Research Article

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Highly thermally conductive boron nitride@UHMWPE composites with segregated structure

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Abstract: Highly thermally conductive boron nitride (BN) ultra-high molecular weight polyethylene (UHMWPE) composites with the segregated structure were fabricated by powder mixing and hot pressing. Scanning electron microscopy and polarizing optical microscopy were used to analyze the dispersion of BN particles in the UHMWPE matrix. The morphology observation shows that BN particles are selectively located at the interfaces of UHMWPE particles and form continuous thermally conductive networks after the compression molding process. As a result, the thermal conductivity of the BN@UHMWPE composite increases to 3.37 W m\(^{-1}\) K\(^{-1}\) with 38.3 vol% BN, which is seven times larger than that of the pure UHMWPE. Furthermore, the incorporation of BN also influences the crystallinity and thermal properties of UHMWPE.

Keywords: boron nitride, thermal conductivity, segregated structure, polymer–matrix composites

1 Introduction

With the integration and continuous miniaturization of electronic devices, heat dissipation has become the main factor that affects the work stability and lifetime of devices (1,2). However, the thermal conductivity of current polymers is quite low, which can hardly satisfy the efficient heat removal requirements of modern electron devices and electrical equipment. To improve the thermal conductivity of polymers, the incorporation of high thermally conductive fillers is the most effective method.

Recently, carbon materials such as graphite (3–5), carbon fiber (6–8), carbon nanotube (9–12), and graphene (13–17) have been widely used as thermal conductive fillers owing to their high thermal conductivity. However, these fillers generally have high electrical conductivity, which may deteriorate the intrinsic insulating properties of the polymer composites and inhibit their usage in microelectronic devices.

Hexagonal boron nitride (h-BN), also called "white graphite," has a hexagonal lattice structure analogous to graphite (18). It exhibits a thermal conductivity of up to 200 W m\(^{-1}\) K\(^{-1}\) in the planar direction and 1–3 W m\(^{-1}\) K\(^{-1}\) in the perpendicular direction (19,20). Furthermore, BN also shows excellent electrical insulation and high breakdown strength due to a wide bandgap (~5.9 eV) (21,22), which makes BN as excellent thermal conductive fillers in composite materials.

It is well known that the interfacial thermal resistance exhibits a great role in determining the thermal conductivity of polymer composites (23,24). Generally, the surface modification of filler can be a widespread strategy for reducing the interfacial thermal resistance and enhancing the filler dispersion in the polymer matrix. Wei et al. (25) utilized sulfonated polyarylene ether nitrile to improve the compatibility between BN and polyarylene ether nitrile. Liu et al. (26) utilized ethylcellulose to promote the dispersion of h-BN in polyimide. Thus, the thermal conductivity of the PI composite film with ethyl cellulose could be twice than of PI film without ethyl cellulose. The interfacial thermal resistance is influenced not only by the filler fraction but also by the topological structure of a thermally conductive network, such as the dispersion and orientation
of fillers, contact area between fillers, and matrix–filler interaction (27,28). The structure of the thermally conductive network may play a vital role in thermal conductive composites (29,30). To obtain a continuous thermal conduction network, the surface of polymer granules is coated with thermally conductive fillers, and then composites with the segregated structure are constructed by compression molding. Thus, the fillers at the interface of resin particles can form a continuous thermal conduction pathway.

In this study, the method of powder mixing followed by compression molding is introduced to prepare thermally conductive boron nitride (BN)@ultra-high molecular weight polyethylene composites with a segregated structure. Vinyl acetate–ethylene serves as a binder to glue BN platelets to the surface of UHMWPE granules. To optimize the efficiency of the filler, a combination of 4 and 15 μm BN platelets is utilized in the composites (31). The large size BN can form the main thermally conductive pathways in composites, while the smaller size BN will fill the gaps between large sizes of BN to enhance more contact (22,32). Finally, the composites with the segregated structure are constructed in which BN flakes are located at the interface of UHMWPE particles by compression molding. Moreover, the crystallinity and thermal properties of BN@UHMWPE composites are also investigated.

![Figure 1: Schematic illustration of the thermally conductive composites fabrication procedure.](image1)

![Figure 2: Particle morphological SEM images of UHMWPE granules (a–c) and BN-coated UHMWPE granules with 4.4 vol% of BN (d–f).](image2)
2 Experimental

2.1 Materials

h-BN (average size 4 or 15 μm) was purchased from Yingkou Liaobin Fine Chemicals (Liaoning Province, China). UHMWPE powder was purchased from Beijing No. 2 Auxiliary Agent Factory (Beijing, China). Vinyl acetate-ethylene resin (VAE 707) was provided by Guangzhou Deep Gen Chemical (Guangdong Province, China).

2.2 Fabrication of BN@UHMWPE composites

The fabrication of the BN@UHMWPE composites is illustrated in Figure 1. UHMWPE and VAE 707 (UHMWPE:VAE707 = 6:1, w/w) were mixed by using a high-speed mixer (800Y, Yongkang Boou Hardware Products Co., Ltd) for 5 min at 25°C. Then, BN flakes (4 μm:15 μm = 3:7, w/w (31)) were added into the mixer and mixed for 5 min. After that, the mixtures were dried in an oven at 60°C for 12 h. Lastly, the BN-coated UHMWPE particles were compression molded via a press vulcanizer at 210°C and 10 MPa for 15 min. The obtained samples were labeled as BN@UHMWPE, in which “@” represents the coating process. For comparison, the BN/UHMWPE composites with random distributed BNs were prepared by melt mixing BN-coated UHMWPE particles in a torque rheometer at 220°C for 15 min. The obtained composites were denoted as BN/UHMWPE, in which “/” indicates melt mixing. The loadings of BN in the composites were 2.1 vol% (5 wt%), 4.4 vol% (10 wt%), 9.4 vol% (20 wt%), 15.1 vol% (30 wt%), 21.6 vol% (40 wt%), 29.3 vol% (50 wt%), and 38.3 vol% (60 wt%).

2.3 Characterizations

The microstructure and surface morphology of the samples were examined by scanning electron microscopy (FE-SEM; Nova Nano 450, FEI, USA) and polarizing optical microscopy.

Figure 3: Optical micrographs of BN@UHMWPE (a–c) and BN/UHMWPE composites (d–f) with 9.4 vol% of BN.

Figure 4: Thermal conductivity of BN/UHMWPE composites made by powder mixing and melt mixing as a function of BN loadings.
The thermal conductivity of the composites at 25°C was measured by LFA-457 (Netzsch, Germany). The differential scanning calorimetry (DSC) analysis of the samples was carried out in DSC 204 HP (Netzsch, Germany) at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) of samples was performed at a heating rate of 10°C/min under a nitrogen atmosphere by STA449 F3 (NETZSCH, Germany).

3 Results and discussion

The morphology of UHMWPE and encapsulated UHMWPE granules was observed via SEM. As shown in Figure 2, it is found that the surface of the raw UHMWPE particle is smooth. This morphology changed obviously after coating with BN flakes. One can see that the surface of the UHMWPE particles is tightly covered by the BN sheets. Meanwhile, larger numbers of BN sheets are embedded into the gullies of UHMWPE particles. BN sheets are successfully coated onto the surface of UHMWPE particles with the help of VAE 707 emulsion. This morphology provides the potential for constructing a segregated conductive network of BN in UHMWPE composites. UHMWPE granules with other contents of BN also show similar structures (Figure A1).

POM was used to observe the distribution of BN in the composites that are shown in Figure 3. The BN and UHMWPE present diverse colors under optical microscopy for their different light transmittances. In Figure 3b, the light-colored part is mainly the UHMWPE phase, while the darker part around the polygon is the BN sheets. It indicates that the BN sheets are not homogeneously dispersed within the polymer matrix, but selectively localized at the interfaces of UHMWPE particles. Similar structures are observed in the POM images of BN@UHMWPE composites with other loadings of BN (Figure A2). Compared with the BN@UHMWPE composites, the BN/UHMWPE composites present homogeneous structure and the BN sheets are randomly distributed in the matrix (Figure 3d–f). Based on the POM observations, it can be concluded that continuous BN conductive networks have been successfully formed.

The influence of the volume fraction of BN on the thermal conductivity of BN/UHMWPE composites with different fabricating methods is shown in Figure 4. The thermal conductivity for both BN@UHMWPE composites and BN/UHMWPE composites increases with a growing BN percentage. The BN@UHMWPE composites exhibit the highest thermal conductivity of 3.37 W m\(^{-1}\) K\(^{-1}\) with 38.3 vol% of BN, which is about sevenfold higher than for the original UHMWPE. Moreover, the BN@UHMWPE composites exhibit higher thermal conductivity than BN/UHMWPE composites at the same filler composition. Compared with the thermal conductivity of BN/UHMWPE composites, the thermal conductivity of BN@UHMWPE composites improved 19.2%, 14.8%, and 55.2% when the...
content of BN is 21.6, 29.3, and 38.3 vol%, and the average thermal conductivity improved by 25.6% at the volume fraction of BN from 2.1 to 38.3 vol%. Segregated structure is much more beneficial to enhance the thermal conductivity of composite compared with the randomly dispersed structure. For the BN@UHMWPE composites, BN is located at the interfaces among UHMWPE particles and formed a continuous thermally conductive network. This tightly stacked structure of BN greatly increases the contact area between the fillers, which reduces the thermal boundary resistance and broadens the heat conduction pathways.

To evaluate the influence of morphology and interconnectivity of fillers on the thermal conductivity of the composites, the Hashin–Shtrikman (HS) model (5,33) is introduced to analyze the thermal conductivity of the composites.

\[
\sigma_{\text{HS}+} = \frac{2\sigma_l + \sigma_p - 2\chi_f (\sigma_l - \sigma_p)}{2\sigma_l + \sigma_p + \chi_f (\sigma_l - \sigma_p)},
\]

\[
\sigma_{\text{HS}-} = \frac{2\sigma_p + \sigma_l - 2\chi_f (\sigma_p - \sigma_l)}{2\sigma_p + \sigma_l + \chi_f (\sigma_p - \sigma_l)},
\]

\[
X_{\text{interconnected}} = \frac{\sigma_{\text{measured}} - \sigma_{\text{HS}+}}{\sigma_{\text{HS}+} - \sigma_{\text{HS}-}},
\]

where \(\chi_f\) is the particle volume fraction, \(\chi_p\) is the volume fraction of the matrix, \(\sigma_l\) is the thermal conductivity of the particle, and \(\sigma_p\) is that of the polymer matrix. In the HS model, the lower boundary of the HS model (\(\text{HS}\)) assumes thermally conductive phase is surrounded by polymer matrix, while the upper boundary of the HS model (\(\text{HS}+\)) is an interconnected filler network. \(X_{\text{interconnected}}\) is a relative parameter to measure the interconnectivity of the thermally conducting network. Figure 5a shows that the thermal conductivity of UHMWPE/BN composites with homogeneously dispersed BN flakes is closer to the lower bound, indicating that the BN sheets are well wetted by the polymer matrix. In Figure 5b, the \(X_{\text{interconnected}}\) of BN@UHMWPE composites with segregated structures show much higher interconnectivity than UHMWPE/BN composites. The higher interconnectivity should be attributed to the interconnected conductive network formed in the BN@UHMWPE composites.

The TGA curves of the UHMWPE and the composites are shown in Figure 6. The thermal parameters obtained from the DSC curves are reported in Table 1. The melting temperature \((T_m)\) of the BN@UHMWPE composites decreased slightly compared with that of neat UHMWPE. This indicates that the lamellar crystallites in the composites are more imperfect than the lamellae in neat UHMWPE, and they will melt at a lower temperature (34).

Furthermore, the degree of crystallinity \((X, \%)\) of the pure UHMWPE and UHMWPE/BN composites was calculated by:

\[
X(\%) = \frac{\Delta H_f}{(1 - \phi) \Delta H_0},
\]

where \(\Delta H_f\) is the heat fusion of the composites, \(\Delta H_0\) is the fusion enthalpy of 100% crystalline PE (293 J/g) (35), and \(\phi\) is the weight fraction of the filler in the composites.

According to Table 1, the degree of crystallinity in composites with 4.4 vol% BN is increased by 7.7% compared with that of UHMWPE. Then, the crystallinity reduces to about 43% when the BN content is over 15.1 vol%. Generally, the fillers affect the degree of crystallinity through nucleation and crystal growth. When an appropriate amount of fillers is added into the polymer, the fillers could act as nucleation sites, which might facilitate the nucleation and increase the crystallinity of the composites. However, enhanced amounts of filler decrease the degree of crystallinity because they hinder the mobility of polymer chains from forming highly order arrangements in the crystal growth (36).

The TGA curves of native UHMWPE and BN@UHMWPE composites are presented in Figure 7.
The corresponding TGA parameters of the composites are listed in Table 2. As shown in Figure 7, two stages of mass loss can be found from the curves of the composites. The first weight loss, which appears at around 300–390°C, is attributed to the decomposition of the VAE 707 emulsion. The second stage at 410–530°C is due to the degradation of UHMWPE resin. From Table 2, with the increasing content of fillers, the $T_{\text{max}1}$ of the composites has no visible change, while the $T_{\text{max}2}$ of the composite shifts to higher temperatures. The $T_{\text{max}2}$ of the composite with 29.3 vol% BN is 11°C higher than that of original UHMWPE. This can be ascribed to the formation of an effective conducting pathway, thus leading to the composite with segregated structure exhibiting much higher thermal conductivity than BN/UHMWPE composites. The HS model reveals that BN@UHMWPE composites with segregated structure show much higher interconnectivity. Furthermore, the incorporation of BN also influences the crystallinity and thermal properties of UHMWPE.

**References**

(1) An F, Li X, Min P, Liu P, Jiang ZG, Yu ZZ. Vertically aligned high-quality graphene foams for anisotropically conductive polymer composites with ultrahigh through-plane thermal conductivities. ACS Appl Mater Interfaces. 2018;10:17383–92.

(2) Wang M, Jiao Z, Chen Y, Hou X, Fu L, Wu Y, et al. Enhanced thermal conductivity of poly(vinylidene fluoride)/boron nitride nanosheet composites at low filler content. Composites Part A. 2018;109:321–9.

(3) Jia Y, He H, Geng Y, Huang B, Peng X. High through-plane thermal conductivity of polymer based product with vertical alignment of graphite flakes achieved via 3D printing. Compos Sci Technol. 2017;145:55–61.

(4) Ren Y, Zhang Y, Fang H, Ding T, Li J, Bai S-L. Simultaneous enhancement on thermal and mechanical properties of polypropylene composites filled with graphite platelets and graphene sheets. Compos Part A: Appl Sci. 2018;112:57–63.

(5) Feng C, Ni H, Chen J, Yang W. Facile method to fabricate highly thermally conductive graphite/PP composite with network structures. ACS Appl Mater Interfaces. 2016;8:19732–8.

(6) Ji T, Feng Y, Qin M, Li S, Zhang F, Lv F, et al. Thermal conductive and flexible silastic composite based on a hierarchical framework of aligned carbon fibers-carbon nanotubes. Carbon. 2018;131:149–59.
(7) Hou X, Chen Y, Dai W, Wang Z, Li H, Lin C-T, et al. Highly thermal conductive polymer composites via constructing micro-pyrormites communis structured carbon fibers. Chem Eng J. 2019;375:121921.

(8) Zhang S, Gao L, Han J, Li Z, Zu G, Ran X, et al. Through-thickness thermal conductivity enhancement and tensile response of carbon fiber-reinforced polymer composites. Composites Part B. 2019;165:183–92.

(9) Du C, Li M, Cao M, Feng S, Guo H, Li B. Enhanced thermal and mechanical properties of polyvinylidene fluoride composites with magnetic oriented carbon nanotube. Carbon. 2018;126:197–207.

(10) Zhang X, Wen R, Huang Z, Tang C, Huang Y, Liu Y, et al. Enhancement of thermal conductivity by the introduction of carbon nanotubes as a filler in paraffin/expanded perlite form-stable phase-change materials. Energy Build. 2017;149:463–70.

(11) Zhang F, Feng Y, Qin M, Ji T, Lv F, Li Z, et al. Stress-sensitive thermally conductive elastic nanocomposite based on interconnected graphite-welded carbon nanotube sponges. Carbon. 2019;145:378–88.

(12) Qi X-d, Wang W-y, Xiao Y-j, Huang T, Zhang N, Yang J-h, et al. Tailoring the hybrid network structure of boron nitride/carbon nanotube to achieve thermally conductive poly(vinylidene fluoride) composites. Compos Commun. 2019;13:30–36.

(13) Chen L, Hou X, Song N, Shi L, Ding P. Cellulose/graphene bioplastic for thermal management: enhanced isotropically thermally conductive property by three-dimensional interconnected graphene aerogel. Composites Part A. 2018;107:189–96.

(14) Liu Z, Chen Y, Li Y, Dai W, Yan Q, Alam FE, et al. Graphene foam-embedded epoxy composites with significant thermal conductivity enhancement. Nanoscale. 2019;11:17600–6.

(15) Liu Y, Wu K, Luo F, Lu M, Xiao F, Du X, et al. Significantly enhanced thermal conductivity in polyvinyl alcohol composites enabled by dopamine modified graphene nanoplatelets. Composites Part A. 2019;117:134–43.

(16) Wu X, Li H, Cheng K, Qiu H, Yang J. Modified graphene/polyimide composite films with strongly enhanced thermal conductivity. Nanoscale. 2019;11:8219–25.

(17) Raiefie M, Nitzsche F, Laliberte J, Hind S, Robitaille F, Labrosse MR. Thermal properties of doubly reinforced fiberglass/epoxy composites with graphene nanoplatelets, graphene oxide and reduced-graphene oxide. Composites Part B. 2019;164:1–9.

(18) Mittal G, Rhee KY, Park SJ. Processing and characterization of PMMA/PPI composites reinforced with surface functionalized hexagonal boron nitride. Appl Surf Sci. 2017;415:49–54.

(19) Partridge I, Inorganic materials V. Ceramic materials possessing high thermal conductivity. Adv Mater. 1992;4:51–54.

(20) Zhang S, Li X, Guan X, Shi Y, Wu K, Liang L, et al. Synthesis of pyridine-containing diamine and properties of its polyimides and polyimide/hexagonal boron nitride composite films. Compos Sci Technol. 2017;152:165–72.

(21) Singh RS, Tay RY, Chow WL, Tsang SH, Mallick G, Teo EHT. Band gap effects of hexagonal boron nitride using oxygen plasma. Appl Phys Lett. 2014;104:163101.

(22) Yu C, Zhang J, Li Z, Tian W, Wang L, Luo J, et al. Enhanced through-plane thermal conductivity of boron nitride/epoxy composites. Composites Part A. 2017;98:25–31.

(23) Ren P-G, Hou S-Y, Ren F, Zhang Z-P, Sun Z-F, Xu L. The influence of compression molding techniques on thermal conductivity of UHMWPE/BN and UHMWPE/(BN + MWNT) hybrid composites with segregated structure. Composites Part A. 2016;90:13–21.

(24) Wang Y, Zhan HF, Xiang Y, Yang C, Wang CM, Zhang YY. Effect of coaxial functionalization on thermal transport across graphene–polymer interfaces. J Phys Chem C. 2015;119:12731–8.

(25) Wei R, Xiao Q, Zhan C, You Y, Zhou X, Liu X. Polyaniline ether nitride and boron nitride composites: coating with sulfonated polyaniline ether nitride. e-Polymers. 2019;19:70.

(26) Liu L, Shen S, Wang Y. Enhanced thermal conductivity of flexible h-BN/polyimide composites films with ethyl cellulose. e-Polymers. 2019;19:305.

(27) Guo Y, Chang C-C, Halada G, Cuillo MA, Xue Y, Zuo X, et al. Engineering flame retardant biodegradable polymer nano-composites and their application in 3D printing. Polym Degrad Stab. 2017;137:205–15.

(28) Wang Z-G, Gong F, Yu W-C, Huang Y-F, Zhu L, Lei J, et al. Synergetic enhancement of thermal conductivity by constructing hybrid conductive network in the segregated polymer composites. Compos Sci Technol. 2018;162:7–13.

(29) Zhou W, Wang C, Ai T, Wu K, Zhao F, Gu H. A novel fiber-reinforced polyethylene composite with added silicon nitride particles for enhanced thermal conductivity. Composites Part A. 2009;40:830–6.

(30) Zhou W, Kou Y, Yuan M, Li B, Cai H, Li Z, et al. Polymer composites filled with core-double shell structured fillers: effects of multiple shells on dielectric and thermal properties. Compos Sci Technol. 2019;181:107686.

(31) Tsai M-H, Tseng IH, Chiang J-C, Li J-J. Flexible polyimide films hybrid with functionalized boron nitride and graphene oxide simultaneously to improve thermal conduction and dimensional stability. ACS Appl Mater Interfaces. 2014;6:8639–45.

(32) Li TL, Hsu SLC. Enhanced thermal conductivity of polyimide films via a hybrid of micro- and nano-sized boron nitride. J Phys Chem B. 2010;114:6825–9.

(33) Weidenfeller B, Höfer M, Schilling F. Thermal and electrical properties of magnetite filled polymers. Composites Part A. 2002;33:1041–53.

(34) Bartczak Z, Argon AS, Cohen RE, Weinberg M. Toughness mechanism in semi-crystalline polymer blends: II. High-density polyethylene toughened with calcium carbonate filler particles. Polymer. 1999;40:2347–65.

(35) Chen Y, Qi Y, Tai Z, Yan X, Zhu F, Xue Q, Preparation, mechanical properties and biocompatibility of graphene oxide/ultrahigh molecular weight polyethylene composites. Eur Polym J. 2012;48:1026–33.

(36) Ren X, Wang XQ, Sui G, Zhong WH, Fuqua MA, Ulven CA. Effects of carbon nanofibers on crystalline structures and properties of ultrahigh molecular weight polyethylene blend fabricated using twin-screw extrusion. J Appl Polym Sci. 2008;107:2837–45.

(37) Zeng X, Yu S, Sun R. Thermal behavior and dielectric property analysis of boron nitride-filled bismaleimide-triazine resin composites. J Appl Polym Sci. 2013;128:3533–9.

(38) Yu B, Xing W, Guo W, Qiu S, Wang X, Lo S, et al. Thermal exfoliation of hexagonal boron nitride for effective enhancements on thermal stability, flame retardancy and smoke suppression of epoxy resin nano composites via sol–gel process. J Mater Chem A. 2016;4:7330–40.
Appendix

Figure A1: Particle morphological SEM images of BN-coated UHMWPE granules with (a–c) 2.1 vol%, (d–f) 9.4 vol%, (g–i) 21.6 vol%, and (j–l) 38.3 vol% BN.
Figure A2: Optical micrographs of BN@UHMWPE with 2.1 vol% (a and b), 21.6 vol% (c and d), and 38.3 vol% (e and f) of BN.