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Aluminum hydroxide–CNT hybrid material for synergizing the thermal conductivity of alumina sphere/thermoplastic polyurethane composite with minimal increase of electrical conductivity

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ABSTRACT

Multi-walled carbon nanotube (CNT) was hybridized with aluminum hydroxide utilizing aluminum trichloride hexahydrate as a precursor to prepare a filler that can be utilized for a thermally conductive yet electrically insulative polymer composite. The thermal conductivity of an alumina sphere/thermoplastic polyurethane (TPU) mixture (100 parts) was enhanced 2 to 3-fold when 5 parts of this hybrid material (Al–CNT hybrid) was added as a synergizer for thermal conduction. This enhancement was better than that by CNT. Moreover, the electrical conductivity increase due to the added Al–CNT hybrid was marginal, whereas the increase was striking when CNT itself was added instead.

Introduction

Efficient thermal management with high-performance thermal interface materials (TIMs) is imperative in the electronic industry because of the continuing miniaturization and increase of power density in electronic devices. Thermally conductive polymer composites, composed of a polymer matrix and a filler with high thermal conductivity, have been predominantly utilized as TIMs due to their excellent characteristics, including good processability, low cost, and light-weight [1,2]. Various ceramic fillers such as alumina, boron nitride, aluminum nitride, and graphite have been utilized as fillers. However, a very high loading of the filler (i.e., >50 vol%) is required to achieve high thermal conductivity, which not only deteriorates the mechanical properties of the composites but also causes processing difficulties [3–5].

Moreover, a thermally conductive yet electrically insulating composite can facilitate a simpler and less expensive design for electrical devices to avert short circuits. In addition, electrical resistivity is desirable to avoid noise or voltage drop, when high-speed signals are applied [1,6,7].

Nanocarbons, such as carbon nanotube (CNT) or graphene, have recently emerged as a promising filler for thermally conductive polymer composites, because their thermal conductivities are extremely high, providing a sufficient thermal conductivity at low loading [8–11]. However, they cannot be utilized for the preparation of a thermally conductive yet electrically insulating polymer composite, because they can create an electrically conductive percolating network in the polymer matrix at very low loading, i.e., <1 vol% [12].

When nanocarbons are hybridized with ceramics such as silica, their electrical conductivity can be reduced effectively. Moreover, the thermal conduction can be improved by an enhanced phonon transfer at the filler/polymer interface because the phonon scattering at the interface due to the modulus mismatch is alleviated by hybridization and the interfacial interaction is improved due to the enhanced compatibility between the filler and polymer [8,9,13,14]. R. Quian et al. utilized alumina-coated graphene to prepare an electrically insulating polymer composite with high thermal conductivity [3]. However, to the best of the authors' knowledge, no paper is available on a polymer composite utilizing an aluminum hydroxide–CNT hybrid as a thermally conductive filler with low electrical conductivity.

In this paper, CNT was hybridized with aluminum hydroxide by thermal decomposition of an aluminum precursor, aluminum trichloride hexahydrate, coated on CNT. Because a large amount of

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nanofiller can embrittle the composite, the aluminum hydroxide–CNT hybrid was utilized as an additive to synergize the thermal conductivity of the alumina sphere/thermoplastic polyurethane (TPU) composite. The synergistic effect of the aluminum hydroxide–CNT hybrid on the thermal conductivity enhancement and the effects on the electrical conductivity and mechanical properties of the composite by the aluminum hydroxide–CNT hybrid were examined and compared with those of CNT.

Experimental

Materials

A multi-walled carbon nanotube (CNT, CM-150, purity; ~90 wt%) was purchased from Hanwha Chemical (Korea). Aluminum trichloride hexahydrate ($AlCl_3{\cdot}6H_2O$, Daejung Chemicals & Metals Co., Ltd., Korea), anhydrous dimethyl formamide (DMF, Aldrich), H_2O_2 aqueous solution (30 wt%, Tokyo Chemical Industry Co., Ltd.), ethanol (SK Chemicals, Korea), alumina sphere with an average particle size of 0.3 μm (ASFP-20, Denka, Japan), and acetone (SK Chemicals, Korea) were used as received. Thermoplastic polyurethane (TPU) based on poly(butylene adipate) (PBA) diol (molecular weight: 1500), 1,4-butane diol, and methylene diphenyl diisocyanate (MDI), of which the soft PBA segment content was 63 wt% and shore D hardness was 36, was used as a matrix polymer. The molar ratio of diols/MDI in the feed for the bulk polymerization of TPU was 1/1, and the number and weight average molecular weights of the TPU were 98,100 and 142,600, respectively.

Preparation of aluminum hydroxide–CNT hybrid

The CNT was treated in 120-fold of strong acid, a 3/1 (v/v) mixture of concentrated sulfuric acid and concentrated nitric acid, at 40 °C for 2 h to remove residual metallic catalysts and amorphous carbon particles and to introduce oxygen-containing functional groups to CNT, which render CNT more compatible with common solvents [15]. The pristine CNT and the CNT treated with strong acid are designated in this paper as p-CNT and a-CNT, respectively.

The a-CNT was oxidized with H_2O_2 to introduce additional oxygen-containing functional groups [16,17], which can act as an anchoring site to attach aluminum trichloride on the CNT's surface. The CNT was treated by mixing in 100-fold of 30 wt% H_2O_2 aqueous solution for 1 day at 60 °C for oxidation. The CNT oxidized with H_2O_2 is designated as h-CNT in this paper.

The CNT hybridized with predominantly aluminum hydroxide rather than alumina was prepared with $AlCl_3{\cdot}6H_2O$ as a precursor of aluminum hydroxide [18]. The h-CNT (0.50 g) was dispersed in ethanol (30.0 g). The aluminum trichloride hexahydrate (1.31 g) was added to this dispersion for reaction with the hydroxyl groups of CNT for 2 h, and the ethanol was then evaporated. The dried mixture was thermally decomposed at 250 °C for 8 h to obtain the aluminum hydroxide–CNT hybrid, which is designated as Al–CNT hybrid in this paper.

Preparation of aluminum hydroxide–CNT hybrid/alumina sphere/TPU composite

The Al–CNT hybrid and alumina sphere were dispersed in DMF and sonicated for 1 h. The TPU was then added to the dispersion and mixed for 8 h at room temperature, affording 15 wt% TPU solution in DMF, dispersing Al–CNT hybrid and alumina sphere. The composite film was cast on a Teflon plate or on a PET film at 80 °C for 1 day under vacuum.

Measurements

Elemental analysis was performed using a Thermo Scientific Flash 2000 CHNS/O analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Fisher K-Alpha spectrometer with Al Kα X-ray radiation. Thermogravimetric analysis (TGA) was performed using a Q50 (TA Instrument) at a heating rate of 10 °C min^{-1} with 6 mg of the sample in a platinum crucible in an air atmosphere.

The morphology of the h-CNT or Al-CNT hybrid was examined using a transmission electron microscope (TEM, JEOL JEM-2100F). A field emission scanning electron microscope (FE-SEM, JEOL JSM 6500F) was used to observe the morphology of the cryogenically fractured surface of the composite. To examine the morphology of h-CNT or its Al–CNT hybrid using TEM, the sample was sonicated for 1 h in DMF. One drop of the suspended sample containing ~0.005 wt% Al–CNT hybrid was placed dropwise onto a carbon film supported on a 200 mesh copper grid, and the DMF was then evaporated at 80 °C under vacuum.

The electrical conductivities of the compressed CNT powders and the compressed Al–CNT hybrid powder were measured using a four-point probe system (CMT-SR 1000 N, AIT Co. Ltd., Korea). The electrical conductivity across an approximate 0.5 mm thick composite sheet was measured with a picoamperometer (Keithley 237) at room temperature. A silver paste was used to ensure good contact between the specimen and the electrodes.

An instrument designed to measure the thermal conductivity according to ASTM D5470-12 was used to measure the thermal conductivity of the composite film. The film with the dimensions of 4 cm × 4 cm × 50 μm was positioned between two isothermal plates, where one plate is heated with an electrical heater and the other plate is cooled with water. The temperature difference (K) between the two isothermal surfaces is divided by the heat flux (W m^{-2}) across the sample to calculate the thermal impedance (K m^2 W^{-1}). The heat flux was estimated from the electrical energy input on the heated plate divided by the area of the sample. Two additional thermal impedances were measured at different sample thicknesses using the samples stacked as two or three layers. The thermal conductivity (W m^{-1} K^{-1}) was calculated from the plot (the thermal impedance versus sample thickness), as the reciprocal of the slope.

The tensile properties were examined using a tensile tester (OTU-2, Oriental TM Co., Korea). The composite film was cut into a micro-tensile specimen with a length, width, and thickness of 25, 5, and 0.5 mm, respectively. The specimen was elongated at a rate of 100 mm min^{-1}.

Results and discussion

Properties of aluminum hydroxide–CNT hybrid

The results of elemental analysis show that the oxygen content of CNT is increased by the treatments with strong acid and H_2O_2 (Table 1). In the XPS survey scan, the ratio of the O_{1s} peak intensity at 532.7 eV relative to the C_{1s} peak intensity at 284.3 eV also increased by the treatments with strong acid and H_2O_2 (Table 2), indicating that new oxygen-containing functional groups were created on the CNT due to the oxidation during the treatment with strong acid and the additional treatment with H_2O_2.

To examine the newly created oxygen-containing functional groups, as shown in Fig. 1, the C_{1s} core level photoemission spectra were deconvoluted into four peaks: C–C carbon (284.5 eV), C–O carbon (285.5 eV), C=O carbon (287.4 eV), and O–C=O carbon (288.9 eV) [19,20]. This Fig. 1 and the deconvolution data in Table 2 shows that the amount of C–C carbon decreased, whereas C–O carbon, C=O carbon, and O–C=O carbon increased with the