder (5 : 1, 6 : 1, 7 : 1, 8 : 1, 9 : 1, wt/wt) was added into the THF solution and stirred at 60 °C for 4 h. Then the THF solution was removed by suction filtration. After the mixture dried at 80 °C for 24 h, the SiO2 coated with BN was obtained and named SiO2@BN. The hybrid filler without any modification was called SiO2&B.

The epoxy monomer and MTHPA (10 : 8, wt/wt) were stirred at 100 °C for 10 min, and 0.1 wt% of 2-ethyl-4-methylimidazole was added as a curing accelerator. Then the 60 wt% content of SiO2@BN fillers with different proportions were added into the mixture and stirred at 100 °C for 30 min. Finally, the blends were poured into cast and cured at 145 °C for 4 h. The epoxy composites filled by the SiO2@BN fillers were called EP/SiO2@BN. The epoxy composites filled with SiO2&B fillers were named EP/SiO2&B, and the EP/SiO2 composites with 60wt% content of SiO2 were prepared as contrast samples.

The SEM images of the power and composites was observed using a scanning electron microscope (SEM, Jeol JSM-6510, Japan). Fourier transform infrared (FTIR) spectroscopy was tested by IS 5 equipment (Thermo scientific). Thermal gravimetric (TG) measurement was obtained by TG 550 (TA Instrument-water LLC). The thermal conductivity of composites were tested using Hot Disk Thermal Analyzer (TPS 2500) at room temperature, and the corresponding dimension of the sample was 30 mm × 30 mm × 8 mm. Thermal images of the samples were taken by an infrared thermograph (FOTRIC 220).

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR) of fillers
In order to verify the modification effect of the fillers, the FTIR spectra of samples are shown in figure 1. For spectra of BN, BNO and f-BN in figure 1(a), the peaks at 1384 cm⁻¹ and 796 cm⁻¹ corresponded to the
stretching and bending vibration absorption of B-N band, respectively [29]. Besides, the new absorption peak in BNO spectra appeared at around 3223 cm\(^{-1}\) was assigned to the stretching vibration of B-OH. In the FTIR spectra of f-BN, the peak at 986 cm\(^{-1}\) was related to the Si-O vibration, which indicated the presence of KH-560 on the surface of BN [30]. In figure 1(b), the SiO\(_2\), m-SiO\(_2\) and SiO\(_2@BN\) showed strong peaks at around 1050 cm\(^{-1}\) and 803 cm\(^{-1}\), corresponding to the characteristic peak of SiO\(_2\). For m-SiO\(_2\), the peaks appeared at 1634 cm\(^{-1}\) and 1381 cm\(^{-1}\) corresponded to the N-H bending vibration and C-N stretching vibration, which demonstrated that the APS has been connected on the surface of SiO\(_2\) [31]. In the FTIR spectra of SiO\(_2@BN\), the peak of B-N band (1385 cm\(^{-1}\)) appeared and the peak of N-H almost disappeared, which was mainly attributed to the reactivity between f-BN and m-SiO\(_2\). These results indicated that the f-BN has been successfully grafted on the surface of m-SiO\(_2\).

3.2. Thermal gravimetric (TG) analyses of fillers

The thermal gravimetric curve of fillers is shown in figure 2. As the temperature increased, the weight of unmodified BN slightly decreased, which may be due to the presence of a small amount of water or other easily decomposed impurities on the surface of BN. The weight loss rate of SiO\(_2@BN\) and f-BN above 300 °C was more significant, which may be due to the decomposition of KH-560 and APS molecules at relatively higher temperatures. In addition, the weight loss rate of f-BN and SiO\(_2@BN\) at 700 °C was 0.48 wt% and 0.51 wt%, respectively, which was slightly higher than that of unmodified BN. Furthermore, compared with f-BN, the weight loss rate of SiO\(_2@BN\) was slightly higher. The TG analyses above indicated that the f-BN has been coated on the surface of m-SiO\(_2\).
3.3. SEM analyses of fillers and epoxy composites

In order to study the coating effect of BN on the surface of SiO$_2$, the morphology of the fillers is shown in figure 3. The SEM images of pure BN and SiO$_2$ can be seen from figures 3(A) and (B). It can be seen that the BN particles exhibited smooth lamellar structure and the particle size was between 2 and 5 $\mu$m. The surface of SiO$_2$ was smooth and the particle size was around 30 $\mu$m. To observe the coating effect of the modified filler, the SEM images of hybrid fillers are shown in figures 3(C)–(F). For SiO$_2$–BN, owing to the absence of interaction between SiO$_2$ and BN, the BN particles were stacked in the gap between SiO$_2$ spheres, which can be seen from figures 3(C) and (E). In this case, there was a large thermal interface resistance between the BN sheets. Figures 3(D) and (F) show the morphology of SiO$_2$:BN hybrid fillers. As the decrease of SiO$_2$/BN ratio, there exhibited increased amounts of BN on the surface of SiO$_2$. When the SiO$_2$/BN ratio is 7:1 (figure 3(D)), the surface of SiO$_2$ spheres can’t be fully coated. However, as the SiO$_2$/BN ratio decreased to 5:1 (figure 3(F)), most of the SiO$_2$ surface was coated with BN, leading to the interconnection among the SiO$_2$ fillers through BN sheets, which formed an efficient thermal conductive path.

In addition, in order to confirm the dispersion of the hybrid fillers in the polymer matrix, the SEM images of epoxy composites are shown in figure 4. The sectional morphology of EP/SiO$_2$:BN can be seen from figure 4(A). It can be found that the rough area was the mixed phase of epoxy and BN, and the surface of the SiO$_2$ sphere was relatively smooth. This may caused by the poor interaction between BN and SiO$_2$, which made BN fall off the surface of SiO$_2$. Figure 4(B) shows the cross-section images of EP/SiO$_2$:BN composites, the BN sheets can be easily found from the surface of SiO$_2$, which played a bridging effect among the SiO$_2$ spheres. In comparison to that of EP/SiO$_2$:BN, the thermal interface resistance in EP/SiO$_2$:BN was lower due to the better interaction between SiO$_2$:BN hybrid fillers. In addition, the BN sheets were contacted with each other, resulting in efficient thermally conductive BN network in the EP/SiO$_2$:BN composites.

Figure 3. SEM images of fillers: (A) BN; (B) SS; (C) SS : BN = 7:1, SS&BN; (D) SS : BN = 7:1, SS@BN; (E) SS : BN = 5:1, SS&BN; (F) SS : BN = 5:1, SS@BN.
3.4. Thermal property of epoxy composites

Figure 5(a) shows the thermal conductivity of the epoxy composites and the addition of fillers in all samples was 60 wt%. The thermal conductivity of EP/SiO₂ was only 0.45 W m⁻¹ K⁻¹ due to the low thermal conductivity of SiO₂ spheres. As the decrease of SiO₂/BN ratio, the thermal conductivity of EP/SiO₂&BN enhanced, indicating that the content of BN in hybrid fillers played an important role to form the continuous thermally conductive network. Compared to that of EP/SiO₂&BN composites, the thermal conductivity of EP/SiO₂@BN exhibited much higher at the same SiO₂/BN ratio. The higher thermal conductivity in EP/SiO₂@BN may cause by the efficient thermally conductive pathway composed of BN sheets. In addition, the interaction between SiO₂ and BN in SiO₂@BN reduced the interface thermal resistance between hybrid fillers, and the thermal conductivity of EP/SiO₂@BN reached to 0.86 W/mK when the SiO₂/BN ratio was 5 : 1. Figure 5(b) shows the thermal conductivity enhancement of EP/SiO₂&BN and EP/SiO₂@BN composites when compared with the EP/SiO₂ composites.

The increased thermal transport properties of pure epoxy and epoxy composites are clearly illustrated by infrared thermographs. The temperature distribution images of neat EP, EP/SiO₂, EP/SiO₂&BN and EP/SiO₂@BN at 0, 60 and 120 s are shown in figure 6(a), and all the samples have the fixed 60 wt% filler level. It can be found that due to the heat process, the color of EP/SiO₂@BN sample changed quickly, indicating that the EP/SiO₂@BN composite had a faster thermal response in comparison with the other samples. Figure 6(b) shows the temperature-time curve of four different samples. For the EP/SiO₂@BN composite, the surface temperature continuously increased at a high rate, which was 17.6 °C higher than that of neat EP after heating for 300 s. Compared to EP/SiO₂&BN, the EP/SiO₂@BN composites exhibited a faster thermal transfer capacity, which made it attractive to potential applications.
The relationship between the thermal interface resistance and thermal conductivity of the composites can be deduced according to the effective medium theory (EMT) developed by Nan et al.\textsuperscript{32} The EMT was valid in this work and the SiO\textsubscript{2}/BN ratio dependence of thermal conductivity data could be calculated as following:

\begin{align}
K_c &= K_{EP/\text{SiO}_2} \times \frac{3 + 2f_{BN}(\beta_1 + \beta_2)}{3 - f_{BN} \times \beta_1} \\
\beta_1 &= \frac{2(d(K_{BN} - K_{EP/\text{SiO}_2}) - 2R_KK_{BN}K_{EP/\text{SiO}_2})}{d(K_{BN} + K_{EP/\text{SiO}_2}) + 2R_KK_{BN}K_{EP/\text{SiO}_2}} \\
\beta_2 &= \frac{L(K_{BN} - K_{EP/\text{SiO}_2}) - 2R_KK_{BN}K_{EP/\text{SiO}_2}}{LK_{EP/\text{SiO}_2} + 2R_KK_{BN}K_{EP/\text{SiO}_2}}
\end{align}

where $K_c$ denotes the thermal conductivity of the composites, $K_{EP/\text{SiO}_2}$ is the thermal conductivity of EP/\text{SiO}_2 samples (Herein, it is assumed that EP/\text{SiO}_2 has a similar thermal conductivity at different SiO\textsubscript{2}/BN ratios, about 0.4 W m\textsuperscript{-1} K\textsuperscript{-1}), and $f_{BN}$ represents the volume fraction of BN, $K_{BN}$ denotes the thermal conductivity of BN (200 W m\textsuperscript{-1} K\textsuperscript{-1}). L = 5 (\mu m) and d (1 \mu m) represent the length and thickness of BN, respectively. $R_K$ is the thermal interface resistance between BN and EP/\text{SiO}_2.

Figure 7(a) shows the relationship between $R_K$ and thermal conductivity of composites. It can be clearly seen that the thermal conductivity of the samples decreased rapidly with the increase of the thermal interface resistance. However, the thermal interface resistance had little effect on the thermal conductivity of the samples when $R_K$ was above $10^{-6}$ m\textsuperscript{2} KW\textsuperscript{-1}, and the thermal conductivity of samples was quite low. As shown in figure 7(b), the experimental data of EP/\text{SiO}_2@BN samples was in good agreement with the EMT model when $R_K$ was 1.15 $\times$ 10\textsuperscript{-7} m\textsuperscript{2} KW\textsuperscript{-1}. The $R_K$ of EP/\text{SiO}_2@BN was lower than that of EP/\text{SiO}_2&BN (1.45 $\times$ 10\textsuperscript{-7} m\textsuperscript{2} KW\textsuperscript{-1}), indicating that the the modification of SiO\textsubscript{2} and BN decreased the thermal interface resistance in EP/\text{SiO}_2@BN composites and the bridging effect between BN and SiO\textsubscript{2} enhanced the continuity of filler network. However, the experimental data of EP/\text{SiO}_2@BN was lower than the data of EMT model, when the SiO\textsubscript{2}/BN ratio reached to 5: 1. This result could be caused by the increased viscosity of the mixture, which made BN fall off from the surface of SiO\textsubscript{2} during mixing process.
4. Conclusions

The modification of the fillers made BN encapsulate on the surface of SiO₂, which formed an efficient thermal network in EP/SiO₂@BN composites. The FTIR spectra and TG analyses showed that the BN had been successfully coated on the surface of SiO₂ and the SEM images confirmed that the interconnected BN had enhanced the thermally conductive pathway. The epoxy composites with 60 wt% SiO₂@BN exhibited a thermal conductivity of 0.86 W m⁻¹ K⁻¹, which was 91% higher than that of EP/SiO₂ samples and around 12% higher than that of epoxy composites with randomly dispersed BN and SiO₂. In addition, the EMT model had successfully confirmed that the EP/SiO₂@BN composites had lower thermal interface resistance and improved thermally network in comparison with EP/SiO₂&BN composites. This method proposed a cost-efficient and practical strategy for the promoting and updating of traditional epoxy packaging composites.

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References

[1] Huang X, Zhi C, Jiang P, Golberg D, Bando Y and Tanaka T 2013 Polyhedral oligosilsesquioxane-modified boron nitride nanotube based epoxy nanocomposites: an ideal dielectric material with high thermal conductivity Adv. Funct. Mater. 23 1824–31
[2] Yang X, Zhu J, Yang D, Zhang J, Guo Y, Zhong X, Kong J and Gu J 2020 High-efficiency improvement of thermal conductivities for epoxy composites from synthesized liquid crystal epoxy followed by doping BN fillers Composites Part B: Engineering 185 107784
[3] Chen H et al 2016 Thermal conductivity of polymer-based composites: fundamentals and applications Prog. Polym. Sci. 59 61–85
[4] Gu J, Zhang Q, Li H, Tang Y, Kong J and Dang J 2007 Study on preparation of SiO₂/epoxy resin hybrid materials by means of sol-gel Polym.-Plast. Technol. Eng. 46 1129–34
[5] Burger N, Laachachi A, Ferriol M, Lutz M, Toniazzo V and Ruch D 2016 Review of thermal conductivity in composites: mechanisms, parameters and theory Prog. Polym. Sci. 61 1–28
[6] Yang X et al 2018 A review on thermally conductive polymeric composites: classification, measurement, model and equations, mechanism and fabrication methods Advanced Composites and Hybrid Materials 1 207–30
[7] Han Y, Shi X, Yang X, Guo Y, Zhang J, Kong J and Gu J 2020 Enhanced thermal conductivities of epoxy nanocomposites via incorporating in situ fabricated hetero-structured SiO₂-BNNS fillers Compos. Sci. Technol. 187 107944
[8] Jiang Y, Liu Y, Min P and Sui G 2017 BN@PPS core–shell structure particles and their 3D segregated architecture composites with high thermal conductivities Compos. Sci. Technol. 144 63–9
[9] Chen J, Huang X, Zhu Y and Jiang P 2017 Cellulose nanofiber supported 3D Interconnected BN nanosheets for epoxy nanocomposites with ultrahigh thermal management capability Adv. Funct. Mater. 27 1604754
[10] Zeng X, Sun J, Yao Y, Sun R, Xu J and Wong C 2017 A combination of boron nitride nanotubes and cellulose nanofibers for the preparation of a nanocomposite with high thermal conductivity ACS Nano 11 5167–78

Figure 7. Experimental and simulated data of epoxy composites: (a) Relationship between thermal conductivity of samples and thermal interface resistance at different SiO₂/BN ratios; (b) Comparison of experimental and theoretical values.
[11] Guo Y, Ruan K, Shi X, Yang X and Gu J 2020 Factors affecting thermal conductivities of the polymers and polymer composites: a review Compos. Sci. Technol. 19 108134
[12] Zhang R, Shi X, Tang L, Liu Z, Zhang J, Guo Y and Gu J 2020 Thermally conductive and insulating epoxy composites by synchronously incorporating Si-sol functionalized glass fibers and boron nitride fillers Chin. J. Polym. Sci. 38 730–9
[13] Chen C, Tang Y, Ye Y, Xue Z, Xue Y, Xie X and Mai Y 2014 High-performance epoxy / silica coated silver nanowire composites as underfill material for electronic packaging Compos. Sci. Technol. 105 80–3
[14] 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 Transfer 92 15–22
[15] Wang J, Wu Y, Xue Y and Liu D 2018 Super-compatible functional boron nitride nanosheets / polymer films with excellent mechanical properties and ultra-high thermal conductivity for thermal management J. Mater. Chem. C 6 1563–69
[16] Zhou H, Deng H, Zhang L and Fu Q 2017 Significant Enhancement of Thermal Conductivity in Polymer Composite via Constructing Macroscopic Segregated Filler Networks ACS Applied Materials & Interfaces 9 29071–81
[17] Alam F et al. 2017 In situ formation of a cellular graphene framework in thermoplastic composites leading to superior thermal conductivity J. Mater. Chem. A 5 6164–9
[18] Qin M, Xu Y, Cao R, Feng W and Chen L 2018 Efficiently controlling the 3D thermal conductivity of a polymer nanocomposite via a hyperelastic double-continuous network of graphene and sponge Adv. Funct. Mater. 28 1803053
[19] Fleming E, Khodmanov I and Shi L 2018 Enhanced specific surface area and thermal conductivity in ultrathin graphite foams grown by chemical vapor deposition on sintered nickel powder templates Carbon 136 380–6
[20] Wang X and Wu P 2018 Melamine foam-supported 3D interconnected boron nitride nanosheets network encapsulated in epoxy to achieve significant thermal conductivity enhancement at an ultralow filler loading Chem. Eng. J. 348 723–31
[21] Zhang Y, Shen Y, Shi K, Wang T and Harkin-Jones E 2018 Constructing a filler network for thermal conductivity enhancement in epoxy composites via reaction-induced phase separation Composites Part A: Applied Science and Manufacturing 110 62–9
[22] Wen B and Zheng X 2019 Effect of the selective distribution of graphene nanoplatelets on the electrical and thermal conductivities of a polybutylene terephthalate / polycarbonate blend Compos. Sci. Technol. 174 68–75
[23] Zhang X et al. 2018 Achieving high-efficiency and robust 3D thermally conductive while electrically insulating hybrid filler network with high orientation and ordered distribution Chem. Eng. J. 334 247–56
[24] Fan B, Liu Y, He D and Bai J 2017 Enhanced thermal conductivity for mesophase pitch-based carbon fiber / modified boron nitride / epoxy composites Polymer 122 71–6
[25] Xiao Y et al. 2016 Largely enhanced thermal conductivity and high dielectric constant of Poly(vinylidene fluoride) / Boron nitride composites achieved by adding a few carbon nanotubes J. Phys. Chem. C 120 6344–55
[26] Pan C, Kou K, Zhang Y, Li Z and Wu G 2018 Enhanced through-plane thermal conductivity of PTFE composites with hybrid fillers of hexagonal boron nitride platelets and aluminium nitride particles Composites Part B: Engineering 153 1–8
[27] Owais M, Zhao J, Imani A, Wang G, Zhang H and Zhang Z 2019 Synergetic effect of hybrid fillers of boron nitride, graphene nanoplatelets, and short carbon fibers for enhanced thermal conductivity and electrical resistivity of epoxy nanocomposites Composites Part A: Applied Science and Manufacturing 117 111–22
[28] Gu J et al. 2017 Synergistic improvement of thermal conductivities of polyphenylene sulfide composites filled with boron nitride hybrid fillers Composites Part A: Applied Science and Manufacturing 95 267–73
[29] Guo Y et al. 2019 Enhanced thermal conductivities and decreased thermal resistances of functionalized boron nitride / polyimide composites Composites Part B: Engineering 164 732–9
[30] Radda S, Abiad C E, Moura N M M, Faustino M A F and Neves M G P M 2019 New hybrid absorbent based on porphyrin functionalized silica for heavy metals removal: Synthesis, characterization, isotherms, kinetics and thermodynamics studies J. Hazard. Mater. 370 80–90
[31] Sun G, Bi J, Wang W and Zhang J 2018 Enhancing mechanical properties of fused silica composites by introducing well-dispersed boron nitride nanosheets Ceram. Int. 44 5002–9
[32] Nan C, Liu G, Lin Y and Li M 2004 Interface effect on thermal conductivity of carbon nanotube composites Appl. Phys. Lett. 85 3549–51