Enhanced thermal-conductive and anti-dripping properties of polyamide composites by 3D graphene structures at low filler content

CrossMark

Xuheng Li [a], Linbo Shao [a,b], Na Song [a], Liyi Shi [a,b], Peng Ding [a,*]

[a] Research Center of Nanoscience and Nanotechnology, Shanghai University, 99 Shangda Road, Shanghai 200444, PR China
[b] College of Sciences, Shanghai University, 99 Shangda Road, Shanghai 200444, PR China

ABSTRACT

In this work, 3D graphene structures constructed by graphene foam (GF) were introduced into polyamide-6 (PA6) matrix for the purpose of enhancing the thermal-conductive and anti-dripping properties of PA6 composites. The GF were prepared by one-step hydrothermal method. The PA6 composites were synthesized by in-situ thermal polycondensation method to realize PA6 chains covalently grafted onto the graphene sheets. The 3D interconnected graphene structure favored the formation of the consecutive thermal conductive paths or networks even at relatively low graphene loadings. As a result, the thermal conductivity was improved by 300% to 0.847 $W \cdot m^{-1} \cdot K^{-1}$ of PA6 composites at 2.0 wt% graphene loading from 0.210 $W \cdot m^{-1} \cdot K^{-1}$ of pure PA6 matrix. The presence of self-supported 3D structure alone with the covalently-grafted PA6 chains endowed the PA6 composites good anti-dripping properties.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Thermal management is becoming increasingly important in the microelectronic packaging, automotive, aerospace industries, etc, because of the need for dissipating heat and preventing the stacking of static charge [1]. Due to its excellent thermal transfer ability and high aspect ratio, graphene has been regarded as new generation of thermal interface material especially as a functional filler in polymer composites [2,3].

Recently, several studies have been reported that a variety of high thermal conductivity fillers were incorporated into polymer matrix to synthesize thermal interface materials [4–7]. One of the most representative thermal conductive mechanisms of polymer composites was conductive chains mechanism. With the increasing of filler content, the thermal conductivity of composites increased slowly until the filler fraction reached a percolation threshold where a rapid increase in conductivity started [8]. Fillers had to form a random close-packed structure to maximize a pathway or network for heat conduction through the polymer matrix [9,10]. In the past researches, the effects of type, shape and size of fillers and interface thermal resistance on thermal performance of composites have been fully addressed. Lee et al. [11] reported the effectiveness of hybrid fillers consisting of different conductive fillers in type and shape on the fabrication of thermally conductive composites. Xu et al. [12] explored the thermal properties of single-walled carbon nanotube/polymer composites. Gojny et al. [13] demonstrated the influence of the type of carbon nanotube (single-walled carbon nanotubes, double-walled carbon nanotubes and multi-walled carbon nanotubes) on the thermal conductivity of polymer composites. Gu et al. [14] introduced methanesulfonic acid/gamma-glycidoxypropyltrimethoxysilan (MSA/KH-560) to functionalize the surface of GNPs. The KH-560 molecules have been successfully grafted onto the surface of GNPs to fabricate GNPs/bisphenol-A epoxy resin (GNPs/E-51) nanocomposites. The thermal conductivity of the fGNPs/E-51 nanocomposites is improved to 1.698 W/m K with 30 wt% fGNPs, 8 times higher than that of original E-51 matri. As our previous work, highly conductive polyamide-6/graphene (PG) composites were produced, which enhanced the thermal conductivity (λ) from 0.196 $W \cdot m^{-1} \cdot K^{-1}$ of neat PA6 to 0.416 $W \cdot m^{-1} \cdot K^{-1}$ of PG composite with only 10 wt% GO sheets loading. According to the "grafting to" strategy, PG composites were synthesized by in situ polymerization. PA6 chains were covalently bonded onto the graphene sheets, which favored the formation of the consecutive thermal conductive paths or networks, and simultaneously avoided the aggregation of reduced graphene oxide (RGO) sheets in PG composite and reduced the interface thermal resistance [15]. However, the irreversible aggregation that caused by increasing the volume of addition of the two-dimensional (2D) graphene made it difficult to fabricate high thermal conductivity composites by improving the filler loading. Thus, we had to solve this problem through other ways.

---

* Corresponding author.
E-mail address: dingpeng@shu.edu.cn (P. Ding).

Recently, graphene foams (GFs), a self-supported three dimensional (3D) interconnected network of graphene have emerged. 3D GFs were prepared by assembling 2D graphene sheets into 3D graphene network. The pore sizes of the GF were in the range of sub-micrometer to several micrometers, which brought about ultralight, high mechanical strength and compressibility, excellent conductivity and adsorption characteristics. The self-supported 3D network morphology could not only prevent individual graphene sheets from aggregating and restacking during the process of assembling, but also endowed high-rate transportation of the phonons and provided multidimensional thermal transport pathways, resulting in excellent thermal conductive performance [16]. Furthermore, multifarious 3D graphene-based macrostructures were prepared using various methods aiming to develop their superior mechanical properties, excellent electrical conductivities, etc [17–19]. The emergence of 3D graphene offers totally new processing routes to fabricate composites with graphene. Chen et al. [20] found that a GF consists of an interconnected flexible network of graphene as the fast transport channel of charge carriers for high electrical conductivity. Even with a GF loading as low as ~0.5 wt %, GF/poly(dimethyl siloxane) composites show a very high electrical conductivity of ~10 S cm^{-1}, which is ~6 orders of magnitude higher than chemically derived graphene-based composites. Tang et al. [21] reported an epoxy/aerogel composites the electrical conductivity value reached 4×10^{-2} S/m with only 0.21 vol% filler, which was almost 13 orders of magnitude higher than that of neat epoxy and nearly 2 orders of magnitude higher than the best value reported for the composites filled with 2D graphene sheets at the similar loading. Zhong et al. [22] produced a phase change material composed of 3D graphene aerogel (GA) and octadecanoic acid (OA). The thermal conductivity of the composite increased about 14 times. Irin et al. [23] demonstrate a novel concept for preparing percolating composites with ultralow filler content by backfilling a thermoset into a pre-existing composite aerogel scaffold. A percolation threshold as low as 0.012 vol% is obtained for graphene-RF cryogel/epoxy composite. Fan et al. [24] developed graphene aerogel (GA)-poly(methyl methacrylate) (PMMA) composites by backfilling PMMA into the pores of the GAs. As graphene loadings increased from 0.67 to 2.50 vol%, the composites exhibited significant increases in electrical conductivity (0.160–0.859 S/m), microhardness (303.6–462.5 MPa) and thermal conductivity (0.35–0.70 W·m^{-1}·K^{-1}) from that of pure PMMA. They demonstrated that composites made from GFs could avoid re-stacking of individual graphene sheets and form 3D conductive paths at a extremely low graphene loading. These were important for conductive graphene composites. However, they have ignored the importance of good interface interaction between graphene and polymer matrices. Poor coupling in vibration modes at the filler-polymer interface will generate Signiant thermal (Kapitza) resistance that was not benefit for the phonon's transfer, and thus decrease the overall λ of the composites.

In this work, owing to supramolecular interaction of RGO, a self-supported 3D interconnected thermal conductive pathways were constructed with RGO sheets. Then, in situ thermal polycondensation method was used to realize polyamide 6 (PA6) chains covalently grafted onto GFs, making a highly conductive polyamide 6/graphene foam composites (PGF) even at a low filler content (Fig. 1). For thermal management materials, safety was as important as thermal conductivity. Thanks for GFs' self-supported 3D interconnected network and in situ thermal polycondensation method, the polymer matrix and filler combined more closely, giving PGF the speciality of anti-dripping. These PGF exhibit high thermal conductivities, flame retardance, and thus were expected to find diverse applications in the thermal interface materials, connectors, and other high-performance thermal management systems, such as the heat-conducting fins in the heat dissipation of automobile, computer, high-power light-emitting diode (LED) and so on.

2. Experimental

2.1. Materials

Expandable graphite were supplied by Jinrilai Co., Ltd. (99.0%, Qingdao, China), concentrated sulfuric acid (98.0% H$_2$SO$_4$, AR), potassium permanganate (KMnO$_4$, SP), hydrogen peroxide (30% H$_2$O$_2$, AR), hydrochloric acid (HCl, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. ε-Caprolactam (CP) and 6-aminocaproic acid (BR) were purchased from Sigma-Aldrich Company Ltd. All the agents were used as received without further treatment.

2.2. Synthesis of PGF composites

The preparation process of the PGF composites was shown in Fig. 1. The GO was prepared by the pressurized oxidation method [25]. In a typical procedure, graphite powder, KMnO$_4$, and H$_2$SO$_4$ were put into the Teflon reactor sealed by stainless steel autoclave and kept at 0–4 °C for 1.5 h and then heated at 80 °C for 1.5 h. The obtained mud was diluted with deionized water and the residual oxidizing agents were removed by H$_2$O$_2$. Then the GO was collected after purification, exfoliation and centrifugation. Graphene hydrogel was prepared by hydrothermal method. Ultrasonic for 30 min, 25–35 ml portion of 7 mg/ml GO aqueous dispersion was sealed into a 100 ml Teflon autoclave and heated at 160 °C for 12 h. Subsequently, the hydrogel was washed with deionized water for several times and then freezing-dried at −50 °C for 48 h to obtain the GFs.

PGF composites were prepared by an in situ bulk polymerization process. GF, ε-caprolactam (18 g) and 6-aminocaproic acid (2 g) were put into a three-neck round-bottom flask (100 ml) and was heated under nitrogen flow to 100 °C for 30 min for pre-polymerization of ε-caprolactam and removing the adsorbed water simultaneously. In order to improve the penetration of ε-caprolactam, vacuum air-removed system was applied. Successively, the mixture was heated to 180 °C for 1 h and then to 250 °C for 3–4 h until the reactant was completely solidified. After cooling to room temperature, the cylindrical PGF sample was obtained by cutting out the excess PA6 according to the GF's shape and then washed in boiling deionized water for 5 h to remove the monomer and oligomers and vacuum-dried at 80 °C for 24 h. The PGF samples were then polished to disk or square shapes for characterization according to the test requirement.

2.3. Characterization

The morphology and microstructure of the samples were investigated by Scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan), Fouriertransform infrared (FTIR, AVATAR 370, Nicolet, USA), X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermofisher, UK), Raman (INVIA, Renishaw PLC, UK), X-ray diffraction (XRD, D/max-2200/PC, Rigaku, Japan), and Federal Aviation Administration Micro Calorimeter (FAAMC, PAA-PCFC, FTT, USA). Thermal gravimetric analysis (TGA) was performed on a Netzsch STA409PC simultaneous thermal analyzer. The data of TGA was collected from room temperature to 700 °C with the heating rate of 10 °C/min under nitrogen atmosphere. The λ of PGF composite was measured by a Netzsch LFA 447 Nanoflash at 25 °C.