Surface modification of BNNS bridged by graphene oxide and Ag nanoparticles: A strategy to get balance between thermal conductivity and mechanical property

Hao Yuan, Ting Li, Yang Wang, Xiaofan Wang, Xuhui Zhang, Bihua Xia, Piming Ma, Tianxi Liu, Mingqing Chen, Weifu Dong *

Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, Wuxi, 214122, China

ARTICLE INFO
Keywords: Thermal conductivity Mechanical property Interfacial interaction Bridging effect

ABSTRACT
Thermal conductive polymeric composites are becoming more and more important in the rapid development of new generation electronic equipment, which can quickly dissipate the heat generated by the equipment to ensure their stable operation with high reliability. Nowadays, the most effective way to prepare thermal conductive polymeric composites is to incorporate efficient thermal conductive fillers into polymers. However, the large thermal resistance at interfaces and degradation of mechanical properties arising from the large filler content restrict their practical applications. Herein, surface modification of BNNS by polydopamine (PDA) was carried out to improve the interfacial compatibility and interaction between fillers and polymer matrix, a simple doctor blading method was adopted to prepare PVA composite films with an aligned structure. In addition, the decoration of silver nanoparticles on BNNS surface and the addition of small amount of GO can help to promote the continuity and reduce the defect of the filler skeleton. Thus, an increase in thermal conductivity (in-plane: 6.54 W m\(^{-1}\) K\(^{-1}\), through-plane: 1.03 W m\(^{-1}\) K\(^{-1}\)) was observed in PVA/BNNS-PDA-Ag (10 wt%)/GO (0.5 wt%) composite film, which also possessed excellent flexibility and a favorable mechanical property of 97.1 ± 5.1 MPa.

1. Introduction
Thermal conductive polymeric composites are in urgent demand. The global fifth-generation (5G) communication technology has opened a new stage of mobile Internet. The intelligent electronic devices in the age of 5G have greater data transmission capacities, faster transmission speeds and computing speeds. However, these will increase the power consumption of chips and make the heat productivity of the core processor increase significantly [1,2]. In addition, the electronic devices in the age of 5G have been more functional and diverse. So their internal structures are more complex and the sealability of the overall mechanism is higher. In such a compact and enclosed space, the heat dissipation of electronic devices has become a serious challenge [3]. With the continuous development of the 5G application market, mobile phones, base stations, Internet of Things, automobiles have put forward higher requirements for thermal conductive polymeric composites. The development of thermal conductive polymeric composites is bound to inject vitality into the 5G market, expanding more applications for downstream VR/AR, unmanned driving, telemedicine, smart factories and other fields.

Thermal conductive polymeric composites have been demonstrated as a promising selection for thermal management materials, owing to their fascinating advantages such as ease of processing, lightweight, low cost, and excellent flexibility. One practicable method for fabricating thermal conductive polymeric composite is often adopted by incorporating efficient thermal conductive fillers [4–6]. Nevertheless, the increase of thermal conductivity is not often as good as we wish it to be. One of the main factors that causes the low thermal conductivity enhancement is the large interfacial thermal resistance between fillers and polymer matrices interface [7–10]. Many studies have shown that the interfacial thermal resistance arises from a poor mechanical or chemical adherence at interfaces. Hence, surface functionalization of fillers to manipulating the interfacial interaction in composites has attracted much attention, since it plays an important role in enhancing the thermal conductivity. Liu [11] et al. modified BNNS with APTES to enhance the dispersion of BNNS in the epoxy and the interface

* Corresponding author.
E-mail address: wfdong@jiangnan.edu.cn (W. Dong).

https://doi.org/10.1016/j.coco.2021.100851
Received 26 March 2021; Received in revised form 19 May 2021; Accepted 18 June 2021
Available online 24 June 2021
2021 Elsevier Ltd. All rights reserved.
conductivity of 5.86 W m\(^{-1}\)K\(^{-1}\) at a filler content of 40 wt \%. Kim [12] et al. provided a method to prepare ozone/TEPA functionalized nanodiamonds (NDs) by chemical bonding with amine termination and the substantial enhancement of thermal conductivity was achieved owing to the improved interfacial interactions between ozone/TEPA functionalized NDs and epoxy matrix. Chen [13] et al. non-covalently attached the amine-terminated ionic liquid to the sidewalls of MWCNTs to reduce the interfacial thermal resistance and improve the thermal conductivity of final epoxy composites. Wang [14] et al. treated the BN NSs with silane coupling agent to enhance interfacial adhesion between polymer matrixes and inorganic fillers thus improving the dispersion and preventing serious agglomeration of the fillers, which was demonstrated to be effective for further enhancement of the thermal conductivity of the composites. As a result, Surface functionalization of thermal conductive fillers has been considered to be an efficient approach to improve the interfacial connections with organic polymers, which can help to improve the thermal conductivity of the composites.

Another main factor can be contributed to how to construct a continuous and effective heat conduction path [15,16,20]. The orientation of fillers in one direction via an external force and an interconnected contact network are of vital importance to create an optimal heat transfer path through filler-filler connectivity. Yoshihara [17] et al. hold the view that the anisotropic thermal conductivity of polymer composites exhibited strong correlation with the orientation of fillers. Thus, the orientation of heat conducting basal plane of fillers should be utilized to realize the directional heat transfer of the composites. Up to now, many new fabrication technologies including electrospinning method [18,19], 3D printing [20], ice-template method [21–23] and melt extrusion or shearing [24] have been developed to design and fabricate 3D interconnected or aligned thermal conductive network. Briefly, these documents have demonstrated that the formation of order hierarchical structures are of great significance to improve the thermal conductive performance of the composites. Recent exploration manifests that the utilization of hybrid fillers with different size, length-aspect-ratio, and/or dimensions, brings extra benefits to enhance the thermal conductivity of the composites. Pokharel [25] et al. finely dispersed three carbon nanomaterials with unique geometric shapes and aspect ratios in the PU matrix and they perform as a single hierarchical filler with high aspect ratio for the improvement of electrical, thermal, and mechanical properties. However, most of these documents ignored or didn’t mention the importance of mechanical strength of the composites, which is also an essential index for practical application. Selbert [26] et al. found that graphene quantum dots (GQDs) could simultaneously improve the mechanical and thermal conductive performances of epoxy composites, and the thermal conductivity increased as much as 144\% for 5 wt \% loading of GQDs in epoxy. Consequently, despite having constructed a continuous thermal conductive network, the increase of thermal conductivity with a relatively high filler loading (>20 wt \%) is usually at the cost of significant deterioration of mechanical properties. How to get a balance between thermal conductivity and mechanical performance is still a great challenge.

In this work, BNNS was prepared by liquid phase exfoliation of h-BN and selected as the main thermal conductive filler owing to its higher thermal conductivity when compared with the bulk h-BN [27,28]. For the purpose of obtaining excellent thermal conductivity and good mechanical properties simultaneously, BNNS was surface modified with polydopamine (PDA) to improve the interface compatibility and interface interaction with PVA matrix. What’s more, the deposition of Ag nanoparticles on BNNS surface during the reduction process assisted by PDA and the small amount of additional GO could act as a “bridge” to connect the adjacent BNNSs and fill the gaps between them, thus promoting the formation of thermal conductive network. Finally, a simple doctor blading method was adopted to prepare PVA composite films with an ordered structure. These obtained PVA composite films exhibit excellent thermal conductivity and favorable mechanical properties, as well as flexibility, and can be used as thermal management materials to solve the heat dissipation problems and prolong the service life of electronic devices.

2. Materials and methods

2.1. Materials

The h-BN powders were obtained from Tianyuan Chemical Research Institute Co., Ltd, Poly (vinyl alcohol) (PVA-1799) was supplied from Sinopac Sichuan Vinylon Works. Dopamine (DA, 98\%) was purchased from Aladdin. Isopropanol, tris(hydroxymethyl)aminomethane, silver nitrate, phosphoric acid (H\(_3\)PO\(_4\)), potassium permanganate (KMnO\(_4\)), hydrogen peroxide (H\(_2\)O\(_2\), 30\%), sulfuric acid (H\(_2\)SO\(_4\), 98\%) were provided by Sinopharm Chemical Reagent Co., Ltd. Graphite powders (99.95\%) were obtained from Qingdao Jinrilai Graphite Co., Ltd.

2.2. Exfoliation of h-BN

The liquid phase exfoliation of h-BN was prepared based on the work of Wong [29] et al. In brief, 2 g h-BN powders were added into a 200 mL mixture solvent of isopropanol and deionized water (volume ratio = 1:1). The mixture was sonicated by ultrasonic cell grinder (JYD-900, Shanghai ZhiXin Instrument Co. Ltd., China) under the ultrasonic power of 400 W. The duration of ultrasound and rest time were 2 s and 3 s respectively, the number of ultrasounds was 100, and the whole process was cycled 72 times. After that, the mixture was let stand for 1 h to make the large h-BN that without exfoliation deposited, the upper solution was collected and washed with deionized water several times to obtain BNNSs.

2.3. Preparation of BNNS-PDA-Ag

Firstly, BNNS-PDA was prepared for later use. In detail, 1 g BNNSs were dispersed uniformly in 200 mL deionized water by ultrasonication. Then 0.5 g dopamine was added into the above mixture and the pH of the solution was adjusted to \(\sim 8\) by adding tris(hydroxymethyl)aminomethane. After that, the mixture was stirred at 500 rpm for 1 h at room temperature (25 °C). After the reaction, BNNS-PDA was filtered through a filtration membrane (pore size: 0.8 μm, diameter: 50 mm), consecutively washed several times with deionized water, and dried in air-circulating oven at 50 °C overnight.

Secondly, BNNS-PDA-Ag was prepared by metal coordination and reduction ability of PDA to Ag\(^+\) [30]. In a typical procedure, 1 g BNNS-PDA was ultrasonically dispersed in 200 mL water into a homogeneous mixture. Then 7 g AgNO\(_3\) was added directly and the mixture was stirred for 5 h at 25 °C (500 rpm). BNNS-PDA-Ag was separated and washed with deionized water by filtration technique and stored in a dry environment away from light.

2.4. Preparation of PVA/BNNS-PDA-Ag/GO composite films

GO was prepared by using an improved Hummers’ method [31]. In the experiment, the desired amount of BNNS-PDA-Ag and 5 mL GO dispersion (1 mg/mL) were added to 20 g PVA solution (in water, 5 wt \%) with stirring and ultrasonication into the uniform dispersion, where the GO content of all samples was the same and the only difference was the weight ratio of BNNS-PDA-Ag. The ratio is on the basic of the weight of BNNS, where Ag and PDA are considered as extra components, and their weights are not involved into the calculation. Then, the mixture was stirred gently at 60 °C for about 4 h to form an 11 wt\% PVA aqueous solution. Composite films with BNNS-PDA-Ag loading between 2 wt\% and 14 wt\% were prepared by using a doctor blade with a height of 500 μm at a speed of 1 cm/s. After that, composite films were dried at room temperature for 12 h until they could be peeled off the polyester
membrane and then further dried in air-circulating oven at 50 °C for 6 h to remove the water completely. The detailed fabrication steps of PVA/BNNS-PDA-Ag/GO composite films were illustrated in Fig. 1.

2.5. Characterisation

The morphology of the h-BN, BNNS and BNNS-PDA-Ag was characterised by scanning electron microscopy (SEM Hitachi S-4800) and transmission electron microscope (TEM JEM-2100plus Japan). Atomic force microscopy (AFM Multimode 8, Bruker Nano, U.S.A.) was used to estimate the thickness of BNNS. The XRD patterns of the composite films and BNNS-PDA-Ag were recorded on a Bruker-D8 X-ray diffractometer (Cu Kα radiation, Germany) in the 2θ range of 5°–90° at a scan rate of 5°/min. The element compositions and chemical characteristics of the BNNS, BNNS-PDA and BNNS-PDA-Ag were examined by X-ray photoelectron spectroscopy (XPS, Axis supra, Kratos, UK). ATR-FTIR examinations were conducted on a Nicolet 6700 FTIR spectrometer (USA). Thermogravimetric analysis (TGA) was performed on Meteler-Toledo 1100SF instrument at a heating rate of 30 °C/min from 30 to 900 °C under N2 atmosphere with a flow rate of 20 mL/min. Thermal conductivity of the composites was measured using the laser flash technique. The schematic illustration of fabricating the PVA/BNNS-PDA-Ag/GO composite films. The in-plane thermal conductivity of PVA/BNNS-PDA-Ag/GO composite films with the same GO content (0.5 wt%), but different BNNS-PDA-Ag filler loadings. The in-plane thermal conductivity improved slightly to 7.04 W m⁻¹K⁻¹ when further increasing the BNNS-PDA-Ag content to 14 wt%, compared with the thermal conductivity of 0.29 W m⁻¹K⁻¹ for pure PVA. When exfoliated by vigorous sonication, the as-prepared BNNS became almost transparent under electron beam, suggesting their thin feature (Fig. S1b). The AFM image and the height profile further showed that the BNNS possess smooth surface and uniform thickness of ~25 nm (Fig. S1d), demonstrating the successful exfoliation of BNNS from bulk h-BN. The size of BNNS and GO measured by Zeta were 2.1 ± 0.7 μm and 3.4 ± 0.7 μm (Fig. S2). BNNS showed a homogeneous dispersion in water and the dispersion was stable for over several days. The clear Tyndall effect further suggested the typical colloidal feature and homogeneous dispersed state of BNNS in water (Fig. S1f).

TEM was adopted to observe the surface morphology of BNNS-PDA-Ag and the result was shown in Fig. 2a. The TEM image showed that the surface of BNNS have been decorated with Ag with the average diameter of about 40–50 nm. XRD has been characterized to verify the successful formation of Ag. According to Fig. 2b, besides the characteristic peaks of BNNS, four additional diffraction peaks appeared at 38.1°, 44.3°, 64.5°, and 77.4°, corresponding to diffractions from (111), (200), (220), and (311) lattice planes of face-centered cubic structure of Ag, respectively [32,33]. The XRD patterns matched well with JCPDS Card No.04-0783. XPS detection of BNNS-PDA-Ag revealed that besides the characteristic peaks of BNNS (Fig. 2c), a strong signal linked to Ag was recorded at 370 eV. The elemental scan of Ag 3d₃/₂ and Ag 3d₅/₂ core level peaks centered at 371.3 eV and 365.3 eV with a spin-orbit splitting of 6 eV can be detected (Fig. 2d), indicating the successful reduction of Ag⁺ to Ag⁰ [34,35]. These results suggested successful synthesis of BNNS-PDA-Ag with zero state silver.

SEM was used to observe the oriented structure and the dispersion state of BNNS-PDA-Ag, as shown in Fig. 3. On the basis of the views along the parallel directions, it can be clearly seen that BNNS-PDA-Ag platelets were aligned along the horizontal plane. The shear force introduced by doctor blading resulted in good orientation of BNNS-PDA-Ag along the force direction. As more and more BNNS-PDA-Ag were added into the PVA matrix, higher and higher filler-filler contact were achieved, thus the thermally conductive path became wider and more continuous. What’s more, it is worth noting that BNNS-PDA-Ag platelets were still well dispersed in PVA without obvious aggregation, implying the importance of surface modification. The hydroxyl as well as amino groups of PDA increased the affinity and interfacial interaction between BNNS-PDA-Ag and the PVA matrix through hydrogen bond.
interfacial thermal resistance. The addition of extra GO would efficiently bridge the adjacent BNNS-PDA-Ag and Ag nanoparticles could help to promote the continuity of thermal conductive network and form effective thermally conductive pathways, affording an exceptional thermal functionality for PVA composites. The synergistic effect of GO and Ag reduced the number of effective phonon scattering centers, leading to the reduced interfacial thermal resistance. As a result, this situation is more favorable for the improvement of in-plane thermal conductivity. Then once the BNNS-PDA-Ag content was high enough to be able to construct a layer-by-layer structure itself similar to the microstructure of natural nacre, for example, 14 wt% BNNS-PDA-Ag content, GO would act as a bridge to connect the adjacent and aligned BNNS-PDA-Ag layers, which lead to a larger enhancement of through-plane thermal conductivity to $2.34 \text{ W m}^{-1} \text{ K}^{-1}$. What’s more, GO was selected as the addition filler due to its excellent phonon match with BNNS. Interfacial thermal resistance between BNNS can be greatly reduced due to large phonon spectral match at the interfaces between BNNS and GO species, which eventually improves the interfacial properties and enhance the thermal

Fig. 2. (a) TEM image of BNNS-PDA-Ag. (b) XRD pattern of BNNS-PDA-Ag. (c) XPS spectra of BNNS-PDA-Ag. (d) Ag 3d XPS spectrum of BNNS-PDA-Ag.

Fig. 3. SEM images of fractured surfaces of PVA composite films with: (a) 0, (b) 2 wt%, (c) 4 wt%, (d) 6 wt%, (e) 10 wt%, (f) 14 wt% BNNS-PDA-Ag. The GO content of all PVA composite films was 0.5 wt%.
conduction performance of the filler skeleton. Table S3 summarizes previously reported BN based thermal conductive polymer composites. One can see that both the in-plane and through-plane thermal conductive performance relative to the filler loading in this work are comparable or superior to some other previously reported thermal conductive composites.

In order to demonstrate the thermal management ability of PVA/BNNS-PDA-Ag/GO composite film, the surface temperature variations

Fig. 4. (a) In-plane and through-plane thermal conductivity of PVA/BNNS-PDA-Ag/GO composite films with different weight ratio. (b) Heating and cooling infrared thermal images of PVA/BNNS-PDA-Ag (10 wt%)/GO (0.5 wt%) composite film. (c) Proposed model of Ag and GO for thermal conduction.

Fig. 5. (a) Stress-strain curves of PVA and PVA/BNNS-PDA-Ag/GO composite films. (b) Digital photos showing the flexibility of PVA/BNNS-PDA-Ag/GO composite film. (c) Stress-strain curves of PVA/BNNS composite films. (d) The corresponding schematic illustration of interfacial interaction in PVA/BNNS-PDA-Ag/GO composite film.
with time during heating and cooling process were captured by an infrared thermal camera. Pure PVA and PVA/BNNS-PDA-Ag (10 wt %)/GO (0.5 wt %) composite film were placed on the same heating stage at 75 °C and the temperature change of the surface was recorded in real time. As shown in Fig. 4b, the surface color became lighter on the samples from left to right, indicating the surface temperature of the PVA/BNNS-PDA-Ag (10 wt%)/GO (0.5 wt%) composite film increases faster than the pure PVA. After that, both the hot samples were quickly transferred to a room temperature platform and detected the surface temperature distribution in the cooling process in time. One can see that PVA/BNNS-PDA-Ag (10 wt%)/GO (0.5 wt%) composite film has a quicker cooling rate and shows a much faster decrease of temperature in comparison with the pure PVA. Those results confirmed that the PVA/BNNS-PDA-Ag (10 wt%)/GO (0.5 wt%) composite film had high heat absorption and heat dissipation capability which could absorb and diffuse heat quickly generated by the heat source.

Despite the excellent thermal conductivity, the composite film should also maintain good mechanical properties to meet the requirements of different working conditions. Typical stress-strain curves of pure PVA, PVA/BNNS-PDA-Ag/GO and PVA/BNNS were shown in Fig. 5. There is no doubt that the addition of BNNS inevitably decrease the mechanical behavior of PVA. The tensile strength and Young’ modulus of the composite films with only 4 wt% BNNS loading dropped to 89.9 ± 15.1 MPa and 3.27 ± 0.27 GPa respectively (Table S2), and further decreased with the increase of BNNS content (Fig. 5c). The main reason for this phenomenon was due to the poor dispersion and interfacial adhesion between the polymer matrix and fillers. For the PVA/BNNS-PDA-Ag/GO composite films reinforced with GO, the mechanical performance increased even with a higher filler loading compared with PVA/BNNS composite films. The tensile strength and Young’ modulus of PVA/BNNS-PDA-Ag (10 wt%)/GO (0.5 wt%) was 97.1 ± 5.1 MPa and 4.07 ± 0.07 GPa, respectively (Fig. 5a, Table S2).

The improvement of the mechanical performance is mainly originated from three aspects. First, the addition of GO act as the reinforced filler plays the role of enhancing the strength of the composite films. Second, the aggregation of BNNS in the polymer matrix can be used as the failure point for the composite. As a result, the excellent dispersion of BNNS-PDA-Ag in PVA matrix can reduce and limit the number of internal defects, thus promoting the improvement of mechanical performance. Third, the improved compatibility and interfacial interaction is also a nonnegligible factor. The abundant amino and hydroxyl groups of PDA play the role of enhancing the strength of the composite films. Therefore, the improved compatibility and interfacial interaction between the matrix and filler. Although the elongation at break of the composite films were decreasing, these composite films show good flexibility can be bent or folded without breaking (Fig. 5b).

4. Conclusion

In summary, PVA composite films containing an oriented network were successfully fabricated by a simple doctor blading method. The significant modification of the surface chemistry, multiple synergistic effects of GO and Ag nanoparticles were employed to improve the thermal conductivity and mechanical performance, simultaneously. 10 wt% BNNS-PDA-Ag and 0.5 wt% GO content was considered to be a relatively favorable choice to fabricate PVA composite film, which possesses excellent thermal conductivity (in-plane: 6.54 W m⁻¹ K⁻¹, through-plane: 1.03 W m⁻¹ K⁻¹) and flexibility, as well as an improved mechanical property. The main reasons for those results can be contributed to the interfacial interaction reinforced by surface modification of BNNS with PDA and the bridging effect of GO and Ag. All those strategies and fabrication process make it a promising candidate for the practical application of next-generation wearable and collapsible electronic devices.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by National Natural Science Foundation of China (21975108), MOE & SAFEA, 111 Project (B13025), and National First-Class Discipline Program of Light Industry Technology and Engineering (LITE2018-19).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jeco.2021.100851.

References


