

ENHANCED THERMAL CONDUCTIVITY OF EPOXY BASED COMPOSITES WITH SELF-ASSEMBLED GRAPHENE-PA HYBRIDS

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ABSTRACT

A high thermal conductivity epoxy-base composite was fabricated via self-assembly of PA microparticles and thermal reduced graphene at 900°C (TrGO-900). The spontaneous self-assembly was ascribed to electrostatic adsorption between PA and TrGO. It was found that the thermal conductivity of the obtained composites increased by 28% than the pure resin when the loading of graphene-PA hydrides was 5 wt%. By contrast, the addition same amount of TrGO-900 (0.5wt%) thermal conductivity of the composite increased by 5%. The increase is attributed to improved phonon conduction pathways and more uniform dispersion for the TrGO-900/PA hydrides in the resin.

1 INTRODUCTION

With the development of large scale integrated circuit and micro encapsulation technology, thermal dissipation of electronic components become more and more important [1,2]. High thermally conductive composites have attracted extremely attention recently due to heat dissipation performance. Conventionally thermally conductive composites used thermal fillers including ceramics (AlN [3], BN [4], etc.), metals (Ag, Cu, etc.), metal oxides (Al₂O₃ [5], Fe₃O₄, etc.). But the loading fraction of the fillers exceed 50% is required to composites with satisfactory thermal conductivities. Owing to intrinsic extremely high thermal conductivity of graphene, graphene-based composites are promising candidates for high-performance thermal interface materials.

The graphene has shown higher efficiency in increasing the thermal conductivity of composites than others fillers [6]. Graphene has extremely high intrinsic thermal conductivity, theoretical simulations and experimental results demonstrate that the thermal conductivity of graphene is as high as 6000 W·m⁻¹·K⁻¹. However it tends to agglomerate, leads to poor dispersion and high interface thermal resistance in epoxy resin [7]. But graphene is expected to replace others fillers.

In our previous work [8-9], the incorporation of epoxy/PA/MWNT-EP membranes substantially improved the dispersion state of MWNT-EP in epoxy resin due to electrostatic self-assembly between MWNT-EP and PA. Also graphene possessed negatively charged surface as same as MWNT-EP. Therefore the self-assembly hybrid fillers fabricated by graphene and PA microparticles would improve the dispersion state and reduce interface resistance of graphene in epoxy resin. the self-assembly hybrid filler of thermal reduction of graphene oxide (TrGO) - polyamides (PA) were directly dispersed in the epoxy resin and the high thermally conductive TrGO/PA modified epoxy composites (GPEP) was fabricated.

2 EXPERIMENTAL

2.1. Materials

The graphite oxide (dimension 1~5 μm) was supplied by Nanjing XFNANO Materials Tech Co.Ltd. The PA microparticles (particle size 20 μm) were supplied by Arkema, France. The epoxy resin (EP, and diglycidyl ether of bisphenol A) was provide Shanghai Huayi Resin Co.Ltd. 3-Aminomethyl-3,5,5- trimethylcyclohexanamine (IPDA) was provided by Aladdin Industrial corporation. Acetone and dichloromethane (CH_2Cl_2) were purchased from Beijing Chemical Agent Co.

2.2. Preparation of hybrid filler

Graphene oxide was prepared from ultrasonic agitation and freeze drying, the as-prepared graphene oxide was placed into a tube furnace and at 900°C for 3h and the obtained production was named as TrGO-900. Subsequently, TrGO-900 was dispersed in acetone ultrasonic agitation for 1h and mixed with PA by a mechanical mixer for 1h. The hybrid filler obtained through self-assembly of TrGO and PA microparticles.

2.3. Composite preparation

The epoxy were added to the mixture solutin and mixed using a high speed shear mixer for 30 min to obtain good homogeneity. The mixture was degassed in a vacuum oven at 60°C until all solvents were evacuated. Then, the IPDA agent (100:23) was added and slurry was stirred for 10 min. The curing condition was 1 h at 80°C , 1 h at 150°C . Four types of composites were prepared: neat epoxy, TrGO/EP, and TrGO/PA/EP.

3 RESULTS AND DISCUSSION

Fig.1 shows the dispersion behavior of the TrGO, PA and the self-assembly hybrid filler in CH_2Cl_2 . The PA microparticles separated and suspended in the upper layer of the solvent, due to great difference in density and polarity between PA and CH_2Cl_2 . The graphene evenly dispersed in the organic solvent. The mixture of TrGO and PA were also found separated and suspended in the upper layer of the solvent. This evidence suggested adsorption force between TrGO and PA.

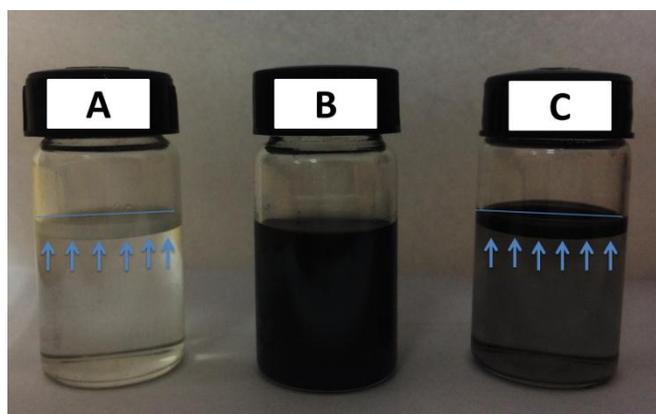


Figure 1. Dispersion behavior of A PA microparticles, B.TrGO, C.mixture of TrGO and PA

Fig. 2a shows the FT-IR spectra of the GO and TrGO-900. The bands at 1058 cm^{-1} , 1390 cm^{-1} and 1738 cm^{-1} indicated the presence of oxygen-containing functional groups of GO corresponding to

C-O-C stretching, C-OH deformation and C=O stretching, respectively. The broad absorption band at 3400 cm^{-1} indicates the presence of the O-H groups, and the peaks at 1630 cm^{-1} were assigned to the skeletal vibrations of the unoxidized graphitic domains. However, oxygen-containing functional groups had been almost entirely removed during reduction with the thermal treatment at 900°C .

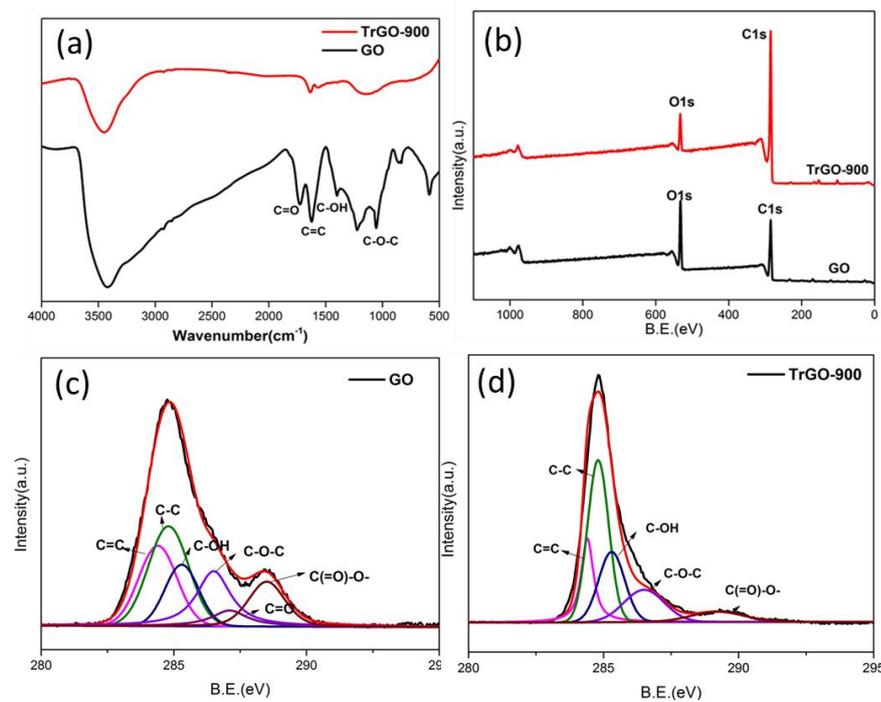


Figure 2. (a) The FT-IR spectra of GO and TrGO-900, (b) XPS survey, the C1s spectra of GO (c) and TrGO-900 (d)

XPS spectra were examined the elemental composition and bonding configuration between GO and TrGO-900. As shown in Fig. 2b, GO and TrGO-900 are composed of two typical peaks, which are C1s and O1s. The C/O atomic ratio values of TrGO-900 calculated from the peak area of C1s to O1s show significantly increase (from 2.55 in GO to 9.99 for TrGO-900). As depicted in Fig. 2c, the C1s XPS spectrum of GO clearly indicates a considerable degree of oxidation with four components that correspond to carbon atoms in different functional groups: the C in C-OH bonds (285.3 eV), the C in C-O-C (286.5 eV), the carbonyl C (287.1 eV) and the carboxylate carbon (O-C=O). However, in the XPS spectrum of TrGO-900, the peaks of the oxygen-containing groups are greatly weakened in intensity and the carbonyl C is disappeared (Fig. 2d).

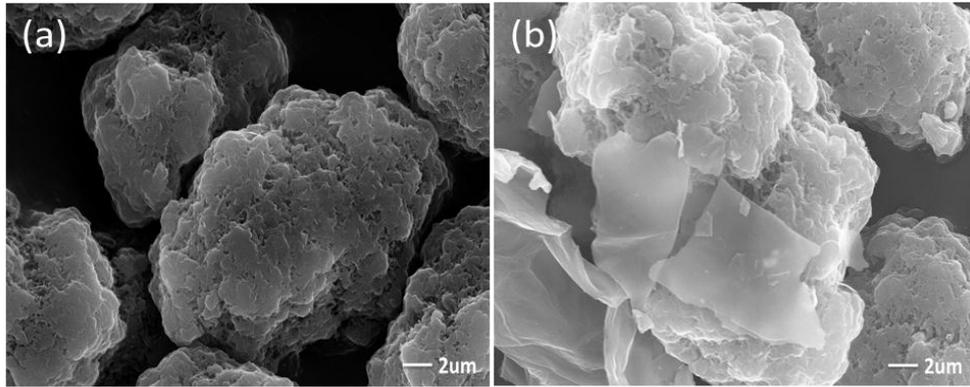


Figure 1. SEM image of PA (a) and graphene-PA hydrides

The surface morphologies of graphene-PA hybrids together, Fig. 3 shows that pristine PA microparticles was anomalous spherical with many holes on the surface and an average size of about 20 μm . Through self-assembly of graphene and PA microparticles, graphene were absorbed on the surface of PA microparticles.

Specimen(wt%)	Thermal conductivity (w/m.k)
Neat epoxy	0.175
TrGO-900(0.5)	0.183
TrGO-900/PA(0.5:5)	0.224

Table 1 Thermal conductivity of composites

Table 1 shows the thermal conductivity of epoxy, TrGO-900/epoxy and TrGO-900/PA/epoxy composites. As can be seen, pure epoxy resin had a low thermal conductivity of $0.175 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. After the addition of filler, TrGO-900 or TrGO-900/PA hydrides, the thermal conductivity increased significantly. Particularly, the thermal conductivity of TrGO-900/PA hydrides reached $0.224 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and increased by 22%.

4. CONCLUSIONS

TrGO-900/PA hydrides were prepared by the electrostatic self-assembly of TrGO-900 and PA. The effects of TrGO-900/PA hydrides on thermal properties of epoxy composites were investigated. The thermal conductivity of TrGO-900/PA composites increased by 22% when the content of 5 wt% of TrGO-900/PA. The increase is attributed to the presence of PA, which improved phonon conduction pathways and more uniform dispersion.

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