Preparation and Properties of High-Conductive Graphene
Nanosheets Reinforced Epoxy Composites

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Abstract. Due to the growing needs of thermal management in modern electronics, epoxy-based composites are increasingly demanded in heat dissipating materials. A simple preparation of composites with high thermal conductivity was developed through the homogeneously dispersed graphene nanosheets in the epoxy matrix. A high thermal conductivity of 0.4843 W/mK (increased by 184\% over that of pure epoxy) could be obtained for the composites with a filler content of 5wt.\%. It was proved that high aspect ratio of GNPs are critical issues of the constitution of a special interface region between the GNPs and epoxy matrix of the composites. The more than mere additive effect on the through-thickness thermal conductivity suggests synergistic physical interactions between graphene nanosheets leading to further enhancement in the through-thickness thermal conductivity. Thus, the graphene-reinforced composites are promising for usage as an efficient heat spreader for heat dissipation applications.

1. Introduction
Graphene, this strictly two dimensional layers of sp2-bonded carbon, is now a rising star in materials science due to its remarkable thermal, mechanical and electronic properties [1-4]. Graphene was first successfully prepared by Novoselov and colleagues with the mechanical stripping method in 2004 [5]. Since its first isolation, many applications have been proposed for graphene and some of its chemically modified forms. The thermal conductivity of graphene is about 5000 W/(mK) [6], which is a dozen times of copper. Some researches show that graphene with the two-dimensional geometry structure and large specific surface area of could combine with the resin matrix strongly [7-9]. Teng et al. [10] added a small amount of graphene into the matrix, the thermal conductivity of composites improved 37.5\% than the pure epoxy resin. Yu et al. [11] showed the thermal conductivity of composites (6.44 W/(mK)) 25 times of neat after 20wt\% graphene addition. A large number of researches [12-17] showed that the addition of graphene significantly could extend increase the thermal conductivity of composites, and the increase of thermal conductivity increased with the addition of graphene content.

To explore the possibility of improving the through-thickness thermal conductivity property, the graphene reinforced composites were prepared in this paper. Micromorphology, thermal conductivity tests were conducted in order to gain insights into the influence of nano-inclusions on the thermal conductivity of graphene / epoxy laminates.
2. Experiments

2.1. Materials and Preparation of Nano-Composites

The multi-layer graphene (supplied by XG Science) used in this study were prepared by a chemical vapor deposition (CVD) method, and the diameter and the thickness ranged between 2–15µm and 7-15nm, respectively. The layers were ranged between 20-40, according to the microstructure pictures analysis. The multi-layer graphene was shown in Fig.1.

![Figure 1. The micromorphology diagram of multilayer graphene.](image)

The epoxy resin (TDE-85 supplied by Tianjin Jindong Chemical Factory) was added into the plastic beaker, then the as-received multilayer graphene and KH560 with the mass of two times of graphene was added into the above plastic beaker. The epoxy/graphene mixture was initially mixed with a glass rod, followed by stirring through magnetic water bath pot at 80°C. The mixture was further dispersed with the method of ultrasound for 1h and 0.5h under high-speed dispersing machine at 10000r/min. Next, the mixture was cooled to room temperature (about 25°C). Then, the curing agent (T-403 supplied by Suzhou Yinsheng Chemical Co., Ltd.) was added at a weight ratio to epoxy of 30:70 into the above mixture and mixed evenly with a glass rod. Finally, the whole mixture was poured into the mold and degassed for 2h to eliminate the entrapped air at the 40°C. The graphene/epoxy mixture was cured for nano-composites at 80°C1h/110°C1h/135°C2h, then the graphene reinforced epoxy nanocomposites was obtained. The preparation process was shown in the following below.

![Figure 2. The preparation process of graphene reinforced epoxy resin casters.](image)
2.2. Characterization and Thermal Conductivity Testing
The scanning electron microscopy (SEM, Hitachi Japan) was used to observe the microstructure and morphology of nanocomposites. The thermal conductivity testing was measured on a DRH-300 thermal conductivity testing instruments (Xiangtan Instruments Co., Ltd.). The nanocomposites of dimension 270mm long × 270 mm wide × 10mm thick were subjected to between a hot plate and a cold plate. Generally the temperature difference between hot plate and cold plate is 20°C. In this paper, the thermal conductivity was tested under 50°C, so the hot plate temperature was setted at 60°C and the cold plate was setted at 40°C. The instrument would work automatically after the temperature was stabilized. The average thermal conductivity would appear after 20 testing data completed. Then the thermal conductivity testing of nanocomposites was completed.

3. Results and Discussion

3.1 Morphology Analysis of Graphene Reinforced Epoxy Composites
The color of pure epoxy resin caster was yellow and the graphene reinforced epoxy composites was black showed in figure 3, and figure 4. The micromorphology showed that the destruction surface of pure epoxy resin caster was very smooth with the typical brittle fracture and uneven of graphene reinforced epoxy composites. Moreover, the uniform dispersion of graphenenanosheets and interface bonding between graphenenanosheets and matrix could be clearly observed. The good interface bonding between graphenenanosheets and matrix could reduce the thermal resistance of the interface in order to facilitate heat transfer. The graphenenanosheets were not closely connected together after adding 1wt% graphenenanosheets, because the low-concentration graphenenanosheets were uniformly distributed in the composites. And the graphenenanosheets were closely connected each other with the higher concentration. And when the concentration of graphenenanosheets was 5%, they piled up together closely without the fluffy feel of low concentration. The effective contact between graphenenanosheets may improve the thermal conductivity of composites sharply.

Figure 3. Physical drawing of pure epoxy resin caster.  
Figure 4. Pictures of graphene reinforced composites.  
Figure 5. Micromorphology of pure epoxy resin caster.
Figure 6. Micromorphology of graphene reinforced composites.

3.2. Thermal Conductivity

Table 1. Thermal conductivity of composites with different concentration of graphene nanosheets

| Materials | Concentration (wt%) | Thermal conductivity (W/(m·K)) | Increasing amplitude(%) |
|-----------|---------------------|-------------------------------|------------------------|
| EP        | 0                   | 0.1702                        | -                      |
| GR01-1    | 1                   | 0.2313                        | 35.90                  |
| GR02-1    | 2                   | 0.2995                        | 75.97                  |
| GR03-1    | 3                   | 0.3572                        | 109.87                 |
| GR05-1    | 5                   | 0.4843                        | 183.55                 |

Figure 7. The coefficient of thermal conductivity of composites.
From the Table 1 and Figure 7, it is shown that the thermal conductivity of composites was increased with the increasing concentration of graphene nanosheets. And when the adding concentration was 5%, the thermal conductivity could increase up to 0.4843 W/(m·K) and 1.84 times of pure epoxy resin caster. Moreover, the thermal conductivity was minor promotion with the low concentration of graphene nanosheets and jumped sharply when the concentration was 5%, and it could also be reflected from the above micromorphology. Percolation theory could explain the thermal conductive property of graphene. A critical probability $P_c$ exists in the network. The isolated node clusters make up the network when the probability is under $P_c$. With the probability increases and it is more than the $P_c$, the nodes form the larger cluster in the entire network. The thermal conductivity of composites increases with the graphene nanosheets concentration increasing. And the thermal conductivity of composites will be greatly improved when the graphene nanosheets interconnect to form the conductive network path, which the concentration of graphene is up to a critical point. When the matrix consists of a small quantity of graphene nanosheets, the graphene nanosheets separate from each other and they could not form effective transmission path to transmit heat rapidly. Therefore the promotion of the thermal conductivity of composites is not obvious. They are formed the thermal conductive pathway with an effective contact between each other with the graphene concentration reaches up to the threshold. Then the transmission path could form through the graphene nanosheets quickly without the matrix, so the thermal conductivity of composites can jump sharply. And the thermal conductivity of composites will continue to increase with the graphene concentration increasing.

4. Conclusions

In this study, thermal conductive composite materials were fabricated successfully. Graphene nanosheets were characterized by HR-TEM and the composites with graphene nanosheets were characterized by SEM. The micromorphology demonstrated the graphene nanosheets were uniformly dispersed in the composites. And the interface bonding between the graphene nanosheets and the matrix showed very strong. The thermal conductivity of the fabricated epoxy composite containing graphene nanosheets was examined as a function of the graphene concentration. The results revealed that the thermal conductivity of the composites increased with the amount of graphene increasing. And the maximum thermal conductivity ($0.4843 W/(m·K)$) was obtained with the addition of about 5 wt.% graphene nanosheets, 2 times of pure epoxy resin approximately. This significant improvement in the thermal conductivity of composites containing graphene nanosheets was better than traditional fillers. The more than mere additive effect on the through-thickness thermal conductivity suggested synergistic physical interactions between graphene nanosheets leading to further enhancement in the through-thickness thermal conductivity.

5. References

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