Influence of electrolessly silver-plated multi-walled carbon nanotubes on thermal conductivity of epoxy matrix nanocomposites

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ABSTRACT

In this work, multi-walled carbon nanotubes (MWCNTs) were electrolessly Ag-plated in order to investigate the effect of plating time on the thermal conductivity of Ag-plated MWCNTs-reinforced epoxy matrix composites. MWCNT surfaces were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS). The thermal conductivity of Ag-plated MWCNT-reinforced epoxy nanocomposites was measured using the thermal equilibrium method with ASTM D5470. From the results, it was found that the thermal conductivity of the composites enhanced with increasing plating time. In particular the Ag-10/EP sample showed more than 150% enhancement of the thermal conductivity compared to the as-received CNTs/EP sample. These results were attributed to the high contents of Ag particles and the increase of the interfacial adhesion between the Ag-CNTs and EP matrix in the composites.

1. Introduction

The continued downsizing of electronic device parts is associated with the problem of heat dissipation, which has emphasized the need for improved thermal interface materials (TIM) in contemporary chip packaging. The reliability of an electronic device is sensitive to the running temperature of the junction [1–3]. A little difference in running temperature (10–15 °C) can result in a twofold reduction in the life of device [4]. Therefore, it is essential that the heat generated in the device is dissipated as soon as possible to maintain the desired device running temperature. Accordingly, a polymer with thermally conductive filler has emerged as a cost-effective way to address the thermal management problem. To obtain TIMs with improved thermal conductivity, composites consisting of various kinds of particles (carbon materials, ceramics, and metals) in epoxy (EP) matrix have been developed.

Among the various thermally conducting fillers, carbon nanotubes (CNTs) attract attention from researchers because of their unique one-dimensional structure and remarkable mechanical, thermal, electrical, and optical properties. Especially, the thermal conductivity of CNTs is known as 6000 for single-walled CNTs (SWCNTs) and 3000 W/mK for multi-walled CNTs (MWCNTs). However, the use of CNTs with EP composites has been largely restricted by their poor dispersion in EP resins and weak interfacial bonding with polymer matrix [5–10].

Surface modification of the CNTs has been used effectively to overcome this problem, thereby improving the functionality of CNTs as reinforcements in polymer composites. Possible surface modifications include oxidation in acid solution [11,12], dry oxidation in oxygen [13], metal plating [14,15], and plasma treatments [16].

These metal-CNT hybrid materials integrate the properties of the two materials and are therefore very useful. As such, many studies have focused on the preparation of metal-plated CNTs and their use in conductive fillers, hydrogen storage. Commercial plating techniques have been used to apply metals such as Ag [17], Ni [18], Cu [19], and Pt [20] to the CNTs in order to increase their thermal conductivity in the composites. Among these options, Ag nanoparticle decoration of CNTs has gained significant attention owing to its potential use in various applications as well as high thermal conductivity and low cost.

This paper proposes the decoration of CNTs with Ag nanoparticles via an electroless-plating-based method. Our aim was to increase the thermal conductivity of the decorated CNTs and

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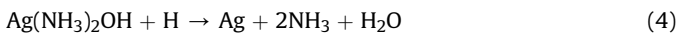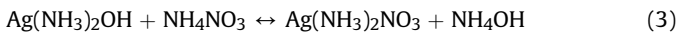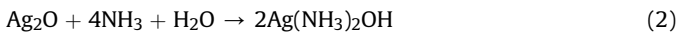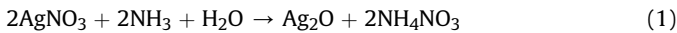** Corresponding author. Tel.: +82 312012565; fax: +82 312026693.
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thereby reduce the contact resistance of CNTs in an EP matrix. We also examined the effects of the Ag content on the structural and surface properties of the Ag-CNTs and the thermal conductivity of the Ag-CNT/EP composites.

2. Materials and methods

The MWCNTs, produced by a chemical vapor deposition (CVD) process, were obtained from Nanosolution Co. of Korea (purity: >95 wt.%, diameter: ≤10 nm, and length: ≤20 μm). Silver nitrate (AgNO$_3$, purity: >99.8%) was obtained from Dae Jung of Korea. Silver-plated MWCNTs (Ag-MWCNTs) were prepared as follows. Prior to deposition, the MWCNTs were stirred into 10 wt.% nitric acid (HNO$_3$) for 30 min in order to remove impurities. They were then sequentially treated in a tin chloride (SnCl$_2$) and palladium chloride (PdCl$_2$) activation solution to form Sn/Pd nuclei for silver reduction. The Ag-MWCNTs were obtained by immersing the treated MWCNTs for 1, 3, 5, and 10 min in a silver bath (pH: 8.5, temperature: 25 °C), thereby yielding Ag-1, Ag-3, Ag-5, and Ag-10 samples, respectively. The pH of the silver-plating solution was adjusted to 8.5 ± 0.1 using ammonia.

The main reaction is as follows.

$$2AgNO_3 + 2NH_3 + H_2O \rightarrow Ag_2O + 2NH_4NO_3 \tag{1}$$

$$Ag_2O + 4NH_3 + H_2O \rightarrow 2Ag(NH_3)_2OH \tag{2}$$

$$Ag(NH_3)_2OH + NH_4NO_3 \leftrightarrow Ag(NH_3)_2NO_3 + NH_4OH \tag{3}$$

$$Ag(NH_3)_2OH + H \rightarrow Ag + 2NH_3 + H_2O \tag{4}$$

The EP resin used as a matrix was the diglycidylether of bisphenol A (DGEBA, epoxide equivalent weight of 185–190 g/eq and density of approximately 1.16 g/m^3 at 25 °C), supplied by Kukdo Chem. of Korea. 4,4′-Diamino diphenyl methane (DDM) was used as a curing agent for the EP. The EP composites were prepared as follows. A three-roll mill (EXAKT 50I, EXAKT, Germany) was used to fabricate the composites. The general configuration of a three roll mill is illustrated in Fig. 1 and consists of three adjacent cylindrical rollers each of which runs at a different velocity. The first and third rollers, known as the feeding (n1) and apron (n3) rollers, rotate in the same direction while the central (n2) roller rotates in the opposite direction. The material to be mixed is poured between the n1 and n2 rollers of the mill. The material was transported between the n2 and n3 rollers where it was dispersed. A scraper system
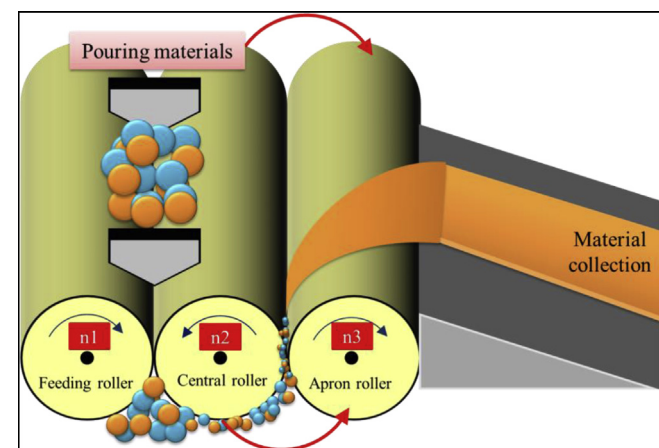
removes the finished product from the n3 roller. This milling cycle can be repeated a few times to maximize dispersion [21,22].

The mixture was subsequently degassed in a vacuum oven at 80 °C for 30 min, injected into a mold, and cured at 150 °C for 1 h. These composites were referred to as Ag-1/EP, Ag-3/EP, Ag-5/EP, and Ag-10/EP, respectively.

A transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) was used to examine the morphological and Ag particles of the Ag-MWCNTs.

In addition, wide-angle X-ray diffraction (XRD, D2 PHASER, BRUKER, Germany) of the Ag-MWCNTs was performed as a function of the plating time with a rotation anode using CuK$_\alpha$ radiation ($\lambda = 0.15418$ nm). The XRD patterns were obtained in 2θ ranges between 10° and 80° at scanning rate of 5°/min.

The X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo scientific, USA) survey spectra of the Ag-MWCNTs were collected using a AlK$_\alpha$ X-ray source ($h\nu = 1486.6$ eV). The base pressure in the sample chamber was maintained within in the range of 10^{-8} to 10^{-9} torr during analysis.

The thermal conductivity of the nanocomposites was measured by using a thermal conductivity measurement system (ThermoCon Tester M100, Metrotech Co., Ltd., Korea). The dispersibility and wettability of MWCNTs within EP matrix was characterized using scanning electron microscopy (SEM, JSM-6701F, JEOL, Japan).

3. Results and discussion

TEM was used to examine the morphological changes in the MWCNTs after Ag plating. Fig. 2 shows TEM images and EDS mappings of the as-received MWCNTs (Fig. 2(a)) and Ag-10 sample (Fig. 2(b, c)). From the TEM images, the as-received MWCNTs have clean surfaces. On the other hand, the surface morphological of Ag-10 sample shows that Ag particles were deposited on the surfaces of MWCNTs without agglomeration. Fig. 2(d) and (e) presents the EDS mapping images of carbon (red) and Ag (yellow), respectively.

Fig. 3 shows the XRD patterns of the Ag-MWCNTs as a function of the plating time. Peaks corresponding to the C(002) and C(100) planes of crystalline graphite-like materials occur at respective 2θ values of 26° and 43°, in the pattern of the as-received MWCNTs. However, those at 38°, 44°, 64°, and 77°, which appear after Ag plating, are associated with the (111), (200), (220), and (311) planes, respectively, of the silver crystals; the positions of these peaks concur with those reported in the literature (JCPDS card, No. 04-0783). The intensity of the peaks, and hence the Ag content, increased with the increasing plating time [23,24].

Fig. 4 compares the XPS wide-scan spectra of the Ag-MWCNTs samples obtained at different plating times. The as-received MWCNTs exhibited mainly peaks associated with the C$_{1s}$ (BE = 285 eV) and O$_{1s}$ (BE = 533 eV). In addition to the C$_{1s}$ and O$_{1s}$, the Ag-MWCNT samples exhibited peaks corresponding to Ag$_{3d}$ (BE = 368.1 eV and 373.8 eV). The enhancement of the O$_{1s}$ peaks on the plated MWCNT surfaces is attributed to the effect of the plating conditions on the surface structure and chemical composition of the MWCNTs; i.e., oxygen-containing groups are introduced to the carbon surface during plating [25,26].

Moreover, high-resolution XPS of the Ag-1 and Ag-10 samples revealed (Fig. 5) peaks corresponding to Ag$_{3d5/2}$ and Ag$_{3d3/2}$ at 368.1 eV and 374.1 eV, respectively, with a spin-orbit splitting of 6.0 eV. The binding energy is archetypal for Ag in metallic form i.e., in zero oxidation form, and is consistent with the XRD results (Fig. 3).

As shown in the figure, the peak corresponding to Ag$_{3d}$ shifts slightly (by 0.3 eV) to a lower binding energy position when the amount of Ag in the MWCNTs is increased. There is also a strong interaction among the Ag nanoparticles [27].

Fig. 1. Schematic showing the general configuration of a three-roll mill and its operating mechanism.