

Graphene Based Core–Shell Additives for Increasing the Thermal Conductivity of Epoxy Nanocomposites

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ABSTRACT

We studied novel technique to enhance the thermal conductivity of epoxy nanocomposites using graphene coated poly-methyl-methacrylate (PMMA) balls. PMMA balls with a diameter in the range of 200–300 nm were synthesized using suspension polymerization. These balls were coated with chemically reduced graphene oxide to form a core–shell additive and dispersed in epoxy. Thermal conductivity measurements of bulk samples of graphene-coated PMMA (GPMMA) epoxy nanocomposite were carried out and compared with baseline samples comprised of graphene nanosheets (not in the core–shell form) dispersed in the epoxy resin. Results show that the addition of 1% (by weight) GPMMA balls increases thermal conductivity by 7-fold. By contrast, the addition of 1% (by weight) of graphene nanosheets (not in the core–shell form) only improves thermal conductivity of the nanocomposite by approximately 3-fold. We attribute this improvement in thermal performance to more uniform dispersion and improved phonon conduction pathways for the GPMMA core–shell additive.

Keywords: Graphene, nanocomposites, thermal conductivity

1 INTRODUCTION

As the global demand for high-density electronic devices rises, thermally conductive polymers have become increasingly important in heat dissipation applications due to their light weight, good chemical resistance and low-cost fabrication [1, 2]. Unfortunately, the thermal conductivity of conventional polymer materials is low, which restricts their applications. Thus, developing polymer-based composites with high thermal conductivity and low fabrication cost is of primary importance [3]. In this work, we present an alternative approach in which the graphene additive is not directly dispersed in the polymer, rather it is coated onto PMMA balls forming a core-shell additive (GPMMA). These additives are then uniformly dispersed in the polymer matrix. The rationale behind this approach is to address the problems of filler dispersion and phonon scattering at graphene-polymer interfaces. Although graphene has very high intrinsic thermal conductivity, it tends to agglomerate (leading to poor dispersion in polymer matrices and high resistance to photon transport at the

graphene-polymer interfaces). Here we demonstrate that organic PMMA particles coated with graphene can be employed to achieve good dispersion. Further the graphene skin coating on the GPMMA particle enables the establishment of long-range thermally conductive pathways that reduce phonon scattering resulting in a significant improvement in the thermal conductivity of the epoxy nanocomposite.

2 EXPERIMENTAL

2.1 Materials

The epoxy resin (Epon 862: diglycidyl ether of bisphenol-F) was provided by Miller-Stephenson Chemical Co., Inc. Expandable graphite (Dixon) was provided by Asbury Carbon. Methyl methacrylate (MMA, Aldrich) was purified by being washed three times with 10% (w/w) sodium hydroxide solution (MMA to NaOH (v/v) = 10 : 1), followed by repeated washing with deionized water (MMA to water (v/v) = 5 : 1) until the pH of the water dropped to 7. Concentrated sulfuric acid (H₂SO₄), potassium persulfate (K₂S₂O₈), phosphorus pentoxide (P₂O₅) potassium permanganate (KMnO₄), hydrochloric acid (HCl), and hydrogen peroxide (H₂O₂) and 2,2-Azobis(2-methylpropionamide) dihydrochloride were purchased from Sigma Aldrich. These chemicals were used as received.

2.2 Preparation of GO Dispersion

Graphite oxide (GO) was prepared by modified Hummers method: Graphite powder (325 mesh) was put into a mixture of concentrated H₂SO₄, K₂S₂O₈ and P₂O₅. The solution was heated to 90 °C while being stirred. Next, the mixture was diluted with deionized water and cooled to room temperature overnight. The pre-oxidized graphite was then re-oxidized by Hummers method. Pretreated graphite powder was put into concentrated H₂SO₄, followed by the gradual addition of KMnO₄ under stirring. Successively, the mixture was stirred and then diluted with deionized water followed by adding H₂O₂ drop by drop. The mixture was filtered and washed with HCl aqueous solution to remove metal ions, followed by ~1 L of deionized water to remove the acid. The resulting solid was dried in air and diluted to make graphene oxide dispersion.

2.3 Preparation of Positively Charged PMMA

Positively charged PMMA beads were prepared by surfactant-free emulsion polymerization. To obtain nano-sized positively charged PMMA, we first added ~87.5 mL of deionized water to the reactor, followed by deoxygenating by extensive bubbling with nitrogen for ~30 min. Subsequently, ~10 g of MMA were added into the reactor. The mixture was stirred at ~350 rpm and bubbled with nitrogen again for ~30 min. The temperature was increased to ~70 °C, followed by the addition of ~0.15 g of 2,2-Azobis(2-methylpropionamidine) dihydrochloride dissolved in ~25 mL of deionized water. The polymerization was carried out under stirring for ~6 h.

2.4 Assembly of PMMA-Reduced Graphene Oxide Composite

Positively charged PMMA (~10 g) and latex was gradually added to the desired volume to the negatively charged graphene oxide (GO) dispersion (~1 mg/mL) under vigorous stirring for ~30 min. The colloidal suspension PMMA-GO composite was reduced with hydrazine (GO/hydrazine 1:10 w/w) at ~80 °C for ~3 h. The obtained colloidal suspension of GPMMA material was filtered, washed with methanol 3 times, and dried at ~80 °C for ~12 h. GPMMA material was then crushed into a fine powder using a mortar and pestle. Samples with various weight fractions of graphene, relative to the PMMA, were fabricated (0, 1, 2, 4, 8 and 16 wt% graphene).

2.5 Epoxy Nanocomposite Fabrication

The composites containing nanoparticles of GPMMA or graphene platelets (GPL) were prepared in laboratory scale, according to a procedure illustrated in Figure 1. The nanoparticles were dispersed in acetone by means of ultrasonication at room temperature to break up any agglomerates. The nanoparticles were dispersed in epoxy resin by tip sonication. Afterwards, the solvent was evaporated in a vacuum oven and the composite was subsequently mixed with hardener via shear force mixing. The mixture was cast into aluminum molds treated with a release agent. Finally, the composite was cured at ~80 °C for ~8 hours. Samples with 0.1, 0.5, and 1.0 wt% total graphene content were fabricated with GPMMA as well as regular graphene platelet (GPL) additives.

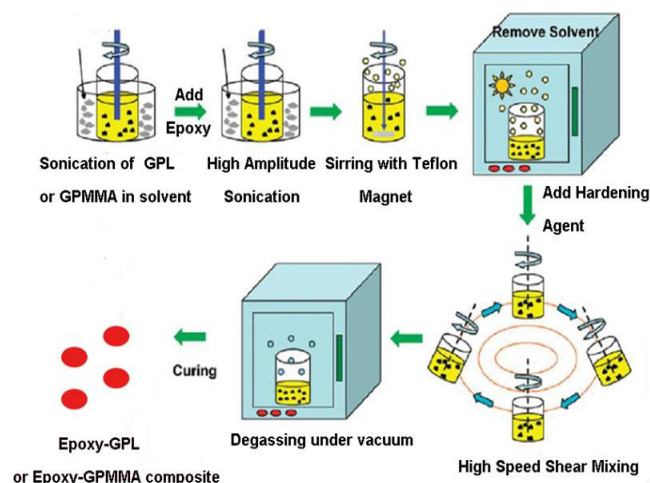


Figure 1. Schematic fabrication of epoxy nanocomposite

2.6 Thermal Conductivity Measurement

To measure the thermal conductivity of the nanocomposites, a steady-state one-dimensional heat conduction method [4] was used. The experimental setup consists of an electrical heater, a heat sink and two thermocouples to measure the temperature gradient (Figure 2). To minimize the interfacial thermal resistance, fine diameter electrically insulated thermocouples were embedded into two soft indium layers to measure the temperature at both sides of a thin cylindrical sample. Pressure is applied using a screw mechanism that is thermally insulated from the sample by a thick Teflon block. The heat losses in the experimental setup were calibrated using glass samples of known conductivity.

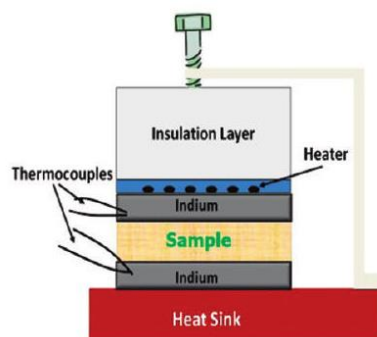


Figure 2. Experimental setup for thermal conductivity measurement

3 RESULT AND DISCUSSION

3.1 Morphological Characterization

In order to investigate the morphology of neat PMMA and GPMMA materials, and to look into finer details of the microstructure, scanning electron microscopy (SEM) was performed. Figure 3 shows SEM images of PMMA and GPMMA materials (1, 2, 8 and 16 wt% graphene). The neat PMMA (Fig. 3a) shows a smooth surface. In comparison, GPMMA materials (Fig. 3b, c, d and e) show a relatively rough texture due to the wrinkled and crumpled graphene sheets that decorate the surfaces of the PMMA balls. For preparation of epoxy nanocomposites we selected the 16wt% GPMMA additive (Figure 3e-f) due to its high graphene content.

We also studied the dispersion of the GPMMA additives in the epoxy matrix by SEM imaging. For this the epoxy nanocomposite samples were freeze-fractured and we characterized the fracture surfaces. Figure 4 shows the typical microstructure for the ~1 wt% GPMMA-epoxy nanocomposite showing spherical GPMMA balls that are dispersed in the epoxy matrix. Note that for the ~1 wt% of GPMMA-epoxy composite, the loading fraction of graphene sheets is ~1 wt% with respect to the total composite mass and is ~16 wt% with respect to the PMMA mass alone.

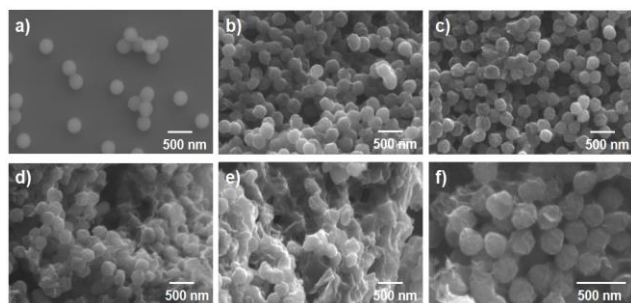


Figure 3. SEM images of a) Pure PMMA, b) GPMMA material (1 wt% graphene), c) GPMMA material (2 wt% graphene), d) GPMMA material (8 wt% graphene), e) GPMMA material (16 wt% graphene), f) higher magnification of 16 wt% graphene material.

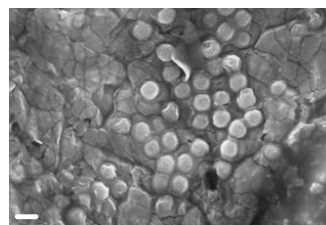


Figure 4. SEM image of the fracture surface of 1 % by weight GPMMA/epoxy composite. The total graphene content in the composite is 1 wt%. The scale bar is 400 nm.

3.2 Thermal Conductivity Measurement

Graphene nanoplatelets (GPL) and GPMMA core-shell particles were dispersed in an epoxy polymer (Epon 862: diglycidyl ether of bisphenol-F) at loading fractions of up to ~1%. Note that loading fraction refers to the total graphene content (weight fraction) in the composite. To compare the effect of graphene, we maintain the amount of graphene in each composite (i.e. GPL/epoxy and GPMMA/epoxy), to be the same. To measure the thermal conductivity of these composites, a steady-state one-dimensional heat conduction method [4] was used. The thermal conductivity of the epoxy measured with this setup (~0.20 W/m-K) matches the value reported in the literature [4].

The thermal transport characterization results are shown in Figure 5. As expected, the thermal conductivity of the epoxy nanocomposites are considerably enhanced by the presence of graphene and graphene-coated PMMA balls. It can be seen that the addition of 1% (by weight) of GPMMA balls increased thermal conductivity by 7-fold, while the addition of 1% (by weight) of GPL (i.e. not in core-shell form) only improves thermal conductivity by approximately ~ 3-fold. It should be noted that since PMMA has a low thermal conductivity (similar to the epoxy), the PMMA is not responsible for the increased thermal conductivity of the composite. The enhanced thermal conductivity can be attributed to two key effects: (1) the GPMMA balls are well dispersed and do not aggregate in the epoxy polymer (Figure 4) and (2) the GPMMA balls provide a path of lower resistance for phonons to travel. We have illustrated this schematically in Figure 6B, where the graphene core-shell particles create a more contiguous phonon conduction pathway as compared to the conventional case (Figure 6A) where phonon scattering at graphene-polymer interfaces limits the phonon transport.

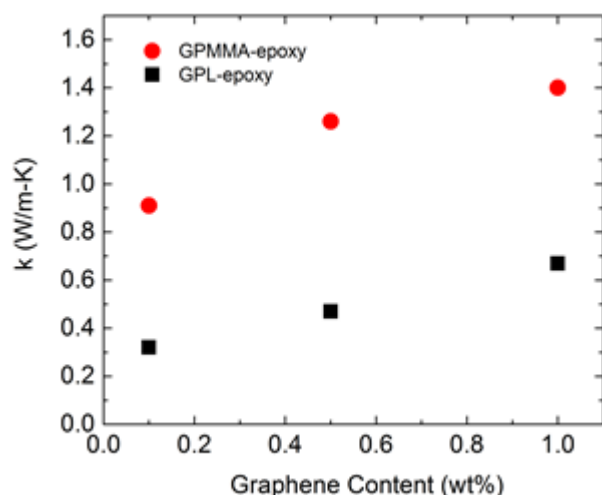


Figure 5. Measured thermal conductivities of the GPMMA/epoxy and GPL/epoxy composites.

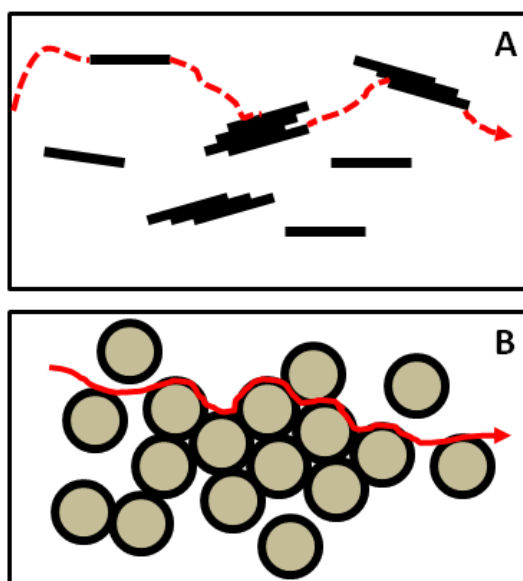


Figure 6. Schematic representation of the mechanism by which the GPMMA/epoxy composite (B) has improved thermal conductivity relative to the GPL/epoxy composite (A) for the same graphene content.

4 CONCLUSION

In this study, we fabricated conventional epoxy nanocomposites with graphene additives as well as epoxy nanocomposites with novel graphene core-shell additives (i.e. graphene skin on PMMA balls). We showed that adding the graphene-coated PMMA balls to the epoxy polymer matrix significantly boosts thermal conductivity. A composite with 1% (by weight) GPMMA balls increased thermal conductivity by 7-fold, while the incorporation of 1% (by weight) of graphene platelets improved the thermal

conductivity of the composite by ~ 3-fold. This shows that the organic PMMA nanoparticles coated with graphene could be employed to promote well-dispersed conditions (with reduced phonon scattering at the graphene-polymer interfaces). Our results indicate that GPMMA are an effective additive for enhancing the thermal conductivity of epoxy thermal adhesive materials and has the potential to be applied to other types of polymers or thermal interface materials.

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