



Exfoliated boron nitride nanosheet/MWCNT hybrid composite for thermal conductive material via epoxy wetting

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ABSTRACT

Herein, we describe the fabrication of thermally conductive composites based on an epoxy matrix with a hybrid filler of hexagonal boron nitride (h-BN) and multi-walled carbon nanotubes (MWCNTs) via the wetting method. The h-BN particles were exfoliated to boron nitride nanosheets (BNNs) by heating in a tubular furnace with steam and sonication. The h-BN particles in the composite were densely packed and oriented almost perpendicular to the bottom. On the other hand, the BNNs were more loosely packed and randomly oriented, and exhibited higher through-plane thermal conductivity despite the low filler content. After the incorporation of MWCNTs, the filler thermal conductivities of both the composites significantly increased. In particular, 9 wt% of MWCNTs was sufficient to increase the thermal conductivity of the BNN composite from 3.12 to 4.25 W m⁻¹ K⁻¹ because of the intercalation of the nanotubes between the BNNs, which provided a three-dimensional heat flow path. Moreover, the MWCNTs interrupted the dense particle packing and the filler concentration was reduced from 56.7 to 43.8 wt%. In the case of h-BN composite, this effect was relatively weak because the nanotubes were agglomerated between the micron-sized BN particles.

1. Introduction

Heat dissipation has been extensively studied from both academic and industrial points of view, as it is an integral aspect of heat exchangers, electronic appliances, and machinery [1,2]. Compact high-power electronic devices require innovative solutions for efficient heat exchange, such as thermal interface materials (TIMs), printed circuit boards (PCBs), heat-absorbing phase-change materials (PCMs), and housing materials. A high thermal conductivity is the most important property for these composites, in order to allow the heat generated at the hot spot to be efficiently transferred outside [3–6].

Polymeric materials have been extensively used as base resins of thermally conductive composites because they are easily processable, light-weight, and cheap. While several highly thermally conductive polymers (thermal conductivity ~1 W m⁻¹ K⁻¹) have been reported, they are generally highly crystalline, contain abundant phenyl groups, and have poor processability and high cost; that is, they do not display most of the important advantageous aspects of polymers [7,8]. On the other hand, since most polymers possess low thermal conductivities (0.1–0.3 W m⁻¹ K⁻¹), combinations of polymeric matrices and thermally conductive fillers can be utilized based on metal (Al and Cu), carbonaceous (graphene and multi-walled carbon nanotubes (MWCNTs)), and ceramic particles (BN, AlN, and SiC). Among the

available variety of fillers, metal particles are not currently used owing to their high density and electrical conductivity, which limits their possible applications. Similarly, carbonaceous particles exhibit disadvantages such as high cost, poor dispersion characteristics, and high electrical conductivity. Therefore, ceramic materials are the most promising thermally conductive fillers for a variety of applications [9–12].

Hexagonal boron nitride (h-BN) is a particularly interesting material as it exhibits the highest thermal conductivity among electrically insulating materials in addition to good thermal and chemical stability. Moreover, its anisotropic properties and two-dimensional sp² honeycomb structure (with a lattice constant similar to that of graphene) have attracted significant attention. The unique physical properties of BN have been extensively utilized for hydrogen storage, catalyst design and fabrication, and biological applications. Furthermore, when isolated BN monolayers or few-layer crystals are stacked layer by layer, a hybrid nanostructure, called the van der Waals heterostructure, is formed. This heterostructure exhibits the advantages of its individual components while displaying new properties and functions for practical applications [13,14]. Recently, some researchers have been studying about exfoliation of boron nitride nanosheets (BNNs) from bulk h-BN. Damm et al. reported the exfoliated BNNs via mechanical milling using various size of ZrO₂ beads. This method could simply control the thickness of nanosheet, however, the size of BNNs were extremely small to

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~50 nm [15]. Lin et al. and Cai et al. prepared the BNNS based on Lewis acid-base interaction and physically functionalized via π - π stacking and partial charge. These physical bonding caused the homogeneous dispersion in solvent [16,17]. Furthermore, the exfoliated BNNSs have been applying to thermal conductive filler in polymeric materials. Lindsay et al. have reported that single-layer h-BN can exhibit a thermal conductivity of over $1000 \text{ W m}^{-1} \text{ K}^{-1}$, which is three times higher than the in-plane thermal conductivity of bulk h-BN [18]. Xiao et al. have reported the exfoliation and functionalization of h-BN via thermal oxidation, which produces numerous hydroxyl groups on the surface and edges of h-BN, providing active sites for chemical bonding with the polymer matrix. This method allows the fabrication of well-dispersed BNNSs in the polymeric matrix, resulting in high thermal conductivity, drug delivery capability, and faster dimensional change upon heating [19]. These results indicate that the exfoliation of h-BN particles not only results in reinforced interactions with the polymeric material but also enhances the thermal conductivity of the composite that is thus produced.

Herein, h-BN was chemically functionalized by water steam treatment using a humidifier and a tubular furnace. Hydroxyl group functionalization and sonication induced the large-scaled BNNS exfoliation. Moreover, introduced hydroxyl groups on BNNS could cause not only enhanced interfacial affinity but also anchor site for further surface modification. The morphology of the particles before and after exfoliation was characterized by field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HRTEM). The Further, h-BN and BNNS/epoxy composites were prepared by epoxy wetting, and their particle dispersions and thermal conductivities were compared. MWCNTs are a promising thermally conductive filler, which is also suitable for use as a secondary filler because of their outstanding aspect ratio and intrinsic thermal conductivity. The thermal conductivities of single strand MWCNT have been reported to $2800\text{--}6000 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature in the longitudinal direction [20]. Therefore, BN/MWCNT/epoxy composites have also been prepared by incorporating a small amount of MWCNTs to improve their thermal conductivity and examine the synergistic effect on the thermal conductivity of the composite [21,22]. Unfortunately, MWCNTs exhibit extremely high electrical conductivity, which limits their maximal loading, electrical conductivities of the BNNS composites with different MWCNT loadings were compared, and the results were rationalized in terms of the formation of a three-dimensional network and the agglomeration between BN particles.

2. Experimental

2.1. Materials

Epoxy-terminated dimethyl siloxane (ETDS) was purchased from Shin-Etsu Silicon (KF-105, epoxide equivalent weight (EEW) = 166.6 g eq.^{-1} , density = 1.20 g cm^{-3}) and used after drying under vacuum at 50°C for 24 h. 4,4'-Diaminodiphenylmethane (DDM) was sourced from TCI Korea and used as a curing agent without further purification. MWCNTs were obtained from LG Electronics in Korea. The diameters of the carbon nanotubes were 10–30 nm and their length was in the range of 5–20 μm . Boron nitride (BN) was purchased from Momentive. The average diameter of the particles was 12 μm .

2.2. Preparation of BN nanosheets (BNNSs)

BN nanosheets were prepared by the exfoliation of micron-sized BN powder, which was loaded in a ceramic boat and placed into the hot zone of a horizontal tubular furnace. Deionized (DI) water was ultrasonically nebulized using a home humidifier (60 MHz, 35 W) and carried by argon gas at a flow rate of 200 mL min^{-1} . The furnace was at 850°C for 2 h and subsequently cooled down to room temperature to collect the hydroxylated BN (BNO). The obtained BNO was dispersed in

DI water by sonicating for 2 h to exfoliate the BN layers, and the mixture was left without sonication for 3 h to allow the sedimentation of BN powder. The resulting milky suspension was vacuum-filtered to obtain BNNSs.

2.3. Fabrication of ETDS matrix

ETDS and DDM were mixed in a 1:2 wt ratio. DDM (1.9 g) was placed in a four-neck round-bottom flask equipped with a reflux condenser and preheated to 90°C . Subsequently, ETDS (9.5 g) was added and the mixture was heated in an oil bath at 90°C for 1 h under a nitrogen atmosphere. Gas bubbles present in the mixture were removed by placing the flask in a vacuum oven for 30 min at room temperature, followed by re-immersion for 10 min into the oil bath held at 50°C under N_2 . Final degassing was performed in a vacuum oven for 1 h at room temperature to remove any remaining air bubble.

2.4. Fabrication of BN-MWCNT/ETDS hybrid composite films

BN particles (2 g) and various amounts of MWCNTs were separately suspended in EtOH by sonicating for 30 min, and the obtained suspensions were mixed to fabricate hybrid fillers with various MWCNT loadings. The mixture prepared in this manner was poured into a glass mold ($r = 0.5 \text{ in}$), placed on a silicon oxide membrane (0.2 μm , Anodisc, Whatman, USA), and vacuum-filtered. The obtained BN/MWCNT filter cake was peeled off from the membrane and annealed at 50°C for 12 h to remove residual solvent. The prepared ETDS resin was then drop-casted onto the BN/MWCNT cake, which easily penetrated it because of the sufficient wettability of BN and MWCNTs. Finally, the obtained BN/MWCNT/ETDS film was cured at 180°C for 3 h.

2.5. Characterization

BN and BNNSs were characterized by X-ray photoelectron spectroscopy (XPS, Thermo UK K-Alpha) using an Al K_{α} X-ray source (1486.6 eV) and a hemispherical analyzer. Constant Gaussian peak widths were used for fitting each spectrum. The crystal structure of BN was characterized by X-ray diffraction (XRD, New D8-Advance, Bruker-AXS) at a scan rate of 1° s^{-1} in the 2θ range of $10\text{--}70^\circ$ using $\text{Cu } K_{\alpha 1}$ radiation ($\lambda = 0.15406 \text{ nm}$). Thermogravimetric analysis (TGA; TGA-2050, TA Instruments) was employed to examine the thermal degradation behavior. In TGA analysis, the samples (4 mg) were heated to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere. FE-SEM (Sigma, Carl Zeiss) and HR-TEM (JEM-3010) were used to examine the morphology of the fabricated composites, and their thermal transport properties were characterized by laser flash analysis (LFA, Netzsch Instruments Co., Nanoflash LFA447) and differential scanning calorimetry (DSC, Perkin-Elmer Inc., DSC-7) at room temperature. The transferred signal initiated a thermal equilibration process in the composite specimen, which was recorded by employing a difference detector at the rear surface and was used to evaluate thermal diffusivity. Specimen bulk density $\rho_{\text{comp}} (\text{g cm}^{-3})$ was measured by using the Archimedes water displacement method. Thermal conductivity (k) was calculated by multiplying composite thermal diffusivity, density, and specific heat capacity. Electrical conductivity was measured by a four-point probe method using a Keithley 2400 source meter. A digital micrometer was used to measure the sample thickness.

3. Results and discussion

Oxidation-induced structural changes of BN particles were observed by XPS and XRD (Fig. 1). XPS wide-scan spectra showed two strong boron and nitrogen peaks at ~ 190.3 and 397.5 eV , along with a small oxygen peak at $\sim 530 \text{ eV}$. The carbon atom peak at 283 eV likely originated from the carbon tape used for particle loading during analysis. After thermal treatment, the intensity of the oxygen peak increased, and

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