

# Improving the thermal conductivity of epoxy resin by the addition of a mixture of graphite nanoplatelets and silicon carbide microparticles

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**Abstract.** In this work, an alternative type of carbon-based nanofiller, graphite nanoplatelets (GNPs) with comparable properties, easier and lower-cost production, were used to improve the thermal conductivity of an epoxy. By adding 12 wt% GNPs or 71.7 wt% silicon carbide microparticles (micro-SiCs) to epoxy, the thermal conductivity reached maxima that were respectively 6.3 and 20.7 times that of the epoxy alone. To further improve the thermal conductivity a mixture of the two fillers was utilized. The utilized GNPs are characterized by two-dimensional (2-D) structure with high aspect ratio (~447), which enables GNPs effectively act as heat conductive bridges among 3-D micro-SiCs, thus contributes considerably to the formation of a more efficient 3-D percolating network for heat flow, resulting in higher thermal conductivity with relatively lower filler contents which is important for decreasing the density, viscosity and improving the processability of composites. A thermal conductivity, 26.1 times that of epoxy, was obtained with 7 wt% GNPs + 53 wt% micro-SiCs, thus not only break the bottleneck of further improving the thermal conductivity of epoxy composites but also broaden the applications of GNPs.

Keywords: polymer composites, nanocomposites, thermal conductivity, graphite nanoplatelets, silicon carbide microparticles

# 1. Introduction

Graphene nanosheet (GNS), a single layer of hexagonally arrayed sp<sup>2</sup>-bonded carbon, has attracted increasing attention recently due to its excellent thermal, electrical and mechanical properties. However, manufacturing GNS-filled composites has been very challenging due to the difficulties in large-scale production of GNSs and their dispersion in matrices. GNSs tend to form irreversible agglomerates or even restack to form graphite through van der Waals interactions during the processing of bulk-quantity GNSs, especially in the drying process [1]. Carbon nanotube (CNT), another type of widely studied and applied high-performance carbon-based nanofiller, also has great challenges in composite applications especially due to its expensive production cost. Instead of trying to discover easier large-scale processes for GNSs or lower cost processes for CNTs, an alternative type of carbon-based nanofiller with comparable properties, which can be produced more easily and cost-effectively in large quantities, has also recently been emphasized. This type of nano-

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filler is herein referred to as graphite nanoplatelet (GNP), which is a stack of platelet-shaped GNSs but is still in the nanoscale in the thickness direction [2]. Increasing energy dissipation, due to the increasing speed and functionality of integrated circuits, calls for methods to increase the thermal conductivity of materials such as epoxy resins which are widely used in electronic industries. Recently, experimental studies have been stimulated to address the heat transport in the GNP/epoxy composites [3-26], and theoretical analysis, e.g. based on effective medium model [2, 11] and normal modes [27], was also conducted to analyze the effective thermal conductivity of the GNP/epoxy composites. Owing to the high thermal conductivity (250 W/(m·K) in basal plane and 80 W/(m·K) across basal plane at room temperature [3]), two-dimensional (2-D) structure and high aspect ratio of GNP, GNPs were found to be more efficient than carbon black (CB) nanoparticles [3-5], single-walled CNTs (SWCNTs) [4-6] and multiwalled CNTs (MWCNTs) [7, 17] in improving the thermal conductivity of epoxy. So far the reported maximum thermal conductivity of GNP/epoxy composites is 6.6 W/( $m \cdot K$ ) obtained using a 40 wt% loading of GNPs [4].

The synergetic effect of GNPs and other nanofillers in improving the thermal conductivity of epoxy was also observed in the case of low total nanofiller loadings, i.e. 18 wt% total loading of GNPs and CB nanoparticles [14], 1wt% total loading of GNPs and MWCNTs [13], 2 wt% total loading of GNPs and MWCNTs [25] and  $\leq 40$  wt% total loading of GNPs and SWCNTs [4].

The addition of 0-D CB nanoparticles helped to increase the thermal conductivity of GNP/epoxy composites by improving the dispersion of GNPs, preventing the settling of GNPs and bridging the gaps among 2-D GNPs [14]. Long and tortuous 1-D CNTs were used to bridge adjacent 2-D GNPs as well as inhibit the aggregation of GNPs, resulting in a high contact area between GNP/CNT structures and epoxy matrix and thus a more efficient percolating nanofiller network with significantly reduced thermal interface resistances, consequently the thermal conductivity of epoxy filled with a mixture of GNPs and CNTs surpassed that of epoxy filled with pure GNPs or CNTs [4, 13, 25]. However, a further increase of thermal conductivity of epoxy by increasing the total nanofiller loading is hard to realize due

to the increased filler aggregation and interfacial thermal resistance as well as dramatically increased viscosity. Recently, epoxy composites with high nanocarbon (GNPs, MWCNTs, GNPs + MWCNTs) loading up to 50 vol% were got by a well-designed fabrication method, however, the method need a special mixer in which the mixture was stirred with a rotation speed and a revolution speed [26]. Therefore, so far, by the routine fabrication method, the reported maximum thermal conductivity of epoxy filled with GNPs and other nanofillers is 4.7 W/(m·K) (obtained with 30 wt% GNPs + 10 wt% SWCNTs [4]), failing to exceed the aforementioned maximum thermal conductivity of GNP/epoxy composites.

Silicon carbide microparticle (micro-SiC) is an attractive 3-D microfiller candidate for high temperature and high power applications in electronic industries due to its high thermal conductivity  $(\sim 390 \text{ W/(m \cdot K)})$  at room temperature), low thermal expansion coefficient (~4.0 ppm/K, a value close to that of Si chip, ~3.5 ppm/K; 300–673 K), etc [28]. However, improving the thermal conductivity of epoxy by combining 2-D GNPs and 3-D micro-SiCs has not been considered yet. In this work, epoxy filled with a mixture of GNPs and micro-SiCs were prepared, aiming at further improving the thermal conductivity of epoxy, thus not only breaking the bottleneck of further improving the thermal conductivity of epoxy composites but also broadening the applications of GNPs. This paper is part of a large project on the development of heat conductive composites reinforced with micro and nanoscale fillers for more demanding applications, such as in nanoelectronics applications, etc.

# 2. Experimental 2.1. Materials

Epoxy resin used in this work was diglycidyl ether of bisphenol-A (DGEBA) supplied by Shanghai Resin Co. Ltd., China. Curing agent, 2-ethyl-4methylimidazole (EMI-2,4), was supplied by Beijing Chemical Reagent Co. Ltd., China. Amino silane coupling agent,  $\gamma$ -aminopropyl-triethoxysilane (A1100), was obtained from Shanghai Chemical Reagent Co. Ltd., China. Other agents utilized were analytically pure grade and supplied by Sinopharm Chemical Reagent Co. Ltd., China.

 $\beta$ -SiC particles with average particle size of 0.75  $\mu$ m and irregularly polyhedral shape were obtained

from Karl Co. Ltd., China. Micrographs of the micro-SiCs and the micro-SiC/epoxy composite can be seen in our earlier works [29, 30], respectively. Carboxyl-functionalized MWCNTs (COOH-MWCNTs) were provided by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, and used as-received. According to the supplier's specification, COOH-MWCNTs were synthesized by catalytic chemical vapor deposition with 50-80 nm diameter, 10-20 µm length and 125-400 aspect ratio. The purity and the specific surface area were greater than 95% and 40  $m^2/g$ , respectively. Before stored in desiccators, COOH-MWCNTs were dried at 110°C for 24 h in vacuum to eliminate the agglomeration caused by hygroscopic absorption, as well as removing planar water, which would hinder the interaction between coupling agent and COOH-MWCNTs. Micrographs of the rod-shaped COOH-MWCNTs and the COOH-MWCNT/epoxy composite can be seen in our previous work [31].

The starting material for GNPs was graphite intercalation compound (GIC) particles (500  $\mu$ m), i.e. sulfuric acid-intercalated graphite, provided by Xinfangyuan Co. Ltd., China. According to the supplier's specification, the content of intercalants was about 15 wt% and the carbon content was higher than 99%. GNPs were prepared according to the method reported in the literature [32]. Briefly, (a) as-received GIC particles were subjected to a thermal shock on rapid exposure to 1000°C for 20 s in a muffle furnace, causing the GIC particles underwent a significant expansion (~440 times) along the thickness direction since the entrapped intercalants within GIC layers decomposed or vapored instantly, (b) the obtained expanded structures were then dipped in absolute ethanol and then broken down to GNPs using a 30 min high speed shear mixing (2400 rpm) followed by a 12 h ultrasonic irradiation (100 W, 80 kHz), (c) the GNP-absolute ethanol dispersion was filtered and the obtained GNPs were dried at 110°C to remove residue solvents. The asprepared GNPs were then kept in a dry desiccator for testing and further use.

Field emission scanning electron microscope (FESEM) micrographs in Figure 1 show that the asprepared GNPs have flat and smooth morphology besides sharp corners. Image analysis calculation results based on 100 GNPs showed that the as-prepared GNPs have average diameter of 21  $\mu$ m with the range of 3–30  $\mu$ m and average thickness of 47 nm with the range of 20–80 nm. Then the aspect ratio can be calculated to be ~447.

Fourier-transform infrared (FTIR) spectrum of asprepared GNPs, shown in Figure 2, illustrates that there are a lot of hydroxyl groups (–OH, intense band at 3650–3050 cm<sup>-1</sup>) and carboxyl functional groups (C=O, band at 1600–1200 cm<sup>-1</sup>) confirmed to exist on the surface of as-prepared GNPs, indicating that the treatment of natural graphite with sulfuric acid and thermal shock of GICs resulted in some carbon double bonds oxidized, leading to the presence of oxygen-containing functional groups on the GNPs, which will facilitate their interactions with coupling agent or micro-SiCs.



**Figure 1.** FESEM micrographs of GNPs,  $5k \times (a)$  and  $60k \times (b)$ 





Figure 2. FTIR spectrum of GNPs

## 2.2. Surface modification of fillers

Oxidation of micro-SiCs involved (a) dipping micro-SiCs in a 10 vol% hydrofluoric acid solution for 20 min, (b) rinsing with acetone by filtration to remove the passivating thin native oxide film on the surface of micro-SiCs, (c) oxidizing micro-SiCs at 900°C for 20 h in a preheated furnace. The oxidized micro-SiCs were left in the furnace, cooling to room temperature, and then stored in desiccators.

Silane treatment of fillers using A1100 involved (a) making a silane-absolute ethanol solution at 0.001 g/mL concentration, and the amounts of A1100 used were 3% by weight of the micro-SiCs and 10% by weight of the nanofillers i.e. GNPs or COOH-MWCNTs, (b) adding filler particles to the solution and stirring with a high speed magnetic stirrer (1500 rpm) at 60°C for 30 min, in addition, dispersing the solution added with nanofiller particles by high intensity ultrasonication for 1 h, (c) rinsing with absolute ethanol by filtration, and drying at 110°C for 1 h in vacuum. Then the silane treated fillers were stored in desiccators.

#### 2.3. Composite preparation

The composites were prepared by solution blending and casting method, which involved (a) stirring DGEBA-absolute ethanol solution at 80°C with a high speed magnetic stirrer for 20 min, (b) adding appropriate amount of as-prepared or pretreated filler particles to the solution and continuing stir for 30 min, in addition, ultrasonicating the solution added with nanofiller particles for 2 h to ensure good homogeneity, (c) cooling to 60°C, (d) adding EMI-2,4, which is 4% by weight of DGEBA, to the mixture and continuing stir for 10 min, (e) casting the mixture in mould and repeatedly degassing the mixture in vacuum drying oven at 60°C until no air bubble appears on the surface of mixture, (f) curing the mixture at 65°C for 1 h, 120°C for 1.5 h, and 160°C for 1.5 h, (g) cooling to room temperature, then demoulding.

#### 2.4. Characterization

In this paper, morphological studies of GNPs and the fracture surfaces of composites were carried out using FESEM (Quanta 3D FEG, FEI Co., USA; LEO1550, LEO Electron Microscopy Ltd., UK). GNPs were pre-coated with a thin platinum layer. The aspect ratio of GNPs was calculated based on the measured dimensions of 100 GNPs from several FESEM images. Composites were fractured in liquid nitrogen and then the fracture surfaces were coated with a thin platinum layer before FESEM study.

FTIR spectrum was recorded on a Thermo Nicolet IS-10 Smart ITR spectrophotometer (Thermo Fisher Scientific Co., Ltd., USA) with the smart iTR<sup>™</sup> ATR (Attenuated Total Reflectance) accessory.

Thermal diffusivity ( $\delta$ , mm<sup>2</sup>/s) at room temperature was measured on disk samples (12.7 mm diameter, 2 mm thickness) by laser flash method (nanoflash LFA 447 system, NETZSCH Instruments Co., Ltd., UK), specific heat (*C*, J/gK) at room temperature was measured on disk samples (6 mm diameter, 1 mm thickness) by DSC (DSC-7 system, Perkin-Elmer Co., Ltd., UK), and bulk density ( $\rho$ , g/cm<sup>3</sup>) of specimen was measured by water displacement. For each measurement, three samples were tested three times. After that, thermal conductivity ( $\lambda$ , W/(m·K)) was calculated by Equation (1):

$$\lambda = \delta \cdot C \cdot \rho \tag{1}$$

The viscosity of epoxy resin and epoxy composites at room temperature was measured using a stress rheometer (ARES9A, TA Instruments, USA) in a steady flow mode. A cone-and-plate geometry was used. A freshly prepared liquid uncured sample was dispensed on the plate before the run and the experiments were conducted under stepped shear rate from 0.01 to  $100 \text{ s}^{-1}$ .

# 3. Results and discussion

Figure 3 presents the filler content dependence of thermal conductivity of the oxidized and silane



Figure 3. Thermal conductivity at room temperature of oxidized and silane treated micro-SiC/epoxy composites. Lines are given only for showing the tendency

treated micro-SiC/epoxy composites. In this work, micro-SiCs were oxidized followed by silane treatment since it was demonstrated that the ability in improving the thermal conductivity of epoxy follows the sequence: oxidized and silane treated micro-SiC>silane treated micro-SiC>untreated micro-SiC [28]. It can be seen that below the percolation threshold (~52.1 wt%), the thermal conductivity of oxidized and silane treated micro-SiC/ epoxy composites rises slowly with the increasing micro-SiC content because of a lack of continuous micro-SiC heat conductive chains, but above the percolation threshold, the thermal conductivity increases rapidly, and when 71.7 wt% oxidized and silane treated micro-SiCs were added, the thermal conductivity reached the maximum, ~20.7 times that of epoxy.

Figure 4 illustrates the nanofiller content dependence of thermal conductivity of the epoxy composites containing GNPs or COOH-MWCNTs. The thermal conductivity approximately increases linearly with the increasing nanofiller content for all the investigated composites. More importantly, at identically low nanofiller contents (<6 wt%), silane treated GNPs produced epoxy composites with higher thermal conductivities than silane treated MWCNTs despite the inherently lower thermal conductivity of individual GNP (250 W/(m·K) in basal plane and 80 W/(m·K) across basal plane at room temperature [3]) as compared with individual MWCNT (3000 W/( $m \cdot K$ ) at room temperature [33]). There are probably two reasons behind this observation: i) the flat surface of 2-D GNPs dramatically



Figure 4. Thermal conductivity at room temperature of GNP/epoxy composites and COOH-MWCNT/epoxy composites

enhances the GNP/epoxy or GNP/GNP contact area, moreover, the rigidity of 2-D GNPs allows for better preservation of their high aspect ratio in comparison with the more flexible 1-D MWCNTs [4], thus 2-D GNPs are more efficient in forming heat conductive networks in epoxy matrix as compared with 1-D MWCNTs, and ii) in sharp contrast to 1-D MWCNTs, the flat surface of 2-D GNPs minimizes the geometric contribution to the thermal interface resistance since the contribution of phonon acoustic mismatch to the interface contact resistance increases with the decreasing radius of nanoparticles [5]. Furthermore, as shown in Figures 3–4, in comparison with 3-D micro-SiCs, GNPs also provided stronger improvement of the thermal conductivity of epoxy at identically low filler contents (<12 wt%) despite the inherently lower thermal conductivity of individual GNP than micro-SiC (~390 W/(m·K) at room temperature [28]). The reason can be attributed to the special morphology of GNPs as well since it is easier for GNPs characterized by 2-D structure to form heat conductive networks in the epoxy matrix, and besides, the high aspect ratio (~447) of GNPs allows a efficient conduction of phonons over a long distance without transitions from particle to particle, whereas the poor contact of micro-SiCs due to their irregularly polyhedral shape along with a low aspect ratio of nearly unity makes it relatively difficult for them to form heat conductive networks.

As seen in Figure 4, a further increase of MWCNT content (>6 wt%) is hard to realize, whereas GNP content can be further increased. It is known that there is only one dimension, i.e. thickness, of 2-D GNP falling within the nanoscale range, which will

induce less dramatically increased viscosity of uncured composites besides less filler aggregation. Therefore 2-D GNP is more desirable for easier composite fabrication as compared with 1-D MWCNT which has two nanoscale dimensions. In this work the maximum content of GNPs can further increase to 12 wt% and accordingly the maximum thermal conductivity of silane treated GNP/ epoxy composites can reach nearly 6.3 times that of epoxy, exceeding that of silane treated COOH-MWCNT/epoxy composites, 2.9 times that of epoxy, with 6 wt% COOH-MWCNTs.

It is known that a strong interface increases the coupling effect of fillers with matrix, damps the phonons' vibrational amplitude at interface, and thus decreases the efficiency of fillers as thermal conductors in matrix [34], moreover, a layer of coupling agent on the fillers acts as a barrier to the phonon transport between filler particles [14], thus silane treatment of GNPs might be adverse to the improvement of thermal conductivity of the GNP/ epoxy composites. However, the functionalized outside layers of GNPs by silane treatment can promote better dispersion of GNPs in epoxy matrix and facilitate the transport of phonons from GNPs to matrix. Relatively homogeneous-dispersed GNPs are easier to form heat conductive paths than aggregated GNPs, moreover, different from aggregated GNPs, the thermal conductivity in basal plane (250 W/( $m \cdot K$ ) [3]) of well-dispersed individual GNPs will play a more important role than the thermal conductivity across basal plane (80 W/( $m \cdot K$ ) [3]) in determining the final thermal conductivity of composites, so silane treatment of GNPs might also be beneficial to the improvement of thermal conductivity of the GNP/ epoxy composites. However, the final overall effect of silane treatment of GNPs on the thermal conductivity of epoxy arises from the antagonistic competition of the two effects discussed above. Micrographs of 3 wt% untreated GNP or silane treated GNP filled epoxy composites are shown in Figure 5. It can be seen that silane treated GNPs were better dispersed in the matrix, which is believed to contribute to the higher thermal conductivity of GNP/ epoxy composites, whereas the dispersion of untreated GNPs was not so good and more agglomeration of GNPs occurred. However, though the distribution of silane treated GNPs was relatively homogeneous, in Figure 5c-5d naked GNPs are observed on the fracture surface and a number of

GNPs were pulled out of the surface instead of being embedded and tightly held to the matrix, indicating that the interfacial bonding between GNPs and matrix is not so strong, thus it is believed that the efficiency of GNPs as thermal conductors in matrix did not decrease to a considerable extent. As a result, as shown in Figure 4, compared with untreated GNP/epoxy composites, higher thermal conductivity was observed for the epoxy composites filled with silane treated GNPs.

However, the obtained highest thermal conductivity of GNP/epoxy composites is far from being expected. A further increase of thermal conductivity by increasing nanofiller content is hard to realize due to the dramatically increased viscosity and the markedly increased filler aggregation. Methods including ultrasonication, high shear mixing and surface treatment have also already been tried. On the other hand, in order to achieve the percolation threshold and obtain high thermal conductivity, very high microfiller loadings must be used, e.g. 71.7 wt% micro-SiCs, to form as more as possible continuous heat conductive chains in the matrix, but high microfiller loadings result in high density and poor mechanical properties. Thus, issues are emerging, i.e. how to further utilize nanofillers, i.e. GNPs, to improve the thermal conductivity of epoxy composites and how to further improve the microcomposites' thermal conductivity without sacrificing their general properties.

It is noticed that the use of inorganic nanofillers has proven to be effective in reducing the filler content required for relatively high thermal conductivity and thereby minimizing the problems associated with density and mechanical properties, and in this work silane treated GNPs did efficiently improve the thermal conductivity of epoxy with low loadings and thus were considered attractively good nanofiller candidates. To combine the high performance of composite at its low nanofiller content and composite at its high microfiller content (>percolation threshold), it is reasonable to partially replace microfiller with nanofiller and expect higher thermal conductivity of composites resulting from the synergistic effect contributed from nano- and microfillers. In this paper, partial replacement method, which partially replaces micro-SiCs with GNPs, was utilized to break the bottleneck of further improving the thermal conductivity of epoxy as well as broadening the applications of GNPs. As



**Figure 5.** FESEM micrographs of 3 wt% untreated GNP/epoxy composite, 1k× (a) and 20k× (b), FESEM micrographs of 3 wt% silane treated GNP/epoxy composite, 1k× (c) and 20k× (d)



Figure 6. Thermal conductivity at room temperature of epoxy resin and epoxy composites (a), viscosity at room temperature of each uncured systems at  $1 \text{ s}^{-1}$  shear rate (b)

shown in Figure 6a, by adding 5 wt% GNPs + 55 wt% micro-SiCs, the thermal conductivity of epoxy composite reached 7.06 W/(m·K) ( $\sim$ 25.2 times

that of epoxy), exceeding that of 71.7 wt%micro-SiC/epoxy composites and also surpassing the previously reported value (24.3 times that of epoxy [28]) of epoxy filled with 5 wt% COOH-MWCNTs + 55 wt% micro-SiCs.

Furthermore, as shown in Figure 6b, the viscosity of epoxy filled with 5 wt% GNPs + 55 wt% micro-SiCs is 6.5 Pa·s, far lower than that of 71.7 wt% micro-SiC/epoxy composites or the previously reported value (7 Pa·s [28]) of epoxy filled with 5 wt% COOH-MWCNTs + 55 wt% micro-SiCs. Moreover, the viscosity of epoxy filled with 12 wt% GNPs is 7.4 Pa·s, even a little lower than that of epoxy filled with 6 wt% COOH-MWCNTs (7.6 Pa·s [28]), therefore GNPs was demonstrated to have advantage in inducing less increased viscosity of uncured composites as compared with MWCNTs, which is more desirable for easier composite fabrication and can be attributed to the aforementioned fact that only one dimension of GNPs, i.e. thickness, falls within nanoscale range. Then, another further increased thermal conductivity, 7.3 W/(m·K) (~26.1 times that of epoxy), was obtained with 7 wt% GNPs + 53 wt% micro-SiCs (further improved total filler content, i.e. >60 wt%, was avoided in consideration of the general properties, such as density, processability, etc).

FESEM micrograph of epoxy composite containing 7 wt% GNPs + 53 wt% micro-SiCs is shown in Figure 7a. GNPs are shown to be surrounded by quite smaller micro-SiCs. Some naked GNPs are also observed on the fracture surface, indicating that the interfacial bonding of GNP/epoxy or GNP/micro-SiC is not so strong. The thermal conductivity of all composites will be determined mainly by the heat transport of the highly heat conductive filler particles, therefore, the formation of heat conductive 3-D

percolating network in matrix is the key parameter, which influences the value of thermal conductivity of the composites. In this paper, the utilized GNPs are characterized by 2-D structure with high aspect ratio (~447), which enables GNPs effectively act as heat conductive bridges among 3-D micro-SiCs, as illustrated in Figure 7b. This kind of morphology of GNPs contributes considerably to the formation of a more efficient 3-D percolating network for heat flow, resulting in higher thermal conductivity with relatively lower filler contents. As is known, lower filler content is important for decreasing the density, viscosity and improving the processability of composites. Thus, with only a small fraction of GNPs, a mixture filler of 7 wt% GNPs + 53 wt% micro-SiCs provided higher thermal conductivity of epoxy composites in comparison with 71.7 wt% micro-SiCs.

# 4. Conclusions

In this study, 2D-GNPs with high aspect ratio (~447) were used to improve the thermal conductivity of epoxy. By adding 12 wt% GNPs or 71.7 wt% micro-SiCs to an epoxy resin the thermal conductivities of the composites reached maxima that were respectively 6.3 and 20.7 times that of the epoxy alone. To further improve the thermal conductivity a composite designing way, i.e. partial replacement method that partially replaces micro-SiCs with GNPs, was utilized to unite the respective advantage of microfiller and nanofiller in improving the thermal conductivity of epoxy. Epoxy composites with a mixture of GNPs and micro-SiCs were prepared, and a thermal conductivity, 26.1 times that of the



**Figure 7.** FESEM micrograph of epoxy composite containing 7 wt% GNPs + 53 wt% micro-SiCs (a) and schematic of heat conductive network in epoxy matrix containing a mixture of GNPs and micro-SiCs (b)

epoxy, was obtained with 7 wt% GNPs + 53 wt% micro-SiCs, thus not only break the bottleneck of further improving the thermal conductivity of epoxy composites but also broaden the applications of GNPs.

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# References

[1] Yan J., Wei T., Shao B., Ma F., Fan Z., Zhang M., Zheng C., Shang Y., Qian W., Wei F.: Electrochemical properties of graphene nanosheet/carbon black composites as electrodes for supercapacitors. Carbon, 48, 1731–1737 (2010).

DOI: 10.1016/j.carbon.2010.01.014

- [2] Lin W., Zhang R., Wong C. P.: Modeling of thermal conductivity of graphite nanosheet composites. Journal of Electronic Materials, 39, 268–272 (2010).
   DOI: 10.1007/s11664-009-1062-2
- [3] Li J., Sham M. L., Kim J-K., Marom G.: Morphology and properties of UV/ozone treated graphite nanoplatelet/epoxy nanocomposites. Composites Science and Technology, 67, 296–305 (2007).
   DOI: 10.1016/j.compscitech.2006.08.009
- [4] Yu A., Ramesh P., Sun X., Bekyarova E., Itkis M. E., Haddon R. C.: Enhanced thermal conductivity in a hybrid graphite nanoplatelet – Carbon nanotube filler for epoxy composites. Advanced Materials, 20, 4740– 4744 (2008).

DOI: 10.1002/adma.200800401

- [5] Yu A., Ramesh P., Itkis M. E., Bekyarova E., Haddon R. C.: Graphite nanoplatelet–epoxy composite thermal interface materials. The Journal of Physical Chemistry C, **111**, 7565–7569 (2007).
  DOI: 10.1021/jp071761s
- [6] Wang S., Tambraparni M., Qiu J., Tipton J., Dean D.: Thermal expansion of graphene composites. Macromolecules, 42, 5251–5255 (2009). DOI: <u>10.1021/ma900631c</u>
- [7] Lazarenko A., Vovchenko L., Matsui D., Prylutskyy Y., Matzuy L., Ritter U., Scharff P.: Electrical and thermal conductivity of polymer-nanocarbon composites. Molecular Crystals and Liquid Crystals, 497, 65397– 75407 (2008).

DOI: 10.1080/15421400802458522

[8] Ganguli S., Roy A. K., Anderson D. P.: Improved thermal conductivity for chemically functionalized exfoliated graphite/epoxy composites. Carbon, 46, 806–817 (2008).

DOI: 10.1016/j.carbon.2008.02.008

- [9] Hung M-T., Choi O., Ju Y. S., Hahn H. T.: Heat conduction in graphite-nanoplatelet-reinforced polymer nanocomposites. Applied Physics Letters, 89, 023117/1–023117/3 (2006).
  DOI: 10.1063/1.2221874
- [10] Debelak B., Lafdi K.: Use of exfoliated graphite filler to enhance polymer physical properties. Carbon, 45, 1727–1734 (2007).
   DOI: 10.1016/j.carbon.2007.05.010
- [11] Veca M. L., Meziani M. J., Wang W., Wang X., Lu F., Zhang P., Lin Y., Fee R., Connell J. W., Sun Y-P.: Carbon nanosheets for polymeric nanocomposites with high thermal conductivity. Advanced Materials, 21, 2088–2092 (2009). DOI: 10.1002/adma.200802317
- [12] Sun X., Ramesh P., Itkis M. E., Bekyarova E., Haddon R. C.: Dependence of the thermal conductivity of two-dimensional graphite nanoplatelet-based composites on the nanoparticle size distribution. Journal of Physics: Condensed Matter, 22, 334216/1–334216/9 (2010). DOI: 10.1088/0953-8984/22/33/334216
- [13] Yang S-Y., Lin W-N., Huang Y-L., Tien H-W., Wang J-Y., Ma C-C. M., Li S-M., Wang Y-S.: Synergetic effects of graphene platelets and carbon nanotubes on the mechanical and thermal properties of epoxy composites. Carbon, 49, 793–803 (2011). DOI: 10.1016/j.carbon.2010.10.014
- [14] Raza M. A., Westwood A., Stirling C.: Carbon black/graphite nanoplatelet/rubbery epoxy hybrid composites for thermal interface applications. Journal of Materials Science, 47, 1059–1070 (2012). DOI: 10.1007/s10853-011-5895-8
- [15] Saw S. W. P., Mariatti M.: Properties of synthetic diamond and graphene nanoplatelet-filled epoxy thin film composites for electronic applications. Journal of Materials Science: Materials in Electronics, 23, 817–824 (2011).

DOI: 10.1007/s10854-011-0499-2

- [16] Sun X., Yu A., Ramesh P., Bekyarova E., Itkis M. E., Haddon R. C.: Oxidized graphite nanoplatelets as an improved filler for thermally conducting epoxy-matrix composites. Journal of Electronic Packaging, 133, 020905/1–020905/6 (2011). DOI: 10.1115/1.4003988
- [17] Teng C-C., Ma C-C. M., Lu C-H., Yang S-Y., Lee S-H., Hsiao M-C., Yen M-Y., Chiou K-C., Lee T-M.: Thermal conductivity and structure of non-covalent functionalized graphene/epoxy composites. Carbon, 49, 5107–5116 (2011).

DOI: 10.1016/j.carbon.2011.06.095

- [18] Seo J., Cha J., Kim S.: Enhancement of the thermal conductivity of adhesives for wood flooring using xGnP. Energy and Buildings, 51, 153–156 (2012).
   DOI: 10.1016/j.enbuild.2012.05.003
- [19] Raza M. A., Westwood A. V. K., Stirling C.: Effect of processing technique on the transport and mechanical properties of graphite nanoplatelet/rubbery epoxy composites for thermal interface applications. Materials Chemistry and Physics, **132**, 63–73 (2012). DOI: <u>10.1016/j.matchemphys.2011.10.052</u>
- [20] Min C., Yu D., Cao J., Wang G., Feng L.: A graphite nanoplatelet/epoxy composite with high dielectric constant and high thermal conductivity. Carbon, 55, 116–125 (2013). DOI: 10.1016/j.carbon.2012.12.017
- [21] Kim J., Im H., Kim J-M., Kim J.: Thermal and electrical conductivity of Al(OH)<sub>3</sub> covered graphene oxide nanosheet/epoxy composites. Journal of Materials Science, 47, 1418–1426 (2012). DOI: 10.1007/s10853-011-5922-9
- [22] Kim J., Yim B-S., Kim J-M., Kim J.: The effects of functionalized graphene nanosheets on the thermal and mechanical properties of epoxy composites for anisotropic conductive adhesives (ACAs). Microelectronics Reliability, **52**, 595–602 (2012). DOI: 10.1016/j.microrel.2011.11.002
- [23] Chatterjee S., Wang J. W., Kuo W. S., Tai N. H., Salzmann C., Li W. L., Hollertz R., Nüesch F. A., Chu B. T. T.: Mechanical reinforcement and thermal conductivity in expanded graphene nanoplatelets reinforced epoxy composites. Chemical Physics Letters, **531**, 6–10 (2012).

DOI: 10.1016/j.cplett.2012.02.006

- [24] Chatterjee S., Nafezarefi F., Tai N. H., Schlagenhauf L., Nüesch F. A., Chu B. T. T.: Size and synergy effects of nanofiller hybrids including graphene nanoplatelets and carbon nanotubes in mechanical properties of epoxy composites. Carbon, 50, 5380–5386 (2012). DOI: 10.1016/j.carbon.2012.07.021
- [25] He Z., Zhang X., Chen M., Li M., Gu Y., Zhang Z., Li Q.: Effect of the filler structure of carbon nanomaterials on the electrical, thermal, and rheological properties of epoxy composites. Journal of Applied Polymer Science, in press (2013). DOI: 10.1002/app.39096

- [26] Huang X., Zhi C., Jiang P.: Toward effective synergetic effects from graphene nanoplatelets and carbon nanotubes on thermal conductivity of ultrahigh volume fraction nanocarbon epoxy composites. Journal of Physical Chemistry C, **116**, 23812–23820 (2012). DOI: <u>10.1021/jp308556r</u>
- [27] Moussa A. A., Mullen K.: Using normal modes to calculate and optimize thermal conductivity in functionalized macromolecules. Physical Review E, 83, 056708/1–056708/8 (2011).
   DOI: 10.1103/PhysRevE.83.056708
- [28] Zhou T., Wang X., Liu X., Xiong D.: Improved thermal conductivity of epoxy composites using a hybrid multi-walled carbon nanotube/micro-SiC filler. Carbon, 48, 1171–1176 (2010). DOI: 10.1016/j.carbon.2009.11.040
- [29] Zhou T., Wang X., Mingyuan G. U., Liu X.: Study of the thermal conduction mechanism of nano-SiC/ DGEBA/EMI-2,4 composites. Polymer, 49, 4666– 4672 (2008).
   DOI: 10.1016/j.polymer.2008.08.023
- [30] Zhou T., Wang X., Gu M., Xiong D.: Study on mechanical, thermal and electrical characterizations of nano-SiC/epoxy composites. Polymer Journal, 41, 51– 57 (2009).
   DOI: 10.1295/polymj.PJ2008173
- [31] Zhou T., Wang X., Liu X. H., Lai J. Z.: Effect of silane treatment of carboxylic-functionalized multi-walled carbon nanotubes on the thermal properties of epoxy nanocomposites. Express Polymer Letters, 4, 217–226 (2010).

DOI: 10.3144/expresspolymlett.2010.28

- [32] Chen G., Weng W., Wu D., Wu C., Lu J., Wang P., Chen X.: Preparation and characterization of graphite nanosheets from ultrasonic powdering technique. Carbon, 42, 753–759 (2004). DOI: 10.1016/j.carbon.2003.12.074
- [33] Yang D. J., Zhang Q., Chen G., Yoon S. F., Ahn J., Wang S. G., Zhou Q., Wang Q., Li J. Q.: Thermal conductivity of multiwalled carbon nanotubes. Physical Review B, 66, 165440/1–165440/6 (2002). DOI: 10.1103/PhysRevB.66.165440
- [34] Gojny F. H., Wichmann M. H. G., Fiedler B., Kinloch I. A., Bauhofer W., Windle A. H., Schulte K.: Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites. Polymer, 47, 2036–2045 (2006). DOI: 10.1016/j.polymer.2006.01.029