International Journal of Heat and Mass Transfer 92 (2016) 15–22

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

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

Functionalized graphite nanoplatelets/epoxy resin nanocomposites with high thermal conductivity

Junwei Gu *, Xutong Yang, Zhaoyuan Lv, Nan Li, Chaobo Liang, Qiuyu Zhang *

Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an, Shaan Xi 710072, PR China

ARTICLE INFO

Article history:
Received 7 April 2015
Received in revised form 3 July 2015
Accepted 25 August 2015
Available online 7 September 2015

Keywords:
Thermally conductive nanocomposites
Graphite nanoplatelets (GNPs)
Bisphenol-A epoxy resin (E-51)
Surface functionalization

ABSTRACT

Graphite nanoplatelets (GNPs) are performed to fabricate GNPs/bisphenol-A epoxy resin (GNPs/E-51) nanocomposites with high thermal conductivity via casting method. And the "two-step" method of methanesulfonic acid/γ-glycidoxypropyltrimethoxysilane (MSA/KH-560) is introduced to functionalize the surface of GNPs (*f*GNPs). The KH-560 molecules have been successfully grafted onto the surface of GNPs. The thermal conductivities of the *f*GNPs/E-51 nanocomposites are increased with the increasing addition of *f*GNPs, and the corresponding thermally conductive coefficient of the *f*GNPs/E-51 nanocomposites is improved to 1.698 W/mK with 30 wt% *f*GNPs, 8 times higher than that of original E-51 matrix. The flexural strength and impact strength of the *f*GNPs/E-51 nanocomposites are optimal with 0.5 wt% *f*GNPs. The thermal stabilities of the *f*GNPs/E-51 nanocomposites are also increased with the increasing addition of *f*GNPs. For a given GNPs loading, the surface functionalization of GNPs by MSA/KH-560 exhibits a positive effect on the thermal conductivities and mechanical properties of the nanocomposites.

1. Introduction

Thermal interface materials (TIMs) play an important role in the electronic components area due to the continued miniaturization and light weight [1–3]. Polymers have gained wider applications in different branches of industry because of their light weight, low cost and excellent chemical resistance, etc. [4–7]. However, the intrinsic low thermal conductivities of the polymers have limited their broader applications, especially in the fields of dissipating heat and maintaining operating temperature.

In our previous work, several thermally conductive polymeric composites have been successfully fabricated by adding single or hybrid thermally conductive fillers, such as silicon carbide (SiC) [8,9], aluminum nitride (AlN) [10], boron nitride (BN) [11], graphite nanoplatelets (GNPs) [12,13] and SiC whisker/SiC particle (SiCw/SiCp) [14,15]. However, the improvement of the thermal conductivities of the polymeric composites is often less than expected from previous theory design. Furthermore, to fabricate polymeric composites with highly thermal conductivity, the excessive addition of thermally conductive fillers can create a significant challenge of processing behavior and mechanical properties of the polymers [16].

Epoxy resins possess high mechanical properties, excellent dimensional & thermal stabilities, low cost and easy processing [17–21]. However, the intrinsic low thermal conductivity of epoxy resins has limited their wider application in microelectronic packaging. Graphite nanoplatelets (GNPs) possess super diameter/thickness ratio, and can contact with each other easily inner the polymeric matrix [12,13]. Moreover, the value of thermal conductivity for GNPs is reported to be as high as 3000–5000 W/mK [22,23], similar to that of graphene (theoretical value of 5000 W/mK) [24–26]. However, the price of GNPs is about 65 dollars/kg, much cheaper than that of graphene (more than 500 dollars/kg). Therefore, it is expected that GNPs are suitable for fabricating the epoxy resins nanocomposites with more highly thermal conductivity and a relatively lower cost.

In our present work, graphite nanoplatelets (GNPs) are introduced to fabricate GNPs/bisphenol-A epoxy resin (GNPs/E-51) nanocomposites with high thermal conductivity via casting method. And the "two-step" method of methanesulfonic acid/γ-glycidoxypropyltrimethoxysilane (MSA/KH-560) is performed to functionalize the surface of GNPs (*f*GNPs). The surface performance of pristine GNPs and *f*GNPs are analyzed and characterized by static precipitation, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) and thermogravimetric analyzer (TGA). In addition, the mass fraction and surface functionalization of GNPs affecting on the mechanical properties, thermal

* Corresponding authors. Tel./fax: +86 29 88431621.
E-mail addresses: gjw@nwpu.edu.cn (J. Gu), qyzhang1803@gmail.com (Q. Zhang).

http://dx.doi.org/10.1016/j.ijheatmasstransfer.2015.08.081
0017-9310/

conductivities and thermal stabilities of the nanocomposites are also investigated.

2. Experiments

2.1. Materials

Graphite nanoplatelets (GNPs), KNG-180, with diameter of 40 μm, super diameter/thickness ratio of 250, are received from Xiamen Knano Graphene Technology Co. Ltd. (Fujian, China); Bisphenol-A epoxy resin (E-51), is received from Xi'an Resin Factory (Shaanxi, China); Both methyl hexahydrophthalic anhydride (MeHHPA) and 2, 4, 6-tris (dimethylaminomethyl) phenol (DMP-30), are purchased from Xi'an Hangang Chemical Group Co., Ltd (Shaanxi, China); Methanesulfonic acid (MSA) is received from Chengdu Kelong Chemical Co. Ltd. (Sichuan, China); γ-glycidoxypropyltrimethoxysilane (KH-560) is supplied by Nanjing Shuguang Chemical Group Co., Ltd. (Jiangsu, China); Acetone, ethanol (EtOH) and tetrahydrofuran (THF) are all supplied by Tianjin Fu Yu Fine Chemical Co., Ltd. (Tianjin, China).

2.2. Surface functionalization of GNPs (fGNPs)

GNPs are firstly immerged in EtOH and THF for 24 h at room temperature for each step, then washed by distilled water, and finally dried at 100 °C in a vacuum oven for 24 h; The obtained GNPs are then immersed in 30 wt% MSA/distilled water for 36 h at 80 °C, and then washed by 10 wt% NaOH and distilled water in sequence; The mixtures of obtained GNPs (HO-*g*-GNPs) and KH-560/EtOH/distilled water (1/50/50, wt/wt/wt) are reacted for 6 h at 70 °C. Finally, the MSA/KH-560 functionalized GNPs (*f*GNPs) are washed by EtOH and distilled water in sequence, and finally dried at 120 °C in a vacuum oven for 24 h.

2.3. Fabrication of the nanocomposites

The mixtures of E-51 matrix, MeHHPA, DMP-30 and GNPs are stirred uniformly firstly, degassed in a vacuum vessel to remove air bubbles, and then poured into the preheated glass mold. Finally the mixtures above are cured according to the following technology: 100 °C/1 h + 120 °C/2 h + 150 °C/4 h, followed by post-curing at 190 °C for another 3 h.

2.4. Analysis and characterization

X-ray photoelectron spectroscopy (XPS) analyses of the samples are carried out by K-Alpha equipment (Thermo Electron Corporation, USA) to measure element components on the surface of GNPs and *f*GNPs; Differential scanning calorimetry (DSC) analyses of the samples are carried out at 10 °C/min (nitrogen atmosphere), over the whole range of temperature (40–200 °C) by DSC1 (Mettler-Toledo Corporation, Switzerland); Thermal gravimetric (TG) analyses of the samples are carried out at 10 °C/min (argon atmosphere), over the whole range of temperature (40–800 °C) by STA 449F3 (NETZSCH, Germany); Scanning electron microscopy (SEM) morphologies of the samples are analyzed by VEGA3-LMH (TESCAN Corporation, Czech Republic); Thermal conductive coefficients of the samples are measured using a Hot Disk instrument (AB Corporation, Sweden) by standard method (Isotropic), which is based upon a transient technique. The measurements are performed on two parallel samples by putting the sensor (3.2 mm diameter) between two slab shape samples. The sensor supplies a heat pulse

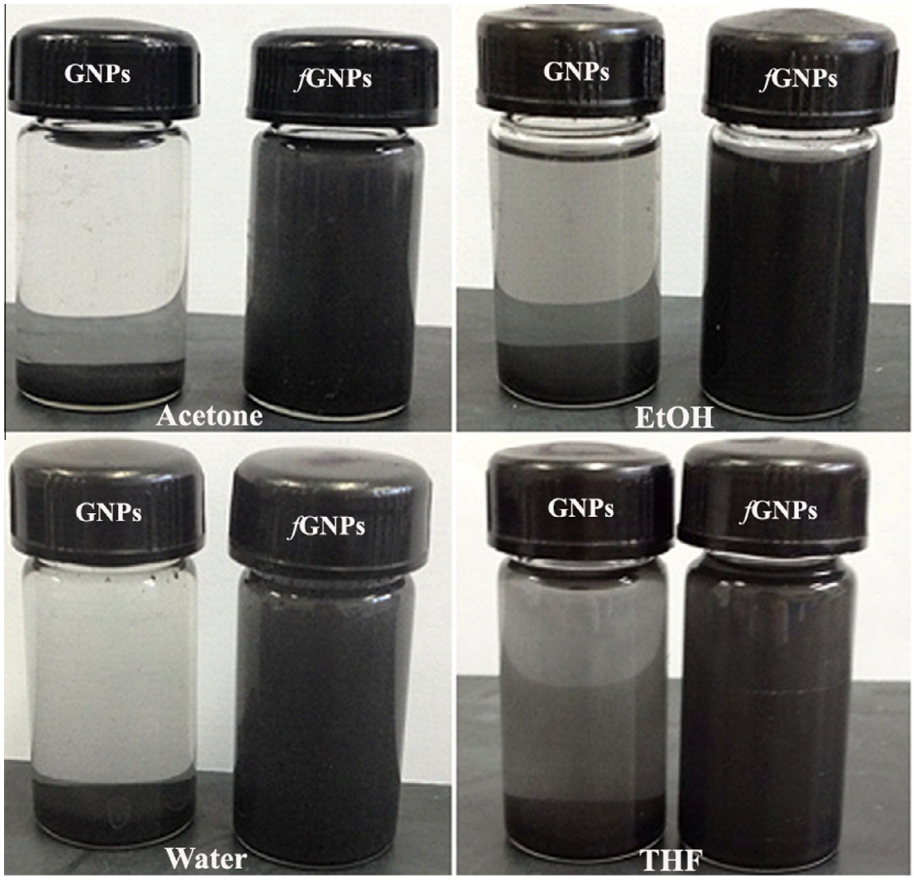

Fig. 1. Dispersion states of pristine GNPs and *f*GNPs in different solvents.