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Enhanced thermal conductivity of functionalized-graphene/boron nitride flexible laminated composite adhesive via a facile latex approach

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ABSTRACT

Flexible fiber-reinforced laminated composite adhesive combining with functionalized-graphene (f-G) layer and hexagonal boron nitride (h-BN) layer was prepared by colloid-blending and self-assembly technology with the assistance of the secondary force and hydrophilic difference. In this system, poly (2-ethylhexyl acrylate) (P2EHA) as the polymer matrix linked the layer of functionalized-graphene and another layer of hexagonal boron nitride like the cross-linker or adhesive via self-assembly technology. Lewis acid-base ($\delta^+-\delta^-$) interaction and π-π stacking improved the compatibility between the filler and the polymer matrix. The effective and successful fabrication of flexible f-G/h-BN laminated composite adhesive has been confirmed by SEM, Raman spectroscopy, and XRD investigations. The oriented stacking and laminated structure resulted in much higher in-plane thermal conductivities (~4.20 W/m K) and insulation in the direction through the plane and good adhesive properties. The procedure was environmental friendly, easy operation, and potential for the practical application in industry.

1. Introduction

With the increase of the power density of electronic devices, heat dissipation is becoming critical [1–3]. High performance thermal interface materials will play a key role in the development of the future high power density microelectronic devices. For polymer composites, one type of solution is to use materials with high thermal conductivity as the filler such as Al_2O_3 [4,5], AlN [6,7], SiC [8], Si_3N_4 [9,10], owing to their easy process and low cost. Recently, new carbon materials have attracted researchers' attention. Carbon-based materials (such as carbon nanotubes or fibers, graphite flakes, and graphene sheets or foam) had been widely used as the fillers to form composite materials due to their high in-plane strength, electrical and thermal conductivity [11–14]. More and more works shed light on the application of graphene in fabricating high thermal conductivity composites due to their super high thermal conductivity [15–18]. However, the high-cost and high electrical conductivity of these carbon materials limit their application, especially in integrated circuit encapsulation materials or thermal interface materials (TIMs) where electrical insulation is required.

Hexagonal boron nitride (h-BN) has a structural analog with graphene. We often use this filler in the preparation of thermally conductive and electrically insulative composites. Because of its good thermal conductivity with the in-plane thermal conductivity ranging from 300 W/m K to 600 W/m K and the excellent electrical insulation [19,20]. In addition, the 2D h-BN is expected to introduce the anisotropic feature on the thermal conductivity of composites [21]. The in-plane thermal conductivity of composites were significantly higher than through-plane thermal conductivity when the microplates h-BN were used as fillers due to the oriented arrangement of fillers towards the in-plane direction [22]. Lewis acid-base complexation was also used to modify h-BN. Lin et al. [23] modified h-BN with either octadecylamine (ODA) or amine-terminated oligomeric polyethylene glycol (PEG) to obtain ODA- or PEG- functionalized h-BN via the interaction between the amino groups and the boron atoms. As we know that graphene has usually high intrinsic thermal conductivity, which estimated to be 4840–5300 W/m K [24,25]. However, its excellent electrical properties limit the application in the field of electronics [26].

Laminated composites consist of laminas (plies) made of fiber-reinforced matrix with various fiber (such as graphene and copper) content had been applied in heat conduction for many years [27,28]. Finite-element modeling was used to investigate the mechanism of thermal conduction in laminated composites [29,30]. Yu et al. [31] enhanced the thermal conduction of carbon

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fiber reinforced polymer composite laminates by coating highly oriented graphite film using the acrylate adhesive. Therefore, we believe that this structure has great advantages in the composites combine with two or more different kinds of materials with huge difference to achieve the synergetic enhancement of performance.

Fig. 1 showed the laminated structure of functionalized-graphene (f-G)/h-BN flexible composites. In general, the technology of deposited (such as chemical vapor deposition (CVD)) or compressed (such as plate vulcanization or plate compression) was used to prepare laminated or overlapping structure [32]. Malekpour et al. improved the thermal conductivity of GL(graphene laminate)-on-PET by the technology of deposition and compression [33]. However, as an efficient and convenient method, colloid blending and self-assembly approach had been used to fabricate the multilayer films. Zhao et al. [34] prepared ultrathin multilayer (PVA/GO)n film through layer-by-layer (LBL) assembly of poly (vinyl alcohol) (PVA) and exfoliated graphene oxide (GO) which GO nanosheets as the building blocks. The mechanical properties of the (PVA/GO)n film was improved significantly. However, the high cost and complex process limit these methods' large-scale application.

In this paper, we prepared the flexible f-G/h-BN composites with laminated structure by deposition and self-assembly method with different mass of h-BN sheets. A simultaneous reduction and surface functionalization of graphene oxide by diethylenetriamine (DETA) was carried out to prepare f-G sheets according to our previous work [35]. Poly(2-ethylhexyl acrylate) (P2EHA) as the polymer matrix act as the adhesive that contact the layer of f-G and h-BN sheets with the assistance of the secondary interaction, such as Lewis acid-base ($\delta^+ - \delta^-$) interaction and π-π stacking. This fabrication method was regarded as an easy and green way owing to its room temperature reaction and no harmful solvents involved. Flexible f-G/h-BN composites with laminated structure presented the anisotropic properties such as electrical conductivity and thermal conductivity. High in-plane thermal conductivity, electrical insulation and adhesive indicated the promising prospect in energy systems or thermal management such as thermal interface materials (TIMs), integrated circuit encapsulation [36–40].

2. Experimental

2.1. Raw materials and experimental methods

The fabrication process of pure poly(2-ethylhexyl acrylate) (P2EHA) latex were reported in our previous works [41]. The loading of functionalized graphene (f-G) for P2EHA/f-G/h-BN composites was fixed at 1.0 wt% in this work. Graphite powder was purchased from Qingdao Huatai Lubricant Sealing S&T Co., Ltd., and used to prepare graphene oxide (GO) by modified Hummers' method. The GO sheets were reduced and functionalized by diethylenetriamine (DETA) subsequently to prepare functionalized-graphene (f-G) [42–44]. Hexagonal BN powder (purity > 99.5%) was provided by Dandong Rijin Science and Technology Co., Ltd. which was sonicated for a few minutes in water prior to use (Figs. S1 and S2). Then the f-G and h-BN were stirred with high speed in water for 1 h and sonicated for 15 min. The P2EHA latex was added into the mixture of f-G and h-BN, which was stirred again with high speed for 2 h and sonicated for 15 min at room temperature. Finally, the mixture was poured into the mold, solidified and kept at 30 °C for few days to get the P2EHA/f-G/h-BN composite films.

2.2. Characterizations

The microstructure of the materials or composites was observed via scanning electron microscope (SEM, Sirion 200, FEI). The morphology and layer number of GO and f-G were measured by transmission electron microscope (TEM, JEM-2010, JEOL) and atomic force microscope (AFM, SPA 300HV). Confocal Raman Microscopy (Renishaw inVia Reflex) was used to obtain the Raman spectra of samples. The water contact angles were measured using CAM200 contact angle goniometer, the values reported were the

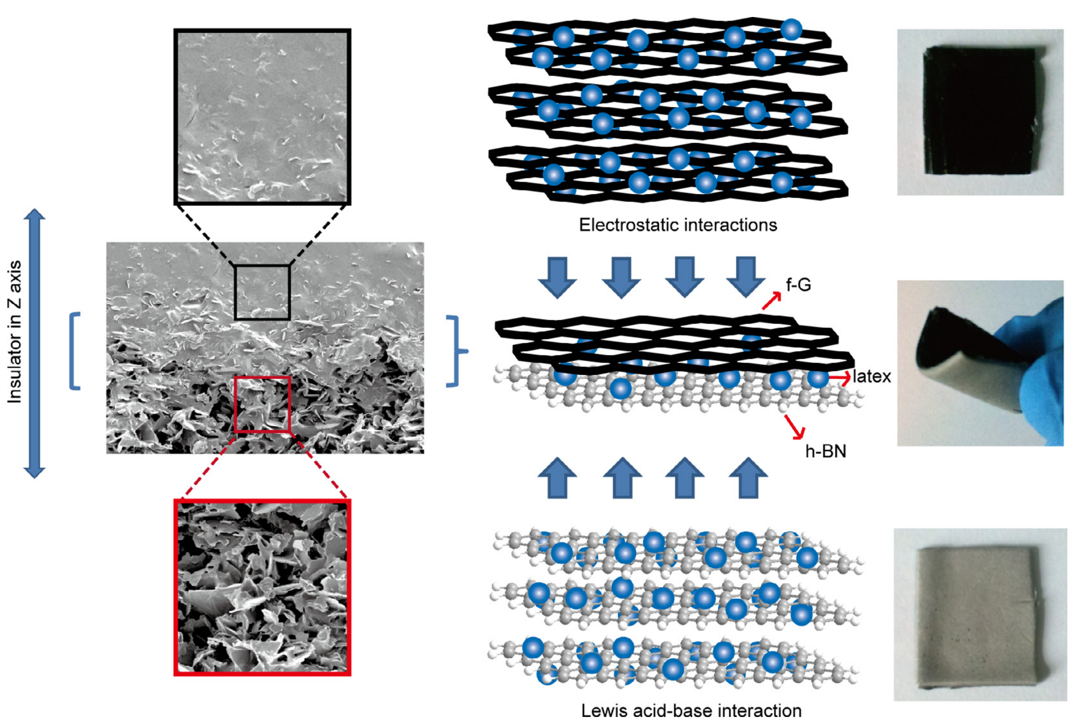

Fig. 1. Laminated structure of flexible f-G/h-BN composites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)