Composites Part B 84 (2016) 52–58

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Synergic enhancement of thermal properties of polymer composites by graphene foam and carbon black

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A R T I C L E I N F O

Article history:
Received 5 March 2015
Received in revised form
19 August 2015
Accepted 22 August 2015
Available online 3 September 2015

Keywords:
A. Polymer-matrix composites (PMCs)
B. Microstructures
B. Thermal properties

A B S T R A C T

A series of novel polymer composites consisting of graphene foam (GF), carbon black (CB) and polydimethylsiloxane (PDMS) were designed and fabricated. Their microstructures and thermal properties were studied. An excellent dispersion of CB was achieved not only in the space of interconnected GF, but also in the interior of GF arms. Bi-network of thermal transfer path in the composites was made up by GF and CB when CB content reached 8 wt%. The synergic effect of GF and CB on thermal properties was well proved by the good performance of CB and GF co-filled composite. The 8 wt% CB/GF/PDMS composite has much better properties, namely, 222% and 72% higher in thermal conductivity, 40% and 10% higher in storage modulus and much lower weight loss compared to pure PDMS and GF/PDMS composite, respectively. Besides, the long term stability at 100 °C of thermal conductivity proves the applicability of the novel composite. These results signify a promising application as thermal interface materials (TIMs) of the CB/GF/PDMS composite.

1. Introduction

Three-dimensional graphene foam (GF) has attracted tremendous attention for its facile fabrication and processing, special interconnected structure since it was firstly fabricated by Chen et al. using chemical vapour deposition (CVD) technique on nickel foam template [1]. Its special structure and good properties hold great promise for potential applications in many fields such as electromagnetic shielding [2], batteries [3–5], supercapacitors [6–8], enzymeless detection [9], water purification [10], composite material strengthening [11], etc. These attempts mainly take advantage of the high specific surface area, outstanding electrical and mechanical properties of GF.

Pettes et al. [12] found that the thermal conductivity of graphene foam architectures composed of few-layer graphene and ultrathin graphite was increased from 0.26 to 1.7 W m^{-1} K^{-1} by changing the etchant for the sacrificial nickel. Ji et al. [13] filled ultrathin-graphite foams into phase change materials (PCMs), and found that the thermal conductivity increased 18 times compared with paraffin wax, with negligible change in the PCM melting temperature or mass specific heat of fusion. Zhang et al. [14] discovered that the thermal interfacial resistance of GF at Si–Al interface was as low as 0.04 cm^2 kW^{-1}. Li et al. [15] reported that the thermal properties of GF were improved with increasing temperature, which was opposite to carbon materials according to the Umklapp phonon scattering theory. Besides, several studies were carried out on two dimensional graphene filled polymer composites, such as graphite nanoplatelet–epoxy composite, fullerene-decorated graphene filled epoxy composite, graphene/poly(vinylidene fluoride) nanocomposite, graphene nanoribbon filled silicone rubber nanocomposite [16–19], etc. Up to now, the use of graphene foam to fabricate polymer composite is still rare, let alone study of its thermal properties. However, due to the interconnected structure of GF, the thermal transportation path is formed naturally in GF/polymer composite. This means that no percolation phenomenon happens, which is different from the filler filled polymer composite. With this advantage, the GF/polymer composite is expected to have good thermal properties. Furthermore, in order to increase the enhancement to greater extent, high conductive particles can be used to fill matrix just as traditional particulate/polymer composite. Then the latter is incorporated with GF to fabricate a new composite which may be endowed with much better properties due to the synergic effect of GF and fillers.

Carbon black (CB) is commonly used as an additive component in polymer composites for reinforcement of both mechanical and

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http://dx.doi.org/10.1016/j.compositesb.2015.08.074

electrical properties [20–25]. It is known that when the content of thermally conductive particles reaches a critical value called percolation threshold, thermal conductivity of composite quickly rises with the particles touching each other to form a conductive path [26]. Agari and Uno [27] reported that the thermal conductivity of polymer-based composite was elevated largely at around 3 vol% of CB. Kim et al. [28,29] prepared the CB/polymer composite by solvent-free processing which achieved a 73% increase in thermal conductivity at 20 wt% loading compared to that of resin. El-Tantawy et al. [30] found that the percolation threshold of CB was 4 wt% for CB/epoxy composite. When the mass fraction of CB particles was less than 4 wt%, they formed isolated islands within the polymer matrix, and there was no physical contact between them.

Following our previous study on graphene foam filled polymer composite [31], a new type of composite composed of GF and CB as reinforcement and polymer as matrix was originally designed and fabricated in this study. Its microstructures, thermal and dynamic thermomechanical properties were investigated.

2. Materials and experimental methods

2.1. Materials

Nickel foam was purchased from Shanghai Zhongwei Materials Co. Ltd. H_2, Ar and CH_4 were supplied by Beijing Longhui gases Co. Ltd. Hydrochloric acid and acetone were purchased from Beijing Chemical Reagent Factory. Carbon black (CB, Alfa Aesar, America) was used as a kind of filler with the specific surface area of 60–80 $m^2 g^{-1}$ and bulk density of 0.135–0.207 gcm^{-3}. Poly(methyl methacrylate) (PMMA, MwD996,000) and polydimethylsiloxane (PDMS, Sylgard184) were purchased from Sigma Aldrich and Dow Corning, respectively.

2.2. GF preparation

The nickel foam of 1.5 mm in thickness and with a density of 3.9×10^{-2} gcm^{-2} was placed in a quartz tube (inner diameter: 53 mm) fixed in a furnace (SGL-1200, Shanghai Daheng Co. Ltd.). It was heated to 1000 °C in an hour under Ar (500 s.c.c.m.) and H_2 (200 s.c.c.m.) and kept for 20 min. Then CH_4 (12 s.c.c.m.) was introduced at ambient pressure for 10 min. Finally, H_2 introduction was stopped and the samples were cooled to room temperature at a rate of 20 °C/min under Ar (500 s.c.c.m.). PMMA (4 wt% in ethyl lactate) was dip-coated on the samples and solidified at 180 °C for 30 min. Then, hydrochloric acid solution (3 M) was used as an etching agent to dissolve Ni at 80 °C for 4 h. The freestanding GF was finally obtained after removing PMMA with acetone and lyophilized (Alpha 1–2 LD plus, Christ).

2.3. Composites fabrication

In this work, pure PDMS, GF/PDMS and CB/GF/PDMS composites were fabricated. For GF/PDMS composite, the fabrication process was described in detail in our previous work [31]. The only difference is that GF weight fraction is 0.5 wt% in this work, instead of 0.7 wt%. The GF content depends on the graphene growth condition such as time duration, flow of CH_4, etc.

For CB/GF/PDMS composites, CB was added into the base agent of PDMS at ambient temperature and was subjected to high speed mechanical agitation for 30 min. Then curing agent (base agent/curing agent = 10/1 in weight) was added under continuous stirring. The mixture of PDMS and homogeneously dispersed CB was poured into GF, degassed and heated at 80 °C for 4 h in vacuum to get the composites with CB loadings of 2 wt%, 4 wt% and 8 wt%, respectively.

2.4. Characterization

A scanning electron microscope (SEM, S-4800, HITACHI) was used to observe the microstructures of studied materials. The thickness of graphene sheets composing GF was identified using atomic force microscope (AFM, MFP-3D-BIO, AR). Thermal conductivity of samples (diameter: 30 mm, thickness: 1.5 mm) was measured by heat flux method (DRL-III, Hunan Xiangyi Instruments Co. Ltd.) in accordance to ASTM D5470. Compared with laser flash method, the heat flux method is more suitable for analyzing transparent and non-uniform polymer composites with low thermal conductivity. What's more, additional properties such as bulk density and specific heat of materials required in the laser flash method are not needed. During the measurement, an onset pressure of 170 kPa was applied to reduce the effect of thermal contact resistance between the sample and copper bars. Thermogravimetric analysis (TGA, Q600 SDT, TA) was performed to test the thermal stability of samples at a heating rate of 20 °C/min in a nitrogen atmosphere. Dynamic thermomechanical analysis (DTMA, Q800, TA) was carried out on samples of $14 \times 3 \times 1.5$ mm^3 from −140 °C to 20 °C at a heating rate of 3 °C/min, and the stretching amplitude was controlled to 10 μm (0.1% strain) at a frequency of 1 Hz in the tensile configuration.

3. Results and discussions

3.1. Morphology

SEM micrographs of CB, GF, GF/PDMS and CB/GF/PDMS composites are shown in Fig. 1 together with AFM image of graphene sheets composing GF. In Fig. 1a, CB was near spherical and had the diameter of about 100 nm. Three dimensional network of GF could be clearly observed in Fig. 1b. Fig. 1c and d–f give the freeze-fractured surfaces of GF/PDMS and CB/GF/PDMS composites, respectively. From Fig. 1c–f, the hollow arm structure of GF was proved by the existence of PDMS inside GF arms. Besides, there was no obvious gap between the GF wall and PDMS, indicating full filling of PDMS inside both GF arms and GF network. The bright dots shown in Fig. 1d–f were CB particles, dispersed well and more densely not only in the space of GF network, but also inside of GF arms with increasing content of CB. In order to know the thickness of graphene layer of GF, several pieces of graphene sheets were peeled from GF, and the thickness measured with AFM was about 4 nm as shown in Fig. 1g.

3.2. Thermal conductivity

Fig. 2 shows the values of thermal conductivity of all materials studied, which has two fast and one slow rising stages. The first fast rising occurred when GF was introduced into PDMS, i.e., an increase of 88% thermal conductivity was achieved for GF/PDMS composite compared to pure PDMS. With the loading of 2 wt% and 4 wt% CB, the thermal conductivities of CB/GF/PDMS composites increased about 2% and 11% respectively, relative to GF/PDMS composite. It means that the contribution of CB to thermal conductivity is not remarkable at low loading. However, as soon as the CB loading reached 8 wt%, the thermal conductivity jumped by 72% and 222% compared to GF/PDMS composite and pure PDMS, respectively. The second fast rising of thermal conductivity marks the transition of heat transfer mechanisms.

For GF/PDMS composite, the enhancement of thermal conductivity comes from the high conductive graphene foam. However, the graphene foam content was only 0.5 wt% in the GF/PDMS composite, so its contribution was much limited. As the interconnected arm space and graphene thickness of GF are decided by