Improved thermal conductivity of polymeric composites fabricated by solvent-free processing for the enhanced dispersion of nanofillers and a theoretical approach for composites containing multiple heterogeneities and geometrized nanofillers

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ABSTRACT

The thermal conductivities of Cyclic Butylene Terephthalate (CBT)-based composites containing nanofillers such as carbon nanotubes (CNTs) and carbon blacks (CBs) were experimentally and theoretically investigated. The recently developed composite manufacturing processing using solvent-free powder mixing and in-situ polymerization for the improved dispersion of nanofillers of various shapes and dimensions within a polymer matrix was applied to prepare nanocomposites. The experimentally measured the thermal conductivity of those composites, comparing the predicted values obtained from micromechanics models, taking into account the effect of both waviness of the nanofillers and multiple heterogeneities. The thermal conductivity of composites was profoundly affected by the waviness of CNTs. In addition, the interphase property between fillers and the polymer matrix was significant in determining the bulk thermal property of composites containing nanofillers.

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1. Introduction

Polymer matrix-based composites (PMCs) reinforced with nanofillers are useful in diverse industries due to advantages such as low weight, chemical and corrosion resistance, good strength, and toughness [1]. With small amounts of thermally conductive materials using carbon-based nanofillers, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), oblate-shaped graphene/graphite, and carbon blacks (CBs), the thermal properties of polymeric composites can be improved to add these sorts of nanofillers within a polymer matrix [2,3]. The thermal properties of polymeric composites dramatically increase by several orders of magnitude [4–9]. However, regardless of these advantages, it is not easy to manufacture these nanofiller-reinforced polymeric composites. There are several reasons for this: 1. effective dispersion of nanofillers depends on the shapes and dimensions of the reinforcements, 2. defects, such as agglomerates of nanofillers, voids, and carbon clusters within polymeric composites, can arise during the manufacturing process, and 3. an interphase or bonding issue between nanofillers and the matrix can also arise [4–9]. Furthermore, the

viscosity of the polymer resin during the manufacturing process can also have a large impact on the conductivity of the composite materials [10].

Manufacturing processes to overcome above difficulties have been established for the better dispersion of nanofillers without any defects inside composites [11–13]. Hu et al. [11] prepared polymer composites by mixing metallic particles and MWCNTs in silicone oil. This method enhanced the thermal conductivity of composites reinforced with two–three volume contents of MWCNTs, but it is difficult to form a solid material with sufficient strength and adhesive properties due to the high concentration of metallic particles. Huang et al. [12] synthesized CNT-reinforced polymer composites by injecting polymers into aligned nanotube arrays. Aligned CNTs can improve the thermal conductivity of composites that are perpendicular to the substrate of CNTs but the processing method is not easy to use for commercial production due to the high cost to prepare aligned nanotube arrays. Noh et al. [13] recently developed a novel nanocomposite preparation method that combines powder mixing and in situ polymerization to induce better dispersion of nanofillers. However, the thermal properties of nanocomposites fabricated by the preparation method have not yet been discussed experimentally and theoretically. If nanofillers within a matrix are evenly dispersed and

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continuously networked, then the thermal properties of nanocomposites can be theoretically enhanced by several magnitudes with a relatively small volume of conductive reinforcements.

In addition to the nanofiller dispersion issue, the thermal properties of nanofiller-reinforced polymeric composites are also determined by the shapes and dimensions of the reinforcements [14–18]. The polymeric composites containing prolate ellipsoids show the highest thermal conductivity compared to other shapes, such as oblate ellipsoids and spheres. As mentioned previously, it is easy to form a conductive network with prolate ellipsoids even though these shapes can easily be wavy, clustered, or agglomerated. The orientation of nanofillers is also a crucial factor to determine the effective thermal properties of nanocomposites [14–18]. There are many approaches and schemes to estimate and model thermal conductivity at various scales of length, such as micro-, macro-, and application scales. Among those, the Mori–Tanaka method (MTM) [19–21] is the best predictor of the effective properties of nanocomposites, due to its definition of nanocomposites, if the fillers are perfectly dispersed within a matrix [17]. Furthermore, the relative size of nanofillers is very small compared to that of a matrix. Thus, this theory can accurately predict the thermal conductivity of the nanofiller-reinforced composites. In this study, the recently developed composite manufacturing processing using solvent-free powder mixing and in-situ polymerization for improving dispersion of various shaped- and dimensioned-nanofillers such as CNTs and CBs within a matrix is applied to prepare nanocomposites, and the experimentally measured thermal conductivities of those composites are compared with the predicted values obtained from micromechanics models with taking the effect of both wavy nanofillers and multiple heterogeneities developed.

2. Experimental

2.1. Materials

MWCNTs (CM 150, Hanwha Nanotech, Seoul, Korea) produced by catalytic chemical vapor deposition have lengths of greater than 10 μm, with diameters of 20–100 nm, and aspect ratios of over 100. The CB with a diameter of 20–50 nm (ENSACO 250G) was supplied by TIMICAL Graphite & Carbon (Bodio, Switzerland). Cyclic Butylene Terephthalate (CBT, CBT 160, Cyclics, NY, USA) is the thermoplastic resin of small molecular-weight cyclic oligomers. The oligomers are ring-opened and melted in a temperature range of 130–150 °C. The melt had a low viscosity of 0.02 Pa s. The used CBT 160 resin was polymerized due to the catalyst incorporated into the matrix at temperatures higher than 160 °C and became polymerized CBT (pCBT), which is a polybutylene terephthalate.

2.2. Preparation of composites

The raw materials were dried overnight at 110 °C to remove moisture before preparing the composites, as moisture can interfere with the polymerization of the CBT oligomer. MWCNT/CBT and CB/CBT composites were fabricated by combining simple powder mixing and in situ polymerization, as shown in Fig. 1. Enhanced dispersion of the mixed nanofillers could be induced because the melt viscosity of the oligomer matrix was as low as 0.02 Pa s during the first heating process. The CBT pellets were crushed into a fine powder using a standard mixer. The powder was then mixed with MWCNT or CB fillers at the target weight ratio using a Thinky mixer (ARE 310, Thinky Corp., Tokyo, Japan) at 2000 rpm for 3 min, as shown in Fig. 1(a) and (b). The mixture was placed in a 4 cm² mold and then hot pressed at 170 °C under 15 MPa for 2 min using a heating press (Dae Heung Science Co., Incheon, Korea) as shown in Fig. 1(c) and (d).

2.3. Characterization of composites

The thermal conductivity of composites was measured at ambient pressure and room temperature using a thermal conductivity analyzer (TPS 2500 S, Hot Disk AB, Gothenburg, Sweden). The analyzer uses the standard ISO 22007-2 hot disk technique. The hot disk sensor is made of a double helix of thin nickel wire and works as a continuous-plane heat source. The hot disk sensor supplies a constant electric power (P) resulting in a temperature increase (ΔT) measured directly by the hot disk itself using a variation of the sensor resistance. Starting at P and ΔT, thermal conductivity can be calculated by solving the Fourier equation of heat conduction. The morphology of the surface of the prepared composites was observed with field emission scanning electron microscopy (FE-SEM, Nova NanoSEM 450, FEI Corp., OR, USA). The surface of the composites was coated with platinum under vacuum conditions for 200 s using a sputter coating machine (Ion Sputter E-1030, Hitachi High Technologies Corp., Japan) and SEM observation was performed at 15.0 kV.

3. Theoretical approach

3.1. Classical micromechanics for effective thermal conductivity

The MTM [19–21] 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 [22], 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 ($\mathbf{q}$) and temperature gradient (∇T) to predict the effective thermal conductivity tensor for the composite [23,24]. The heat flow in a composite may be characterized in terms of the far-field applied heat flux vector (q), i.e.,

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

where $\overline{\mathbf{K}}$ is the effective second-rank thermal conductivity tensor and ∇T is the continuum averaged temperature gradient. Similar to the classical Eshelby solution for linear elasticity [22], where the strain field inside each heterogeneity is constant, the resulting temperature gradient inside each heterogeneity is also constant when calculating effective thermal properties. For a composite with a matrix phase (0) and a nano-reinforcement phase (1), the second-rank effective thermal conductivity tensor ($\overline{\mathbf{K}}$) can be expressed as:

$$\overline{\mathbf{K}} = \mathbf{K}_{(0)} \cdot \{\mathbf{I} + c_1(\mathbf{S}_{(1)} - \mathbf{I}) \cdot (\mathbf{A}_{(1)} - \mathbf{S}_{(1)})^{-1}\} \cdot \{\mathbf{I} + c_1\mathbf{S}_{(1)} \cdot (\mathbf{A}_{(1)} - \mathbf{S}_{(1)})^{-1}\}^{-1} \tag{2}$$

where

$$\mathbf{A}_{(1)} = (\mathbf{K}_{(0)} - \mathbf{K}_{(1)})^{-1} \cdot \mathbf{K}_{(0)} \tag{3}$$

is the second-rank thermal gradient concentration tensor for heterogeneity, $\mathbf{K}_{(0)}$ and $\mathbf{K}_{(1)}$ are the second-rank thermal conductivity tensors for the matrix and heterogeneity, c_1 is the heterogeneity volume fraction, $\mathbf{S}_{(1)}$ is the second-rank Eshelby tensor for heterogeneity, $\mathbf{I}$ is the second-rank identity tensor, and a middle dot is used to denote the tensor single dot product. The Eshelby tensor ($\mathbf{S}_{(1)}$) accounts for the influence of the aspect ratio/geometry of the heterogeneity on the local temperature field. Eshelby tensors for specific reinforcement shapes (spheres, platelets, fibers, etc.) are readily available in the literature [23,24].