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Highly anisotropic thermally conductive polyimide composites via the alignment of boron nitride platelets

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ABSTRACT

In this work, highly anisotropic thermally conductive polyimide/boron nitride (PI/BN) composites were successfully prepared by a simple method called "ball milling, high-pressure compression and low-temperature sintering". The in-plane thermal conductivity of the PI composites with 30wt% BN reached as high as 2.81 W/mK, while the out-of-plane thermal conductivity was 0.73 W/mK, about 3.2 times and 2.4 times of pure PI, respectively. The great improvement of the thermal conductivity was attributed to the in-plane alignment of BN platelets, which constructed highly connected thermally conductive pathways. The thermally conductive BN networks were observed to be more dense and sufficient in the in-plane direction, more favorable for the heat dissipation, compared to the out-of-plane direction.

1. Introduction

In recent years, with the rapid development of the electronics industry, electronic components have rapidly developed toward the direction of miniaturization, resulting in the increase of the cable density. Therefore, heat dissipation problem has been increasingly severe, becoming a major issue affecting the efficiency, safety, and longevity of electronic devices. Polyimide (PI) has been widely used as electronic packaging materials due to its good thermal and mechanical properties [1]. In particular, it possesses low dielectric constant and loss tangent, high thermal stability and storage modulus. However, the intrinsic thermal conductivity of pure PI is only in the range of 0.1–0.4 W/mK [2,3], far from being the thermally conductive materials. To meet the practical application, highly thermally conductive fillers have generally been introduced into the matrix to fabricate thermally conductive PI composites. These fillers could be metals or metal oxides (silver nanowires [1,4], zinc oxide [5,6], Al_2O_3 [7] etc.), carbonaceous materials (carbon nanotube [8,9], graphene [10,11] etc.), and ceramic materials (boron nitride (BN) [12–15], SiC [2,16] etc.).

When using metals, metal oxides or carbonaceous materials as fillers, the electrical conductivity of the composites is also increased [17–19], which prolongs the time of signal propagation of electronic devices and thus limit their application in certain electronic packages. As a kind of two-dimensional material, hexagonal BN has a layered structure analogous to the graphite, which not only possesses high thermal conductivity (around 600 W/mK) in the planar direction but also excellent electrical insulation [20]. With those features, BN makes itself highly suitable to be the thermally conduct filler and has thus been studied by numerous researchers. Generally, disorderly and uniformly dispersed BN platelets incorporated into polymer matrix could make the property enhanced at some extent [21–23]. In the conventional PI/BN composites, BN platelets are randomly distributed, and a higher volume fraction ($>$ 40 vol %) is usually needed to obtain thermal conductivity values higher than 1 W/mK at room temperature [24]. It is worth noting that BN exhibits a lower thermal conductivity in the layered direction (about 1–3 W/mK) [25]. To make full use of the high in-plane thermal conductivity of BN as much as possible, composites in which BN platelets are aligned in-plane have thus been prepared. Many methods have been reported to assist the alignment, including doctor blading [26], magnetic field alignment [27], oscillatory shearing [28], electric field [29], electrospinning [12], etc. With these methods, the effective thermally conductive pathways were constructed by densely stacked BN platelets, and the resultant composites exhibited high in-plane thermal conductivity. Zhang et al. [30] prepared poly(vinyl alcohol)/BN composites by vacuum filtration and subsequent poly(vinyl alcohol) wetting. At a BN content of 27 vol%, the maximum

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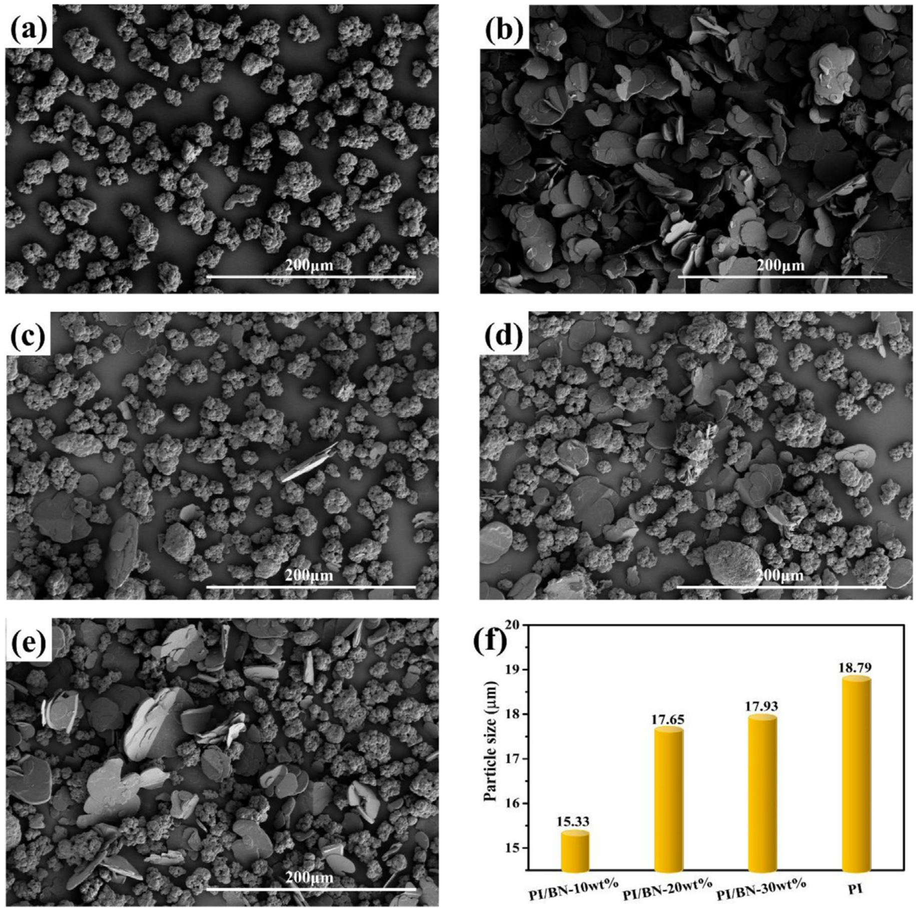

Fig. 1. SEM images of PI powder (a), BN (b), PI/BN mixtures with different BN loadings: 10 wt % (c), 20 wt % (d) and 30 wt % (e). The average size of PI particles in PI/BN mixtures after the ball milling and the original average particle sizes of pure PI without the ball milling (f).

thermal conductivities along the through-plane and in-plane directions were 1.63 W/mK and 8.44 W/mK, respectively. Zhang et al. [31] prepared polyvinylidene fluoride/BN composites with the electrospinning method and the in-plane thermal conductivity reached 7.29 W/mK with the content of 30 wt% BN. Therefore, with the assistance of high in-plane thermal conductivity of BN, polymer/BN composites could possess a high thermal conductivity in the orientation direction of BN platelets.

Analogously, to assist the BN's orderly arrangement in the PI composites, special methods were also needed. Gu et al. [12] designed and fabricated thermally conductive PI/BN composites using in-situ polymerization followed by electrospinning-hot press technology. However, they only tested the out-of-plane thermal conductivity, which is only 0.696 W/mK. Wang et al. [32] applied a solution-casting process to prepare PI composites with BN nanosheets as the thermal conduct filler. The in-plane thermal conductivity of PI composite films with 7 wt% BN nanosheets loading was up to 2.95 W/mK, which was increased by 1080% as compared to that of neat PI. Whereas, the out-of-plane thermal conductivity of the composites was only 0.44 W/mK, with an increment of only 76%. For PI is one type of special engineering plastics, either its processing temperature is high, or it is insoluble and does not melt, so that the normal molding is not acceptable. To fabricate thermally conductive PI/BN composites, in-situ polymerization technique was usually adopted. With regard to the procedure of in-situ polymerization, the synthesis process is much complex, hard to control and for the large-scale fabrication. Therefore, easy methods that can fabricate highly anisotropic thermally conductive PI/BN composites are still in demand.

Inspired by powder sintering for polymers with the characteristics of insolubility and non-melting, a simple method called “ball milling, high-pressure compression and low-temperature sintering” was adopted to fabricate PI/BN composites in our work. The PI/BN composites with highly in-plane alignment of BN platelets were successfully prepared, which demonstrated a significantly improved thermal conductivity. Our work provides a new idea for the fabrication of polymer composites with high thermal conductivity, especially for the special engineering plastics.

2. Experimental

2.1. Materials

PI powder (trade name: YS-20), with an average particle size of 18.79 μm, were supplied by Shanghai Synthetic Resin Research Institute Co. Ltd., China. BN platelets with an average particle size of 30 μm and the thickness of 20–35 nm were kindly offered by Ya'an Bestry Performance Materials Co. Ltd., China. All the chemicals were analytical grade and were used as received without further treatments.

2.2. Sample preparation

PI powder were physically mixed with a specified amount of BN platelets (0 wt%, 10 wt%, 20 wt% and 30 wt%) using a ball milling at 500 r/min for 1 h. Then, the as-prepared mixtures were compressed into semi-finished round products with diameter of 20 mm and thickness of 2 mm at 130 °C for 10 min under 200 MPa, and then sintering for 30 min at 290 °C without pressure to get PI/BN composites.