



Core-shell structured carbon nanotube-poly(methylmethacrylate) beads as thermo-conductive filler in epoxy composites



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ABSTRACT

A facile and novel method has been developed for the preparation of highly thermo-conductive epoxy-based composites. The core-shell structure is formed with 'functionalized carbon nanotubes (sCNTs)' as shell encapsulated on the plasma-treated poly(methylmethacrylate) (pPMMA) as core. Effective thermo-conductive pathways are realized through core-shell structured bead-bead conduction throughout the composites. The core and shell have been characterized by Fourier transform infrared analysis and zeta potential measurement. The core-shell arrangement has visualized by scanning electron microscopy, which supported the expectation that the shell being positively charged would be assembled on the negatively charged core forming a highly conductive outer surface of the non-conductive core. The thermal conductivity of the epoxy composites increased from $0.19 \text{ W m}^{-1} \text{ K}^{-1}$ of neat epoxy to $0.96 \text{ W m}^{-1} \text{ K}^{-1}$ at 1 wt% of sCNTs in sCNT@pPMMA beads. The method developed in this work introduces a new approach of using non-conductive polymer beads as constituting element in conductive framework formation.

1. Introduction

The development of electronic devices towards smaller design, higher power consumption and multiple functions requires fast heat dissipation. A small difference in operating temperature could affect the reliability, performance, and service time of electronic devices. Thermal conductivity of most of the commercial polymeric materials are quite low (for example, in the order of $0.2 \text{ W m}^{-1} \text{ K}^{-1}$ for epoxy resin) at room temperature and they could not meet the heat dissipation requirement of the electronic devices [1–4]. Over the last decade, thermally conductive polymer-based composites, however, has drawn much attention for application in a wide variety of fields, especially in electronic devices for heat removal applications, due to their exclusive material properties such as light weight, good processability, high thermal stability, outstanding chemical resistance, low cost, etc. [5,6]. There have been many efforts to improve thermal conductivity of polymer composites using a wide range of fillers such as, metal particles including aluminum, copper, silver, gold [7–10], and ceramic compound including aluminum nitride, boron nitride, silicon carbide [11–13]. Although these fillers can improve the thermal conductivity of polymeric materials, their introduction in high content may cause deterioration of the processability, mechanical properties, and so on.

Carbon nanotubes (CNTs) have received considerable attention for

possessing extraordinary combination of properties: excellent mechanical strength, and super high electrical and thermal conductivity [14–16]. They have high thermal conductivity ($\sim 3000 \text{ W m}^{-1} \text{ K}^{-1}$), and if filled in high aspect ratio could effectively form heat transfer paths in a polymer matrix [17,18].

Many investigations have been conducted on the method of dispersion of the CNTs in a polymer matrix in order to fabricate polymer composites suitable for thermal management applications. Song et al. dispersed CNTs in epoxy matrix by sonicating CNTs-epoxy resin mixture in ethanol solvent. They have reported that the thermal conductivity of the epoxy composite so prepared was $0.26 \text{ W m}^{-1} \text{ K}^{-1}$ at 1.5 wt% of CNTs [19]. Cai et al. presented a method to improve the dispersion of CNTs in polymer matrix using a latex technology and the thermal conductivity increased from $0.15 \text{ W m}^{-1} \text{ K}^{-1}$ for pure poly (urethane) (PU) to $0.47 \text{ W m}^{-1} \text{ K}^{-1}$ for of the PU composites with 3 wt % of multi-wall carbon nanotubes (MWCNTs) [20]. The thermal conductivity achieved by these dispersion techniques (simple mixing or sonication) could not be considered satisfactorily high to meet requirements in thermal management applications of modern electronic systems.

Yang et al. loaded chemically functionalized CNTs into an epoxy matrix and achieved a thermal conductivity of $1.3 \text{ W m}^{-1} \text{ K}^{-1}$ i.e. 271% higher than that of the pure epoxy, for 10 vol% of the filler [21].

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Another research group used benzene tricarboxylic acid as organic molecules to modify CNTs by Friedel-Crafts reaction and prepared epoxy-modified CNT composites. The highest thermal conductivity of the composite was $0.96 \text{ W m}^{-1} \text{ K}^{-1}$ at 10 vol% of filler loading [22]. Both the groups concluded that the significant improvement of thermal conductivity of the epoxy composites was due to the well dispersion of the surface-modified CNTs and the low thermal interfacial resistance between the filler and the matrix. These are excellent achievements in terms of the thermal conductivity, but insertion of high concentration of non-compatible filler material in the composition, would definitely increase the filler cost of the composites.

Huang et al. infiltrated polydimethylsiloxane matrix into aligned CNT arrays. The thermal conductivity of the composite with 0.4 vol% of CNTs was as high as $1.21 \text{ W m}^{-1} \text{ K}^{-1}$ [23]. The complicated preparation step using the aligned CNTs arrays was not suitable for mass production of the composites, but it gave clear indication that high conductivity could be achieved even with very low CNT-concentration as opposed to those reported in [15,16] and provided a good conductive framework throughout the matrix.

Polymer core with shell of high thermal conductivity has proved to be an effective element for the construction of interconnected conductive filler network in a polymer matrix and to obtain composites with high thermal conductivity [19]. Koo et al. fabricated core-shell structure by electroplating poly(styrene) (PS) beads with copper, and with these filler obtained composites with thermal conductivity as high as $26.14 \text{ W m}^{-1} \text{ K}^{-1}$ at 23 vol% of copper [24]. Jiang et al. modified hexagonal boron nitride (h-BN) with a silane and assembled it with poly(phenylene sulfide) (PPS) beads by electrostatic interactions. The core-shell structure of h-BN in PPS matrix resulted in the composites with thermal conductivity of $4.15 \text{ W m}^{-1} \text{ K}^{-1}$ at 40 vol% BN, which is 16 times higher than that of the neat PPS resin [25]. The authors found that the core-shell structure of the filler formed effective thermal pathways that led to significant improvement in thermal conductivity as compared to that of the composite with randomly distributed filler. But still the high conductivity has been achieved at the expense of high concentration of conductive components. It is presumed that the selection of core material similar to that of the matrix material might have caused partial mixing of the core with the matrix due to high compatibility, and thus resulting in the partial destruction of the core-shell structure of the conductive filler. To avoid such potential disadvantages, the core material was chosen incompatible with the matrix.

From the literature survey, it becomes evident that intensive researches are underway to find effective method for the preparation of polymer composite applicable for thermal management of electronic systems, and core-shell structured conductive filler appears to be high prospective. In this work, we have developed a facile and low cost method for the preparation of core-shell structured highly conductive filler element consisting of plasma-treated poly(methylmethacrylate) (pPMMA) micro-beads and silanized CNTs (sCNTs). The core material pPMMA has been chosen to be incompatible with the matrix material (epoxy-based) to preserve the core-shell structure of the filler in the ultimate composite mass. The epoxy composite with this filler shows high thermal conductivity at low CNT-concentration and would meet the requirements for application in electronic systems. This is a cost effective method and has the potential to find mass scale production.

2. Experiment

2.1. Materials

Poly(methylmethacrylate) microbeads (PMMA, MH-5FD, diameter: $5 \mu\text{m}$) were purchased from Kolon Co., Korea. Multi-wall carbon nanotubes (CNTs, CM-95, length: $10\text{--}20 \mu\text{m}$, diameter: $10\text{--}25 \text{ nm}$), was ordered from Hanwha Nanotech Co., Korea. 3-aminopropyltrimethoxy silane (APTMS-99%) was purchased from Sigma Aldrich Co., USA. The low viscosity epoxy resin (YDF-170) and curing agent (KH-818B) were

obtained from Kukdo Chemical Co., Korea. These chemicals were used as received from the supplier without further purification.

2.2. Preparation of positively charged sCNTs

0.1 g of CNTs was oxidized using 80 ml of a mixture of acids (H_2SO_4 : $\text{HNO}_3 = 1:3 \text{ v/v}$) at 60°C for 2 h under mild stirring. Then the oxidized CNTs (oCNTs) were filtered and washed using deionized (DI) water until $\text{pH} = 7$. After that, the oCNTs were dispersed in DI water (100 ml) by mild sonication for 30 min. APTMS (1 ml) was added to the oCNTs-suspension dropwise in a round-bottom flask and heated to 80°C under magnetic stirring for 6 h. The final product, silanized CNTs (abbreviated as sCNTs), was filtered and washed thoroughly with DI water.

2.3. Preparation of negatively charged PMMA beads

The negatively charged PMMA beads were prepared by introducing oxygen functional groups on PMMA bead-surface. The beads were plasma-treated under oxygen atmosphere using a capacitively coupled plasma chamber. The PMMA beads were dried in a vacuum oven at 80°C to remove absorbed moisture. Then the powder was cast on a plastic petri dish and placed between two parallel electrode plates in cylindrical plasma reactor. The reactor chamber was evacuated by a rotary vacuum pump until the inside pressure dropped to about 8.0 Pa. Afterwards, the chamber was charged with oxygen and set to 20.0 Pa with 30 standard cubic centimeters per minute of oxygen. The sample was treated for 5 min with radio frequency of 13.56 MHz emitted from a plasma source of 30 W. After the plasma treatment, the sample was exposed to oxygen for 10 min to form further radicals and oxygenated functional groups. To enrich the functional groups on the PMMA surface, the procedure was repeated 3 times, the product was named as pPMMA (plasma-treated PMMA).

2.4. Preparation of core-shell structure of sCNTs@pPMMA filler

The core-shell structure of sCNTs@pPMMA filler was prepared employing electrostatic interaction between positively charged sCNTs and negatively charged pPMMA beads in ethanol solvent. Typically, 10 ml of sCNTs suspension (1 mg ml^{-1}) was dropped into the well-dispersed 245 ml of pPMMA suspension (2 mg ml^{-1}) in a beaker under gentle stirring. The interaction continued at 70°C for 2 h. The positively charged sCNTs assembled on the surface of negatively charged pPMMA beads. As the stirring stopped, the sCNTs@pPMMA beads settled down at the bottom of the beaker. Finally, the precipitate was centrifuged and washed with DI water several times and freeze-dried for 24 h to obtain sCNTs2@pPMMA (around 2 wt% of shell material 'sCNTs' with respect to the core material 'pPMMA beads'). In this way, sCNTsx@pPMMA (where x is the nominal wt% of sCNTs) samples with various weight contents of sCNTs (*i.e.*, 0.5, 2, and 4 wt%) were prepared. Samples with targeted weight percentage was obtained by controlling the feed concentration of sCNTs suspension. The procedure of preparing the sCNTs@pPMMA filler is schematically presented in Fig. 1.

2.5. Preparation of epoxy-based composites

The epoxy-based composites containing (i) only sCNTs, (ii) a mixture of sCNTs and PMMA beads, and (iii) sCNTs@pPMMA beads were prepared by a solvent-free method. For the (iii) type composition, typically, the epoxy resin was placed in an oven at 80°C for 30 min to reduce the viscosity. Then sCNTsx@pPMMA filler was added in the epoxy resin and mixed by a mechanical mixer for 10 min. Afterwards, the mixture was cooled and the hardener was added into the above mixture (epoxy resin: hardener = 2:1, wt/wt) and mixed for 10 min by a mechanical mixer. The mixture was poured carefully into a mold and degassed under vacuum for 30 min. Finally, the composition was cured at 80°C for 4 h and at 150°C for 2 h. The procedure is the same for the two composition type (i) and (ii).

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