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Synergistic effect of hybrid graphene nanoplatelet and multi-walled carbon nanotube fillers on the thermal conductivity of polymer composites and theoretical modeling of the synergistic effect

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ABSTRACT

We found that the thermal conductivity of polymer composites was synergistically improved by the simultaneous incorporation of graphene nanoplatelet (GNP) and multi-walled carbon nanotube (MWCNT) fillers into the polycarbonate matrix. The bulk thermal conductivity of composites with 20 wt% GNP filler was found to reach a maximum value of 1.13 W/m K and this thermal conductivity was synergistically enhanced to reach a maximum value of 1.39 W/m K as the relative proportion of MWCNT content was increased but the relative proportion of GNP content was decreased. The synergistic effect was theoretically estimated based on a modified micromechanics model where the different shapes of the nanofillers in the composite system could be taken into account. The waviness of the incorporated GNP and MWCNT fillers was found to be one of the most important physical factors determining the thermal conductivity of the composites and must be taken into consideration in theoretical calculations.

1. Introduction

Polymer-based thermally conductive composites have been considered for use in electroluminescent devices, gate dielectrics, electrical energy storage, and touch panel devices due to their high flexibility, low temperature processing conditions, and simple fabrication process [1,2]. While the electrical properties of composites rapidly increase at a certain level of filler content, which is consistent with percolation theory, the thermal conductivity of polymer composites has shown linear improvement with increasing filler content [3,4]. Given theses characteristics, there have been many attempts to effectively enhance composite thermal conductivity by incorporating two or more types of fillers and identifying possible synergistic effects [5–7]. Yung and Liem [6] reported that the simultaneous introduction of high thermal conductivity fillers of different sizes synergistically contributed to improving the thermal conductivity of composites. Pak et al. [7] reported that incorporating a small amount of MWCNTs with a long aspect ratio induced a synergistic improvement in the thermal conductivity of polymer composites due to the formation of an efficient three-dimensional (3D) thermally-conductive network.

The thermal conductivity of polymer composites filled with nanocarbon fillers has been studied widely because of their excellent thermal conductivity. Nanocarbon fillers such as graphene and carbon nanotube (CNT) have been reported to have thermal conductivities in the range of 3000–6500 and 1950–5000 W/m K, respectively [8–12]. Synergistic effects of hybrid GNP and CNT fillers on the thermal properties of polymer composites have also been previously reported [13]. Yu et al. [13] reported that the thermal conductivity of composites was synergistically enhanced by the simultaneous incorporation of GNP and CNT, but at high filler content it ended up being lower than that of composites containing GNP alone, as the synergistic effect decreased with the increasing content of the fillers. However, analysis of the synergistic effect has not been systematically discussed from a theoretical perspective.

From a theoretical viewpoint, the morphology of the fillers is also a critical factor in determining the thermal conductivity of composites, because it can result in interrupted thermal transfer, and influence the formation of clusters and networking between heterogeneities. In general, even small wavy heterogeneities such as those of GNPs and CNTs can result in a significant decrease in composite thermal conductivity. To consider the effect of wavy heterogeneities on thermal conductivity, the theoretical approach of the Mori–Tanaka method (MTM) can be modified to account

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for the perturbation of the thermal gradient by wavy heterogeneities subjected to a constant far-field heat flux, as applied to steady-state heat conduction problems. Yu et al. [14] originally modified the analytical approach for estimating the elastic properties of composites containing wavy prolate heterogeneity. Kim et al. [3] incorporated this developed method into a micromechanical framework to investigate the effects of wavy GNPs on thermal conductivity. The Modified MTM (M-MTM) developed in the present study also takes into account the effect of wavy fillers on the thermal conductivities of composites. Further details are in the literature [14–17].

In this study, we found that the thermal conductivity of polymer composites was synergistically improved by the simultaneous incorporation of GNP and MWCNT fillers into the matrix. The optimized composition of the hybrid fillers was investigated experimentally in order to enhance the thermal conductivity. The theoretical objective of the current study is to compare and to verify the estimated values obtained from the modified micromechanics approach developed in this work with the experimentally measured properties of composites filled with hybrid fillers. These results can verify the synergistic effect of hybrid fillers on the thermal conductivity of composites containing multiple geometrized fillers.

2. Experimental

2.1. Materials

GNP (M5) with a thickness of 6–8 nm and a diameter of 5 μm was obtained by XG science (Lansing, MI, USA). MWCNTs (CM 150) with lengths greater than 20 μm and diameters of 20–100 nm were supplied by Hanwha Chemical (Seoul, Korea). A linear polycarbonate (PC, LUPOY PC 1300-03, LG Chemistry Co., Gyeonggi-do, Korea) was used as the polymer matrix. The melt flow rate of the resin was measured to be 3 g per 10 min as determined by ASTEM D1238.

2.2. Preparation of nanocomposites

The carbon fillers and PC matrix were dried at 80 °C for 2 h to remove moisture. The dried materials were mixed at their respective contents using a Haake Rheomix internal mixer (HAAKE™ Rheomix 600R OS Mixer, Thermo scientific Inc., Marietta, GA, USA) at a temperature of 260 °C and a screw speed of 60 rpm for 30 min. The fabricated composites were pelletized and thermally conductive composite samples with a rectangular shape of 2 mm thickness and 4 cm^2 area were prepared using a heating press (D3P-30J, Daehung Science, Incheon, Korea) at a pressure of 15 MPa for 10 min at 250 °C, and then quenched to 30 °C.

2.3. Characterization

2.3.1. Morphology

The geometrical shapes of the carbon fillers and composites were observed using a field emission scanning electron microscope (FE-SEM, Nova NanoSEM 450, FEI Corp., OR, USA). GNP and MWCNT fillers of 0.5 mg were dispersed for 10 min in 10 ml of ethanol using a ultrasonic bath (JAC-2010P, Kodo Technical Research Co. Ltd, Gyeonggi-do, Hwaseong, Korea) and the dispersions were coated onto silicon wafer at 3000 rpm for 30 s using a spin coater (Spin-1 2000, MIDAS, Daejeon, Korea). The composite samples to be used for measuring the thermal conductivity were fractured after freezing in liquid nitrogen. The samples were surface-coated with platinum for 120 s in a vacuum using a sputter coating machine (Ion Sputter E-1030, Hitachi High Technologies, Tokyo, Japan). The prepared SEM samples were observed with a voltage of 10 kV applied under a nitrogen vacuum. For atomic force microscopy (AFM) measurement, GNP fillers of 0.5 mg were dispersed for 2 h at 750 W in 100 ml of ethanol using a horn type ultrasonic machine (VCX750, Sonics & Materials. INC., CT, USA) and then coated onto a silicon wafer at 3000 rpm for 60 s using a spin coater (Spin-1 2000, MIDAS, Daejeon, Korea). After the sampling, an AFM (NX-10, Park systems Corp., Suwon, Korea) was utilized to measure the thickness of the GNPs. The diameters of the MWCNT fillers were observed with a transmission electron microscope (TEM, Tecnai F20, FEI Corp., OR, USA). The MWCNT fillers were dispersed in ethanol and sonicated for 5 min, and subsequently the dispersion was dropped on a lacey-carbon coated film on the Cu grid. The TEM analysis was performed at 120 kV and the accelerated electron exposure time was minimized to avoid electron radiation damage.

2.3.2. Tomography

X-ray micro-computed tomography (MICRO-CT, Skyscan 1172, Bruker Co., USA) was used to observe the dispersion and network structures of the fillers in the composites. The X-ray source was irradiated at a voltage of 56 kV and a current of 173 μA under normal pressure.

2.3.3. Thermal conductivity

The bulk thermal conductivities of the composites were measured under room temperature and ambient pressure conditions using a thermal conductivity analyzer (TPS 2500 S, Hot Disk AB, Gothenburg, Sweden), according to the ISO 22007-2 standard. The sensor consisted of a double spiral of thin nickel wire and served as a plane heat source. The sensor was designed to generate a temperature rise (ΔT) by providing a defined amount of power (P) and measure temperature changes obtained from changes in sensor resistance at the same time. The thermal conductivities of the samples were calculated using the Fourier equation for heat conduction based on the provided power and generated temperature changes.

2.3.4. Transient heat transfer

The transient temperature response behavior of the fabricated composite specimens was evaluated using an infrared camera (FLIR T420, Wilsonville, OR, USA). The composite specimens were put on an isothermal hot plate at a constant temperature of 100 °C. Thermal images of the specimens were recorded after 20 s. The composite specimens with a constant temperature of 100 °C were placed on a metal plate at room temperature. Also, thermal images of the specimens were recorded after 20 s during the cooling.

3. Theoretical approach

3.1. Classical micromechanics for effective thermal conductivity

The MTM [18–20] considers a single ellipsoidal heterogeneity embedded within an infinite homogeneous matrix domain subjected to a constant far-field heat flux, as applied to steady-state heat conduction problems. The MTM departs from the Eshelby method [21], which posits that the thermal gradient field is not perturbed by the existence of heterogeneities within a matrix. The MTM takes the opposite view and uses the continuum averaged heat flux vector ($\boldsymbol{q}$) and temperature gradient (∇T) to predict the effective thermal conductivity tensor for the composite [22–23]. The heat flow in a composite may be characterized in terms of the far-field applied heat flux vector ($\boldsymbol{q}$), i.e.,

$$\boldsymbol{q} = -\overline{\boldsymbol{K}} \cdot \nabla T \tag{1}$$