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Optimization of Hybrid Filler in Thermally Conductive Composite Formation

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Carbon nanotubes, alumina and carbon black were combined with graphite nanoplatelets in an epoxy resin in order to reach compromise between increase in thermal conductivity and composite formation. The results confirm that carbon nanotubes with a fiber structure can enter the boundary between adjacent graphite nanoplatelets and can construct an effective thermally conductive network. The carbon nanotubes-graphite nanoplatelets/epoxy composite was also found to exhibit improved moldability compared with solo graphite nanoplatelets filler content. Alumina-graphite nanoplatelet/epoxy and carbon black-graphite nanoplatelet/epoxy composites both exhibited good moldability, but the aggregate shapes from spherical particles in alumina and carbon black were unfavorable due to the increase in thermal conductivity.

Keywords: Composites, Molding, Synthesis, Processing.

1. INTRODUCTION

Composite/hybrids consisting of two or more constituent materials with significantly different physical or chemical properties have attracted attention in the rapidly growing area of current materials research. The characteristics of these composites will be different from the individual components which remain separate and distinct. Polymer matrix composites are plastics in which reinforcements are embedded. The most commonly used composite reinforcement materials are fibers, particles and layered materials. Although high strength-to-weight ratios provide polymeric composites with a range of potential advantages over conventional materials and makes them popular for industrial use, but present challenges still exist in design and formation.

To overcome the problems associated with heat dissipation in the electronics industry, thermal interface materials (TIMs) based on polymers filled with thermally conductive reinforcements have been explored. In general high fractions of thermally conductive filler such as silver, alumina, or silica are required to achieve high thermal conductivity at room temperature in conventional TIMs.[1,2] Among the candidates for improving performance of polymeric composites, carbon nanotubes (CNTs) and grapheme have been utilized as efficient fillers because of their superior properties in previous studies.[3–8] However, the practical application of carbon nanotubes as fillers in TIMs must still be improved in order to address weak thermal coupling at the carbon nanotube/matrix interface and the difficulty in homogeneously dispersing the carbon nanotubes in the polymer matrices.[9] The current interest in the extraordinary electronic properties of graphene has offered an alternative for to TIMs. Graphene can be described as a one-atom thick layer of graphite. An optimized mixture of graphene and multilayer graphene was reported to lead to an extremely strong enhancement of the cross-plane thermal conductivity of a composite. It was also determined that a relatively high concentration of single-layer and bilayer graphene flakes must exist simultaneously with a thicker multilayers of large lateral size to attain the observed unusual thermal conductivity enhancement.[9] Graphite nanoplatelets (GNP) prepared from thermally exfoliated natural graphite, as efficient fillers for epoxy composites, can also provide a substantial enhancement of thermal conductivity enhancement.[10] A sheet-form layered structure allows graphite nanoplatelets form an ideal

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thermally conductive skeleton in the polymeric composites, but such structure is not beneficial for the moldability of a composite compared with a fiber or particle structure. Interestingly, a synergistic effect arising from the combination of different fillers in polymeric composites has been confirmed. A hybrid filler indicates that two or more traditional filler materials were used by combining the advantages of the different materials. Such new family of composite with hybrid filler exhibits improved composite performance compared with corresponding single filler system.[11–16] The use of hybrid filler was found to be effective in increasing the thermal conductivity of composites, which is likely due to the enhanced connectivity offered by structuring filler with high aspect ratio in hybrid filler.[17]

This study combines carbon nanotubes (superior thermal conductivity), alumina (moderate thermal conductivity) and carbon black (poor thermal conductivity) with graphite nanoplatelets to form hybrid fillers. We investigate the optimization of the graphite nanoplatelet-based hybrid fillers in epoxy resin to reach a compromise between increase in thermal conductivity and composite formation.

2. EXPERIMENTAL DETAILS

2.1. Materials and Characterization

The epoxy resin used in the experiment was a Bisphenol-A type liquid epoxy resin (0174-type, Wuxi Resin Factory, China). The curing agent was a low molecular polyamide (651-type, Beijing General Research Institute of Mining and Metallurgy), and the carbon nanotubes (multi-wall) were provided by Chengdu Institute of Organic Chemistry. Carbon black particles were purchased from the Guangzhou Sunny Plaza Trading Co., LTD. Alumina powders and acetone were supplied by the Beijing Chemical Company. Natural graphite was purchased from the Aldrich company.

The SEM (Scanning Electron Microscope) were conducted on a HITACHI SU8020. Raman spectra of the prepared composites were recorded on a Labraw HR Evolution from the HORIBA International Corporation. The thermal conductivity was obtained from a thermal

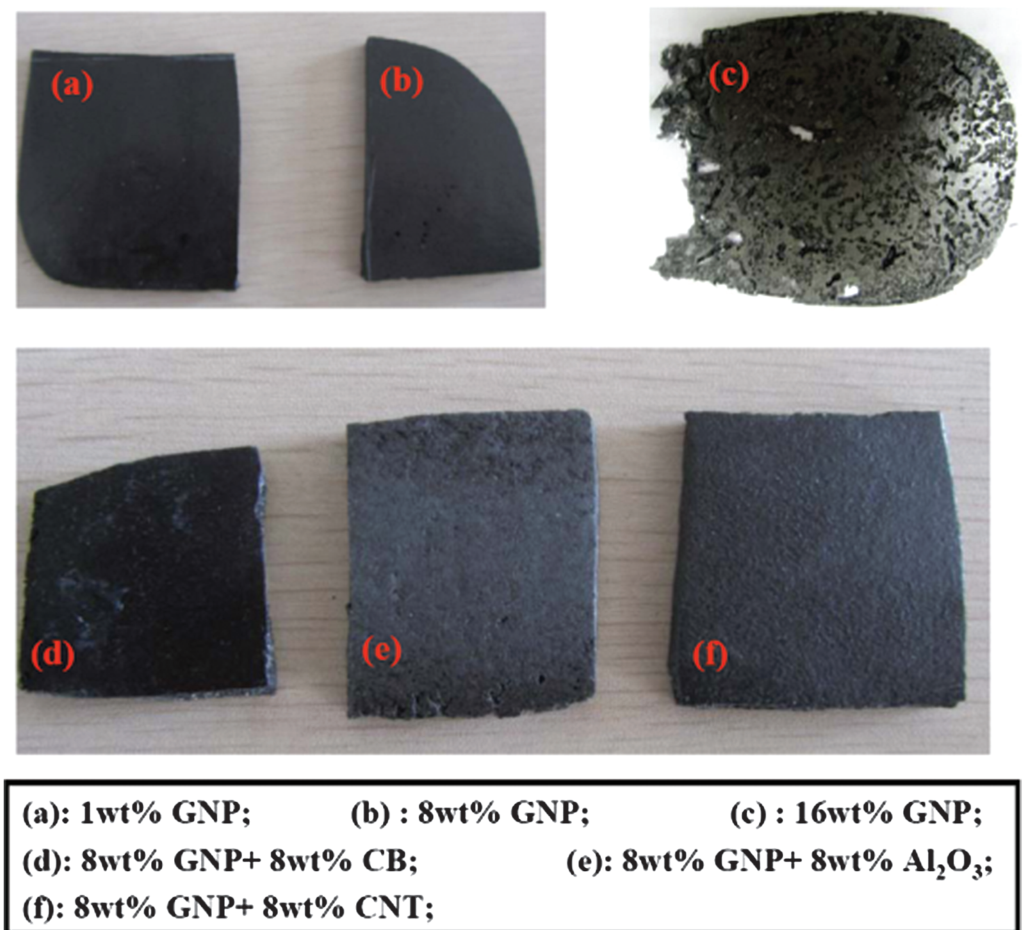

Fig. 1. Pictures of the final composite samples with different fillers; (a): 1 wt% GNP; (b): 8 wt% GNP; (c) 16 wt% GNP; (d): 8 wt% GNP and 8 wt% carbon black; (e): 8 wt% GNP and 8 wt% alumina; (f): 8 wt% GNP and 8 wt% carbon nanotube.

conductivity detector (TC3010, the Xi'an Xiaxi Electronic Technology Co., Ltd.)

2.2. Preparation of Graphite Nanoplatelets

Preparation of the graphite nanoplatelets (GNP) was based on existing experimental procedure.[18] Natural graphite flakes were intercalated in a mixture of concentrated sulfuric and nitric acids (3:1) and treated overnight at room temperature in order to get intercalated graphite. The acid-treated natural graphite was washed and dried to remove any remianing water. Then air-dried natural graphite was then exfoliated by thermal shock through a rapid exposure to 800 °C in nitrogen. The exfoliated graphite nanoplatelets were immersed in acetone in an ultrasonic bath for 10 h and retained for further use.

2.3. Composite Processing

To fabricate monoliths of the GNP-based epoxy thermally conductive composites, the epoxy resin and the fillers were both immersed in acetone to decrease viscosity and allow fillers more homogeneous dispersion of the fillers under continuous strong stirring. The mixture was heated to 60 °C to remove the acetone until the curing agent was added. Finally the mixture was cast into a plate mold, degassed and heated in a vacuum for curing in an oven at 75 °C for 12 h.

3. RESULTS AND DISCUSSION

3.1. Filler Optimization in Composite Formation

Figure 1 presents the final composite samples with different fillers. Composites with only GNP as thermally conductive fillers are shown in Figures 1(a)–(c). Smooth surface and excellent moldability were observed in the samples with 1 wt% and 8 wt% GNP fillers. When the content of GNP fillers increases to 16 wt%, moldability becomes difficult as indicated in Figure 1(c). To maintain good moldability of the composite, hybrid fillers were utilized and the samples were displayed in Figures 1(d)–(f).

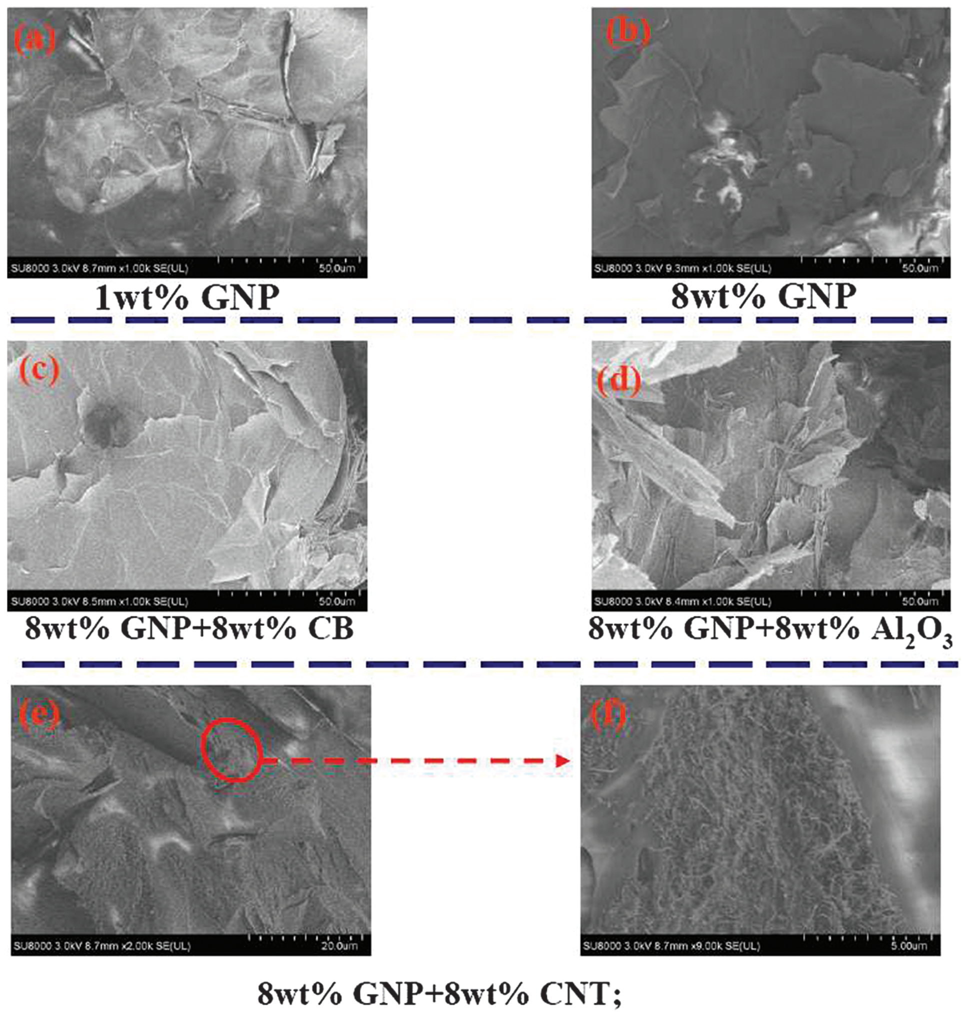

Fig. 2. SEM images of the fracture surfaces of epoxy composite; (a): 1 wt% GNP; (b): 8 wt% GNP; (c): 8 wt% GNP and 8 wt% carbon black; (d): 8 wt% GNP and 8 wt% alumina; (e): 8 wt% GNP and 8 wt% carbon nanotube with different scale bar.

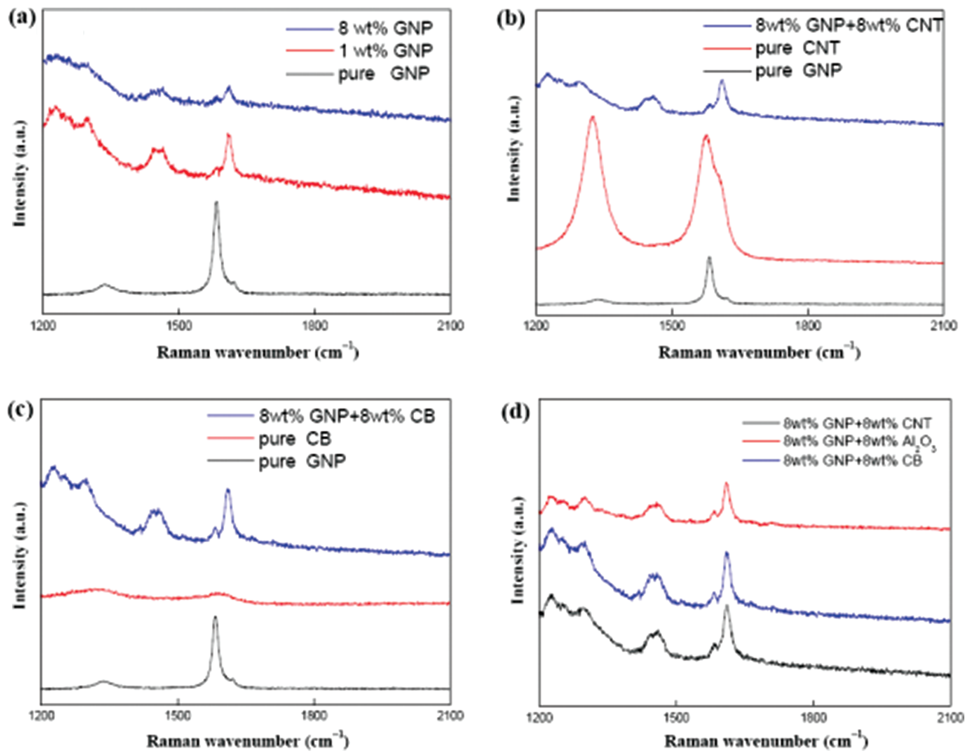

Fig. 3. Comparison of Raman spectra between fillers and composites; (a): only GNP filler and its composite; (b): GNP, carbon nanotube filler and its composite; (c): GNP, carbon black filler and its composite; (d): composits with diffeent hybrid fillers.

The 8 wt% GNP and 8 wt% other fillers were used together to maintain moldability and increase thermal conductivity. The results reveal that the moldability with the same content fillers was improved for the hybrid fillers compared with those of the pure GNP fillers.

3.2. SEM Characterization

Figure 2 shows SEM images of the fracture surfaces of the epoxy composites with only GNP fillers (a and b) and hybrid fillers (c, d and e). The results reveal that the GNP fillers randomly dispersed in the epoxy matrix and an obvious boundary was observed between adjacent GNP. When alumina and carbon black particles were combined with GNP as hybrid fillers, the internal structure of the composites did not significantly change. For the composite with GNP and carbon nanotubes as hybrid fillers, the boundary between adjacent GNP was filled with carbon nanotubes as shown in Figure 2(e).

3.3. Raman Spectra

Raman spectra of these composite samples were recorded and are shown in Figure 3. Distinctive peaks at approximately 1330 and 1580 representing the *D* band and *G* band in the GNP and carbon nanotubes were confirmed. In the final composites, the peak attributable to *D* band disappears (neither weak intensity for GNP, nor strong intensity for carbon nanotube) and an upshift of the *G* band was indicated (Figs. 3(a–c)). The disappearance of the *D* band and the upshift of the *G* band may be a consequence of strong forces associated with the epoxy matrix on the fillers.

3.4. Thermal Conductivity

The thermal conductivity of the different composites is shown in Figure 4. The results clearly confirm the improvement of thermal conductive performance of the composites with increasing GNP content (from 0.28 W/mK for 1 wt% GNP to 1.08 W/mK for 8 wt% GNP). Compared with the

	A	B	C	D	E
Composition	1 wt% GNP	8 wt% GNP	8wt% GNP + 8wt% CNT	8wt% GNP + 8wt% Al_2O_3	8wt% GNP + 8wt% CB
Thermal Conductivity (W/mK)	0.28	1.08	1.7	1.04	0.8

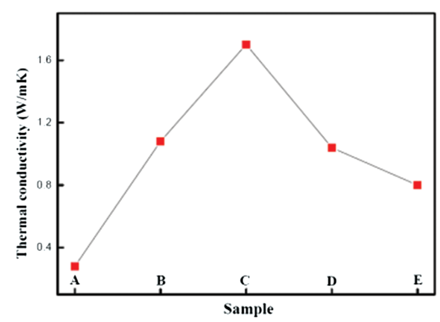

Fig. 4. Thermal conductivity of different composites.

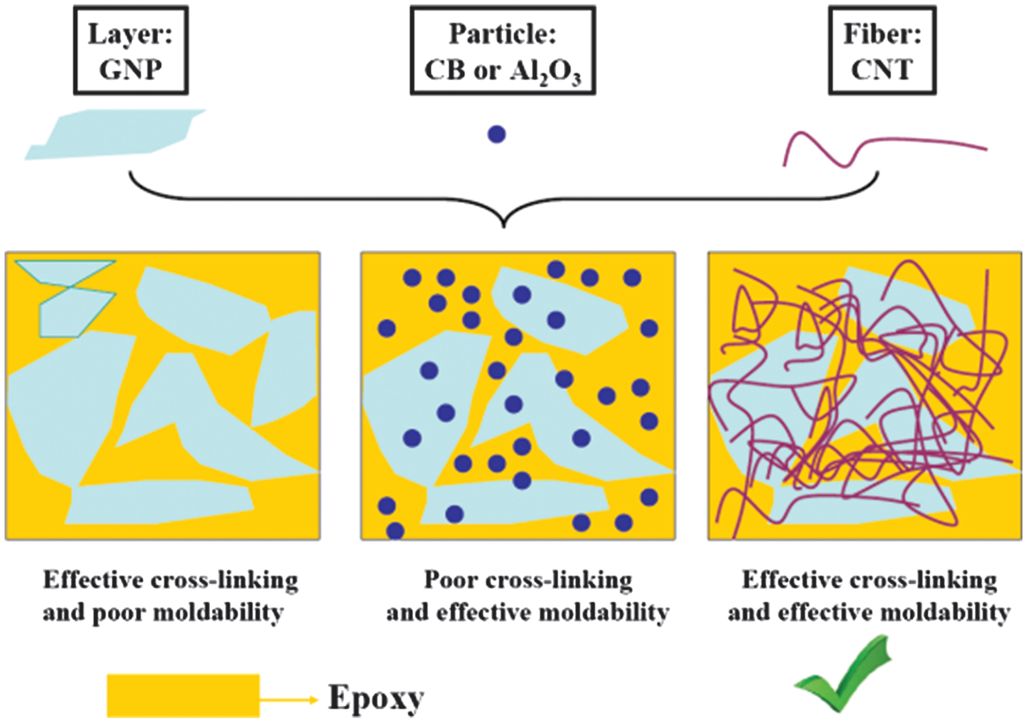

Fig. 5. Schematic representation of thermally conductive fillers with different structures (layer, particle and fiber) in epoxy matrix.

thermal conductivity for the composite with only 8 wt% GNP fillers, the change is slight for the composite with 8 wt% GNP and 8 wt% alumina hybrid fillers (1.04 W/mK) and even decreases for the composite with 8 wt% GNP and 8 wt% carbon black hybrid fillers (0.8 W/mK). The thermal conductivity was effectively enhanced to be 1.7 W/mK for 8 wt% GNP and 8 wt% carbon nanotube hybrid fillers. Based on these results, graphite nanoplatelets and carbon nanotube hybrid fillers in epoxy resin can achieve a compromise between increase in thermal conductivity and composite formation. The key for preparing high thermally conductive composite is to construct an effective thermally conductive network and decrease the thermal interface resistance between the fillers. Figure 5 illustrates the schematic representation of these thermally conductive fillers in an epoxy matrix. It is certain that GNP is one of the best choices because of its high thermal conductivity and high volume/mass ratio. An effective thermally conductive network can form in a polymer matrix using GNP fillers, but its sheet-form layered structure is not well suited for composite formation. Although particle fillers can have good moldability, they can not effectively form a cross-linking network with GNP effectively and are not ideal for increasing thermal conductivity. As shown in Figures 2(e) and (f), carbon nanotubes can enter the boundary between adjacent GNP and construct an effective thermally conductive network through their fiber structure. Carbon nanotube-graphite nanoplatelets/epoxy composite also exhibit good moldability. Our results confirm that the optimization of hybrid fillers can reach a compromise between an increase in thermal conductivity and composite formation.

4. CONCLUSION

In summary, graphite nanoplatelets can be used as primary fillers to construct effective thermally conductive skeleton in epoxy composites and optimization of hybrid fillers can achieve a compromise between an increase in thermal conductivity and composite formation. A synergistic effect arising from the combination of different fillers in epoxy composites was confirmed to be an economical solution for the development of thermal interface materials.

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