



Improved thermal conductivity of graphene encapsulated poly(methyl methacrylate) nanocomposite adhesives with low loading amount of graphene



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ABSTRACT

Adhesive nanocomposites, which have potential use as light-weight thermal interface materials for heat removal in electronic devices, were prepared by using graphene-encapsulated poly(methyl methacrylate) microparticles with two different loading amounts of graphene (0.9 and 0.09 wt.%), and their thermal conductivities were compared. Three different types of graphene-encapsulated microparticles (large, small, and those with a rough surface with an internal pore structure) were fabricated and characterized. Adhesive nanocomposites were UV cured easily to a solid state via thiol-ene reaction. The thermal conductivity of the nanocomposites prepared in this study was 200% higher than that of a simple blend of poly(methyl methacrylate) and graphene, despite the low amounts of graphene encapsulation. The results suggest that an improvement in thermal conductivity can be achieved by effective adhesion of graphene to the surface of microparticle. This new approach can be applied where light-weight or transparency is required in addition to transport performance.

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1. Introduction

Graphene-based polymer nanocomposites are attracting considerable attention for various potential applications owing to their exceptional physical, chemical and thermal properties [1–4]. In particular, graphene-based polymer nanocomposites have emerged as potential thermal interface materials (TIMs) that offer lightweight, and highly efficient thermal management solutions in current and next-generation electronic devices, wherein heat removal has become crucially important issue. Thus far, nanocomposites of graphene with various polymers, such as epoxy [5], polypropylene [6], and polystyrene [7] have been reported to show improved thermal conductivity. In addition, graphene as filler for TIMs application have been reported [8–11].

Nevertheless, the thermal conductivity of graphene-based polymer nanocomposites is much lower than that of pristine graphene. This is because the dominant heat transfer process in such systems is governed by the phonons or lattice vibrations. The poor phonon coupling in the vibrational modes at the polymer-filler and filler-filler interface cause thermal resistance called Kapitza resistance that decreases the overall thermal conductivity of the material

[12,13]. It is suggested that the heat conducting fillers should be continuously connected to form a network, in order to reduce the number of contacts that increase the heat resistance [14].

In addition, the strong, attractive van der Waals forces between the graphene sheets tend to cause re-aggregation during the fabrication procedure [15]. Therefore, ensuring uniform dispersion of graphene in the matrix is also mandatory to obtain nanocomposites with improved thermal conductivity.

Furthermore, it has been reported that the electrical and thermal transport properties of such systems are related to the long-range connectivity, defined by the percolation threshold, and the loading should exceed a certain amount in order to obtain efficient increase of the property [16]. However, high filler loadings generally result in low mechanical strength, heavy weight, and poor processability [17]. Thus, low filler content and good graphene dispersions are necessary to obtain desirable polymer composites. Earlier attempts to improve the thermal conductivity of graphene-based polymer nanocomposites indicate that the nature of the nanofiller/matrix interface plays a key role in determining the polymer nanocomposite design and behavior [18]. However, it has always been a continuous challenge to develop new design of composites with a low percolation threshold.

Herein, we demonstrate a new approach to prepare graphene-based polymer nanocomposite using graphene loaded microparticles

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packed in UV curable formulation, which could potentially be used as a TIMs between the heat sources and heat sinks for efficient thermal management.

2. Experimental

2.1. Materials

Graphene was purchased from Graphene Supermarket. Poly(methyl methacrylate) (PMMA) (IF 870, LG MMA, $M_w = 86,000$) was used as received. Poly(ethylene glycol) dimethacrylate (PEGDMA, acryl monomer) ($M_w = 526$) and pentaerythritol tetrakis (3-mercaptopropionate, thiol monomer) were purchased from Aldrich. 2-Methylpentane (TCI, Japan) was used as an inert organic phase change material (PCM) for the fabrication of particles with rough surface. Poly(vinyl alcohol) (PVA, 87–89% hydrolyzed, $M_w = 13,000$ – $23,000$, Aldrich) was used as a stabilizer for the aqueous solution at the concentration of 1 wt.%.

2.2. Preparation of graphene-encapsulated PMMA microparticles

In this study, three different types of graphene-encapsulated microparticles were fabricated by using the spontaneous emulsification method [19]. Briefly, graphene was dispersed in dichloromethane (DCM) (concentration of 1 mg/mL or 0.1 mg/mL) under sonication at 25 °C for 30 min. To this mixture, PMMA was dissolved at the ratio of PMMA/DCM = 10:90, to prepare the organic phase solution. Subsequently, the as-prepared organic phase solution was added to 1 wt.% PVA aqueous solution either by drop-wise addition under magnetic stirring or by homogenization (4000 rpm for 180 s), resulting in the formation of larger (mean diameter = 209 μm) and smaller (mean diameter = 28 μm) microparticles, respectively (Fig. 1). Microparticles with rough surfaces were prepared by modifying the method previously reported in the literature [20]. In the typical process, PCM was initially incorporated at the ratio of PMMA:PCM = 7:3 in organic phase solution, followed by the same procedure adopted for the preparation of larger microparticles. In this study, two different samples were prepared by varying the amount of graphene in PMMA (0.09 wt.% and 0.9 wt.%). All the microparticles were vacuum dried for 1 d before use.

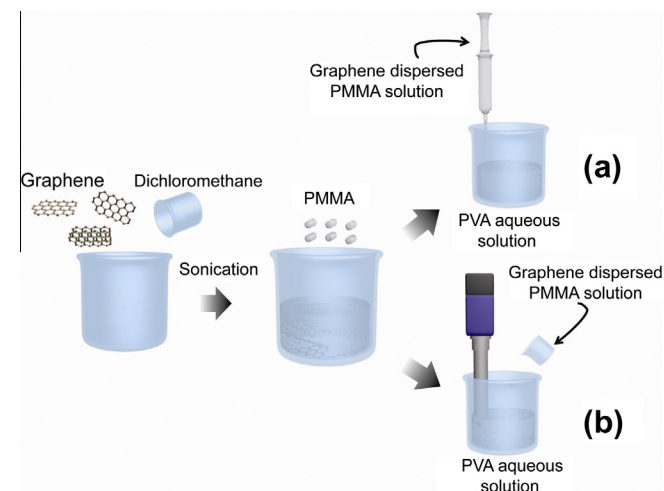


Fig. 1. A schematic illustration of the procedure adopted for the fabrication of graphene-encapsulated PMMA microparticles by (a) drop-wise addition method and (b) homogenization method.

2.3. Fabrication of thermally conductive adhesive nanocomposites

The as-prepared graphene-encapsulated PMMA particles were spread onto a glass slide (coating area of 1.0 cm \times 1.0 cm and, thickness 500 μm), followed by the addition of two drops of methyl methacrylate (MMA). As MMA can solubilize PMMA, the addition of a few drops of MMA slightly dissolves the surface of PMMA microparticles, establishing connection between them. Subsequently, UV-curable viscous adhesive mixture was prepared by mixing pentaerythritol tetrakis (thiol monomer) and PEGDMA (acrylate monomer) under a light-protected condition. This was added onto the microparticles layer spread on the glass slide. Following that, the viscous UV-curable adhesive nanocomposite was solidified via UV irradiation (1 kW/cm²) for 7 min at ambient condition by the thiol-ene mechanism (Fig. 2).

2.4. Characterization

Surface and cross-sectional morphologies of the three different types of graphene-encapsulated PMMA microparticles prepared in this study were observed by using scanning electron microscopy (S-4800, Hitachi, Japan). Using an image-processing program (Photoshop CS5, Adobe, San Jose, CA), false color images of the graphene-encapsulated PMMA microparticles were obtained, wherein the graphene was coded green. The average particle size and size distribution of graphene encapsulated PMMA microparticles were measured by using a Microtrac S3500 Particle Size Analyzer (Microtrac, USA). Thermal properties of the graphene-encapsulated microparticles were evaluated by using differential scanning calorimeter (DSC, Q20, TA instruments, USA). The thermograms are obtained in the temperature range of 40–200 °C at a heating and cooling rate of 10 °C/min. In addition, thermogravimetric analysis (TGA) was performed using a Q50 (TA instruments, USA) in the temperature range of 25–800 °C at a heating rate of 10 °C/min under N₂ atmosphere. The transmittance spectra of the cured, thermally conductive, adhesive nanocomposite film were observed at room temperature using a UV-Vis spectrometer (Optizen 2120 UV plus, Mecasys, Korea) in the wavelength ranging from 400 nm to 800 nm. Thermal conductivity of the rectangular (dimension of sample: 1.0 cm \times 1.0 cm) composite films was measured using a steady-state heat flow measurement apparatus (LFA 457-Nanoflash, Netzsch) with an accuracy of about 3% and 5% for thermal diffusivity and specific heat capacity, respectively. Flash power was 1535 V and duration was 500 ms for the measurement.

3. Results and discussion

3.1. Fabrication of graphene-loaded microparticles

Fig. 1 schematically illustrates the procedure adopted for the fabrication of graphene-encapsulated PMMA microparticles. The resulting microparticles exhibit different sizes depending on the methods used for the addition of organic phase solution into the aqueous medium (drop-wise addition or homogenization). Furthermore, low-concentration graphene (1 mg/mL and 0.1 mg/mL) was dispersed in DCM in order to realize stable dispersion of graphene in the organic solvent [21]. For comparison, graphene-encapsulated microparticles with rough surface and internal pore structure were also prepared by modifying the drop-wise addition method.

Fig. 3 shows the particle size of the graphene-encapsulated microparticles obtained by the drop-wise addition and homogenization methods. As seen from the figure, the graphene-encapsulated PMMA microparticles prepared by drop-wise addition method have particles sizes ranging from 148 μm to 320 μm , with the mean diameter of 209 μm (Fig. 3a). On the other hand, homog-

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