Composites Science and Technology 125 (2016) 17–21

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Thermal properties of epoxy resin based thermal interfacial materials by filling Ag nanoparticle-decorated graphene nanosheets

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ARTICLE INFO

Article history:
Received 10 September 2015
Received in revised form
18 December 2015
Accepted 15 January 2016
Available online 18 January 2016

Keywords:
Functional composites
Thermal properties
Graphene sheets
Silver nanoparticles

ABSTRACT

Epoxy resin based thermal interfacial materials (TIMs) with high thermal conductivity have been obtained by filling Ag nanoparticle-decorated graphene nanosheets (GNSs) as thermal conductive fillers. The thermal conductivity (k) enhancement of epoxy resin based TIMs increases with the thermal filler loading. The more decoration of Ag nanoparticles on the GNS surfaces, the higher thermal conductivity enhancement of epoxy resin based TIM is. It is proposed that the bigger Ag nanoparticles acting as "spacers" increase the distance between the graphene sheets more than the smaller ones. It is not easy for graphene sheets to form stacked graphitic structures and the high specific surface area as well as other unique properties exhibited by 2D graphene are retained. Furthermore, the larger particle size is desired to minimize the scattering of phonons because of low interfacial thermal barrier. The obvious enhancement of thermal properties should be also attributed to the high intrinsic k of graphene and the effective thermal conductive networks forming by graphene and Ag nanoparticles. The synergistic effects including the stronger phonon Umklapp scattering, better phonon transmission trough the interfaces, decreasing Kapitza resistance, and decreasing ability of heat transfer by electrons result in the slight variation of k with the temperature. The weak temperature dependence of k is beneficial for TIM applications and can be obtained by controlling the addition of hybrid thermal fillers and quantity of decorated silver nanoparticles.

1. Introduction

Graphene nanosheet (GNS) as one of nanostructure carbon materials exhibits a unique structure of two-dimensional sheet composed of sp^2-bonded carbon atoms with one-atomic thickness [1]. GNSs have large specific surface area, extraordinary physical properties [2], and strong interactions towards metals [3–5]. Which make it possible that GNSs can be used as supporting materials for dispersing the metal nanoparticles directly on their surfaces. Because of their extraordinary electrical and thermal conductivity (k), thermal stability, and excellent mechanical strength, GNSs and its derivatives are important thermal conductive filler materials for polymer composites [6,7]. This kind of polymer composites with high k are urgently needed for the progress in information, communication, and energy storage technologies. The rapidly increasing power densities in electronics makes it a crucial issue to efficiently remove heat for the performance and reliability of modern electronic, optoelectronic, photonic devices, and systems [8,9]. In the thermal management, it is essential to apply a special material, thermal interface materials (TIMs), between heat sources and heat sinks [10–13]. The attempts of utilizing highly thermal conductive nanomaterials, for example, GNSs as fillers in TIMs, may not lead to practical applications because on drying the graphene dispersion, the isolated sheets aggregate and form an irreversibly precipitated agglomerate, like other dispersions of nanomaterials with high aspect ratios. And the advantage caused by the ultrahigh surface area of 2D GNS is lost. As a result, the aggregated GNS behaves similar to the particulate graphite platelets with relatively low surface area [14]. Si et al. has verified that the introduction of nanoparticles into the dispersion of graphene sheets impeded the formation of a stacked graphitic structure [14]. The metal nanoparticles functioning as a "spacer" increase the distance between the graphene sheets to several nanometers, thereby making both the faces of graphene accessible even in its dry state. It can be deduced that the metal nanoparticles decorating on GNS surfaces also can act as spacers to ensure that the high specific surface area as well as other unique properties

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http://dx.doi.org/10.1016/j.compscitech.2016.01.011
0266-3538/

exhibited by 2D graphene is retained when it is dispersed into polymer materials to form TIMs. Decoration of GNSs with metal nanoparticles (NPs) has also been extensively presented using reducing agents in solution or external electron sources [15–18]. Those widely spread methods do not allow good reproducibility in the fabrication process in terms of number of layers, stacking on the transducer when drying or homogeneous transducer coverage, and thus do not lend themselves easily to mass production [19]. Lin et al. [20] reported a rapid, solventless, and readily scalable method to prepare various metal nanoparticle-decorated carbon nanotubes from the thermal decomposition of metal acetate/carbon nanotube solid mixtures without the use of any reducing agent. This simple but effective "mix-and-heat" method was also successfully applied to various other carbon substrates with the use of many different metal acetates. This reported method makes it possible to prepare TIMs with Ag-GNSs as thermal conductive fillers in mass production.

In this paper, "mix-and-heat" method is applied to prepare Ag-GNSs. Different loadings of Ag nanoparticles on the GNS surfaces are studied. The scanning electronic microscopy (SEM) is applied to obtain the morphology of Ag-GNSs. X-ray diffraction is also employed to characterize the obtained product. The obtained product as thermal conductive fillers is used to prepare epoxy resin based TIMs. The k of TIM samples is tested by using thermal conductivity meter (C-THERM TCI). The results show that the Ag-GNSs are perfect thermal conductive fillers due to lower loading of fillers can make great k enhancement of epoxy resin based TIMs. The weak temperature dependence of k is beneficial for TIM applications and can be obtained by controlling the addition of hybrid thermal fillers and the loading of silver nanoparticles.

2. Experimental

2.1. Synthesis of thermal conductive fillers

The Ag-GNSs as thermal conductive fillers are synthesized by using the reported method [20]. In this report it has realized the decoration of Ag nanoparticles on the surfaces of carbon nanotube, carbon nanofiber, expanded graphite, and carbon black. It also deduces that other metal nanoparticles such as Au, Ni, Co, and Pd also can decorate the surfaces of the mentioned carbon materials. Typically, a certain proportion of silver acetate powders and GNSs with a total weight of 5 g (0.5 mol % Ag loading) are first manually mixed at room temperature via a mortar and pestle. The acetate/GNS mixture is heated in a nitrogen atmosphere above the silver acetate decomposition temperature (about 400 °C). The silver acetate will convert into metal silver and form nanoparticles on the surfaces of the GNSs. The obtained Ag-GNSs can be used as thermal conductive fillers directly.

2.2. Preparation of epoxy resin based TIMs

The direct mixing dispersion method is applied to prepare epoxy resin based TIMs with Ag-GNSs as thermal conductive fillers. A certain amount of Ag-GNSs is dispersed in acetone by using ultrasonic dispersion technology. Subsequently the epoxy resin is added into the acetone dispersion with mechanical agitation and ultrasonic dispersion technology. The obtained dispersion is kept in the vacuum drying oven and dried at 70 °C and vacuum condition. After being dried the epoxy resin based TIMs with Ag-GNSs as thermal conductive fillers are obtained. The composites can be massively prepared at low cost by using this simple method. Furthermore, the thermal conductive fillers can also be uniformly dispersed in the epoxy resin to ensure good micro interfacial contact between the thermal conductive fillers and the epoxy resin.

2.3. Characterization

The morphology of Ag-GNSs is characterized by field-emission scanning electron microscope (SEM) (S4800, Hitachi, Tokyo, Japan). The crystal structure of the obtained samples is studied by X-ray diffractometer (XRD) (D8 Advance, Bruker, Karlsruhe, Germany) equipped with a copper target and nickel filter. X-ray wavelength used in the ananlysis was 0.154 nm of Cu Ka. The thermal conductivities of the epoxy resin based TIMs with Ag-GNSs as thermal conductive fillers are measured by a thermal conductivity analyzer (C-Therm TCi, C-Therm Technologies Ltd., Fredericton, Canada), which is based on the modified transient plane source principle. The TCi thermal conductivity analyzer includes a sensor, power control device, and computer software. A spiral-type heating source locates at the center of the sensor, and the heat generated from the center will enter the materials through the sensor. During this process a voltage decrease occurs rapidly at the heating source, and the voltage decrease data is used to calculate the k of samples. The testing capabilities of the system is 0–100 W/mK across a wide range of temperature (−50 °C–200 °C). The temperature of the test system is controlled by using a constant temperature box (Shanghai Boxun Industry &Commerce Co., Ltd.). For a measurement, the samples were filled into the mould with a thickness of 2 mm. The uncertainty of this test method is estimated to be within ±1.0% resulting from the test instrument. The k of each sample is tested for at least five times to get the average.

3. Result and discussion

3.1. Morphology of Ag nanoparticle-decorated GNSs

The formation of Ag nanoparticles on the GNS surfaces is achieved by using a straightforward "mix-and-heat" process [20] and the SEM images of Ag-GNS nanohybrid with different Ag loadings are shown in Fig. 1. Fig. 1(a) clearly shows that the GNSs are multilayer ones, which supply wide surfaces for depositing Ag nanoparticles. As shown in Fig. 1(b) the average size of the Ag nanoparticles is about 30 nm except several bigger ones as the Ag loading is 0.5 mol %. With the increase of Ag loading, such as 1.0 mol %, the average size of Ag nanopartilces also increases and reaches about 50 nm, which can be seen from Fig. 1(c). The same effect of Ag loading on the average size of Ag nanoparticles also can be seen from Fig. 1(d) with Ag loading 1.5 mol %. The average size of Ag nanoparticles is about 100 nm. And the size of Ag nanoparticles is somewhat uniform. The TEM image result given by Lin et al. [20] identifies that the Ag nanoparticles are grown using the carbon nanotube surface as the template rather than by loose attachment after nanoparticle growth. It can be proposed that Ag nanoparticles also grow on the GNS surfaces.

One sample of Ag-GNS nanohybrid with Ag loading 1.0 mol % is investigated by XRD and the results can be seen from Fig. 2. The result shows typical patterns of Ag metal (JCPDS 04–0783) at 38.0, 44.2, 64.3, and 77.2°, corresponding to the (111), (200), (220), and (311) crystal planes of Ag, respectively. There are no silver acetate diffraction patterns appearing in the spectrum of the final nanohybrids, which suggests that the salt-to-metal conversion was essentially complete. The peak at 26°, corresponding to the (002) GNS graphitic sidewall, suggesting the GNS structure is well preserved.

3.2. Thermal conductivity of TIMs containing Ag-GNSs

The k enhancements of the epoxy resin based TIMs as a function of weight fraction of thermal filler is depicted in Fig. 3. In this article, k and k_0 represent the thermal conductivities of the epoxy