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High thermal conductivity of flexible polymer composites due to synergistic effect of multilayer graphene flakes and graphene foam

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ABSTRACT

Research on flexible thermal interface materials (TIMs) has shown that the interconnected network of graphene foam (GF) offers effective paths of heat transportation. In this work, a variant amount of multilayer graphene flakes (MGFs) was added into 0.2 vol% GF/polydimethylsiloxane (PDMS) composite. A remarkable synergistic effect between MGF and GF in improving thermal conductivity of polymer composites is achieved. With 2.7 vol% MGFs, the thermal conductivity of MGF/GF/PDMS composite reaches 1.08 W m^{-1} K^{-1}, which is 80%, 184% and 440% higher than that of 2.7 vol% MGF/PDMS, GF/PDMS composites and pure PDMS, respectively. The MGF/GF/PDMS composite also shows superior thermal stability. The addition of MGFs and GF decreases slightly the elongation at break, but observably increases the Young's modulus and tensile strength of composites compared with pure PDMS. The good performance of MGF/GF/PDMS composite makes it a good TIM for possible application in thermal management of electronics.

1. Introduction

Heat dissipation has become a serious problem with the miniaturization and integration of electronic devices. Thus thermal interface materials (TIMs) with high thermal conductivity, applied between heating element and heat sink, are needed to remove the heat quickly to decrease the hot-spot temperature [1–5]. Traditional TIMs made of metal-matrix materials or rigid polymer-matrix composites bring the mismatch with the electronic devices as a result of the surface roughness, which increases the thermal interfacial resistance [6,7]. Thermal grease as traditional TIM is unrecoverable and its thickness is difficult to control, which is easy to penetrate or pump out on account of its liquidity, maybe causing unreliability and pollution to the devices [4,8,9]. What's more, traditional polymer-matrix TIMs require high loading of metal particles (above 50 vol%) to achieve the thermal conductivity of 1–5 W m^{-1} K^{-1}, which is high-cost and increases dramatically the viscosity of polymer, bringing the enormous difficulty in removing bubbles to get qualified samples [10–12].

Recently, graphene has attracted tremendous attention as the most promising filler to improve the thermal conductivity of polymer composites due to its high intrinsic thermal conductivity (3000–5300 W m^{-1} K^{-1}) and large specific surface area [13–17]. Multilayer graphene flakes (MGFs) made from expandable graphite are almost identical to pristine graphene, low-cost and possible for high-volume production. They show better enhancement in thermal conductivity of polymer compared with carbon nanotubes (2000–6000 W m^{-1} K^{-1} along the tube axis) [18–21]. Shahil and Balandin [12] mixed 10 vol% of single-layer and multilayer graphene sheets with epoxy resin and got 2300% enhancement in cross-plane thermal conductivity. Wang et al. [22] combined graphene nanoplatelets (85 wt% GnP) and cellulose nanocrystals (CNC) to fabricate flexible hybrid thin film by hot-pressing method, and obtained in-plane and through-plane thermal conductivity of 41 W m^{-1} K^{-1} and 1.2 W m^{-1} K^{-1}, respectively. Goli et al. [23] added 20 wt% graphene into the hydrocarbon-based phase change material (PCM), making its thermal conductivity be increased by more than two orders of magnitude while preserving its latent heat storage ability.

Graphene foam (GF) with interconnected network has a thermal conductivity of 0.26–1.7 W m^{-1} K^{-1} and low thermal interfacial resistance of 0.04 cm^2 K W^{-1} at Si–Al interface [24–26]. Recently, Li et al. [27] reported the abnormal characteristic of GF that its thermal properties were improved with increased temperature, different from other carbon materials. In our previous work [28], the thermal conductivity of 0.7 wt% GF/polydimethylsiloxane (PDMS) composite reached 0.56 W m^{-1} K^{-1}, i.e., 200% higher than that of pure PDMS. Ji et al. [29] embedded the ultrathin-graphite into PCM to improve the thermal conductivity up to 18 times

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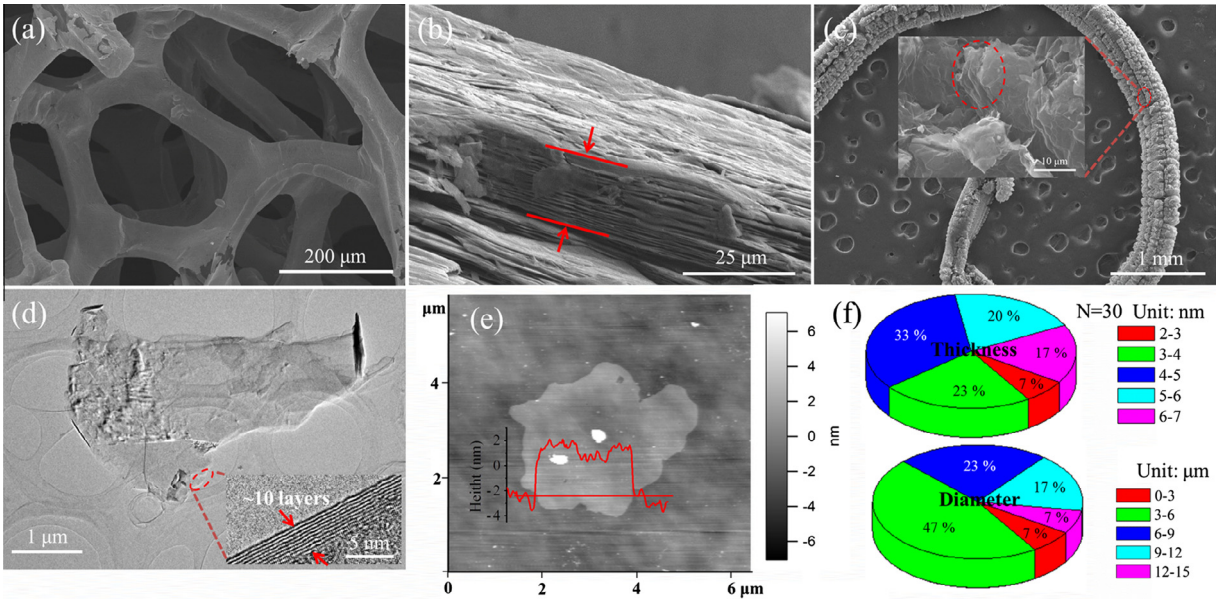

Fig. 1. SEM images of (a) GF, (b) expandable graphite and (c) expanded graphite (inset: multilayer structure of the expanded graphite). (d) TEM (inset: graphene layers) and (e) AFM images of MGF. (f) Thickness and diameter distribution of MGFs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

compared with wax at very low loading of 1.2 vol%. Jia et al. [30] prepared the 0.2 wt% GF/epoxy composite which had a notable increase of T_g by 31 °C, as well as 53% and 38% enhancements in flexural modulus and strength, respectively.

Furthermore, some researchers utilized the synergistic effect of graphene and other fillers to further improve the thermal properties of composites. Yu et al. [31] filled 7.5 wt% graphite nanoplatelets (GNPs) and 2.5 wt% single-walled carbon nanotubes (SWNTs) into epoxy, and got a thermal conductivity of 1.75 W m^{-1} K^{-1}. Yu et al. [32] added only 1 wt% graphene into the thermal grease with 63 vol% Al_2O_3 particles, the thermal conductivity was increased from 2.70 to 3.45 W m^{-1} K^{-1}. Chen et al. [33] modeled and analyzed the synergistic effect of hybrid filler-GNPs and SWNTs on thermal conductivity enhancement of polymer composites, providing an instruction to predict the optimal ratio of the hybrid filler.

Although the 3D structure of GF is beneficial to both the thermal and mechanical properties of composites, restricted by the chemical vapor deposition (CVD) method and the density of Ni foam, the content of GF in composites cannot be increased significantly, impeding a further improvement of thermal conductivity of composites. So, MGFs were added to increase the thermal conductivity of polymer matrix. It is known that the performance of composites depends greatly on the filler content. Despite the different forms of GF and MGF, the shape change is not as important as filler content to the thermal conductivity of composites. A dramatic improvement in thermal conductivity is not expected by merely adding GF. So, a combination of GF and MGF is more meaningful. In this paper, on the basis of our previous works [28,34], a new series of polymer composites were fabricated with hybrid fillers – MGFs and GF. The thermal and mechanical properties are investigated systematically.

2. Materials and experimental methods

2.1. Raw materials and composites fabrication

The fabrication process of GF, GF/PDMS composite and pure PDMS was reported in our previous work [34]. The loading of GF for GF/PDMS composite is 0.2 vol% (0.5 wt%) in this work.

Expandable graphite powder with average diameter of 300 μm was purchased from Qingdao Jinrilai Graphite Co. Ltd., and fully expanded at 800 °C for 1 min in the atmosphere of Argon. Then the expanded graphite was sheared and stirred at high speed in acetone for 2 h and then sonicated for 20 h to get multilayer graphene flakes (MGFs). Next, the base agent of polydimethylsiloxane (PDMS, Sylgard184, Dow Corning) was added into the mixture of MGFs and acetone, which was again sheared and stirred at high speed for 30 min. Acetone was removed completely when the mixture was continuously stirred in 60 °C water bath. Then, the curing agent (base agent/curing agent = 10/1 in weight) was added and stirred. Finally, the mixture was poured into the GF which was previously placed in a mold, vacuumized and solidified at 80 °C for 4 h to get the MGF/GF/PDMS composite. For comparison, the MGF/PDMS composites were also prepared in the same way.

2.2. Microstructures and characterization

The microstructures of studied materials were observed by scanning electron microscope (SEM, S-4800, HITACHI). The morphology, size and layer number of MGFs were measured by transmission electron microscope (TEM, JEM-2100F, JEOL) and atomic force microscope (AFM, MFP-3D-BIO, AR). The thermal conductivity of samples with the diameter of 30 mm and thickness of 2.0 mm was tested by heat flux method (DRL-III, Hunan Xiangyi Instruments Co. Ltd.) on the basis of ASTM D5470. An onset pressure of 170 kPa was applied to increase the contact area between the sample and copper block. Thermogravimetric analysis (TGA, Q600 SDT, TA) was performed from room temperature to 900 °C at a heating rate of 20 °C min^{-1} in an atmosphere of nitrogen. The tensile tests were carried out with a miniature tensile testing machine (2000, MiniMat) at a loading rate of 1.5 mm/min. Three samples of each kind of studied materials were tested. The thickness and length of dumbbell shape samples are 2 mm and 35 mm, respectively. The valid parallel part of sample is 2 mm in width and 12 mm in length according to GB/T 528-92.