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Effect of incorporating carbon nanocoils on the efficiency of electromagnetic-wave shielding of carbon-nanomaterial composites

Gi-Hwan Kang, Sung-Hoon Kim*

Center for Green Fusion Technology and Department of Engineering in Energy & Applied Chemistry, Silla University, Busan 617-736, Republic of Korea

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ABSTRACT

Carbon nanocoils (CNCs) were deposited on Al_2O_3 substrates using C_2H_2 and H_2 as source gases in a thermal chemical vapor deposition system. Composites of CNCs in polyurethane (CNC@PU) and CNCs plus other carbon-based materials, such as carbon microcoils (CMCs) and carbon nanotubes (CNTs), in polyurethane (CNC + CMC@PU, CNC + CNT@PU) was fabricated. The electromagnetic-wave-shielding effectiveness of the CNCs-incorporated composites were examined and compared with those of other carbon-based materials in the measurement-frequency range of 0.25–4.0 GHz. The incorporation of CNCs in CMC@PU composites reduced the shielding effectiveness; on the other hand, it slightly enhanced the shielding effectiveness of CNT@PU composites within the measurement frequency range of 0.5–3.0 GHz. Based on the resulting shielding effectiveness, we conclude that the incorporation of CNCs was useful for the materials that exhibited reflection-based shielding effectiveness although the CNCs themselves had poor electrical conductivity.

1. Introduction

Carbon coils have recently emerged as promising materials for electromagnetic-wave absorbers because their unique spring-like geometry can effectively induce a current through an inductive electromotive force [1–3]. The geometry of carbon coils are usually classified into two groups, carbon nanocoils (CNCs) and carbon microcoils (CMCs) [4,5]. CNCs usually have a twisted-rope-type morphology, while CMCs display a unique and well-developed DNA-like morphology [3–6].

So far, several researchers have attempted to enhance the microwave-absorbing properties of a polymer composite by incorporating CMCs [7–10]. Du et al. reported fabrication of a composite consisting of CMCs with paraffin wax as a dielectric-loss material with small magnetic loss and diamagnetism in the Ku band (12.4–18 GHz) [7]. Electromagnetic-wave-absorption properties of composite beads of CMCs and polymethyl methacrylate (CMC–PMMA) in the W band (75–105 GHz) were studied by Motojima's group [8]. They suggested that a small portion (1–2 wt.%) of the added CMCs in PMMA beads is much more effective. In our previous report, we confirmed that the CMC–polyurethane (PU) composite will be applicable even in the mobile communication region (around 1–2 GHz) [9]. We also reported that the electromagnetic-wave-shielding properties were enhanced in the measurement frequency range of 2.0–3.5 GHz by the incorporation of CMCs in a carbon-nanotube–PU composite [10].

Meanwhile, only a few researchers have investigated the effectiveness of CNCs for enhancing the electromagnetic-wave-shielding properties of the CNC–polymer composite. Zhao et al. reported that CNCs exhibit superior microwave absorption compared with the larger CMCs [2]. It was understood that the composite having the shielding mechanism of both reflection and absorption characteristics would be an ideal shielding material of EMI in the wide frequency region [11]. In this respect, we paid close attention to the CNT + CNC composite for an effective shielding material in the wide range of the frequency.

In this work, we investigated the effect of CNC incorporation on the electromagnetic-wave-shielding properties of other carbon nanomaterials (CNMs) such as CMCs and carbon nanotubes (CNTs). We first fabricated composites of CNCs in polyurethane (CNC@PU). Then we proceeded to prepare composites of CNCs + CMCs in polyurethane (CNC + CMC@PU) and composites of CNCs + CNTs in polyurethane (CNC + CNT@PU). The electromagnetic-wave-shielding properties of the CNC@PU composites were examined and compared with those of CNC + CMC@PU and CNC + CNT@PU composites in the measurement-frequency range of 0.25–4.0 GHz. Based on these results, we will discuss and suggest in this paper the role of CNCs incorporation in CMC or CNT-based composites regarding the electromagnetic-wave-shielding properties.

* Corresponding author. Tel.: +82 51 999 5619; fax: +82 51 999 5335.
E-mail address: shkim@silla.ac.kr (S.-H. Kim).

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Table 1
Experimental conditions for the deposition of CNCs and CMCs.

	C_2H_2 flow rate (sccm)	SF_6 flow rate (sccm)	Substrate temp. (°C)	Total pressure (Torr)	Deposition time (min)
CMCs	500	40	750	100	60
CNCs	500	40	550	100	60

2. Experimental details

A thermal chemical vapor deposition (TCVD) system was employed for the deposition of carbon coils. Acetylene (C_2H_2) was used as the source gas, and sulfur hexafluoride (SF_6), an additive gas, was injected into the reactor during the reaction. The flow rates of C_2H_2 and SF_6 were fixed at 500 and 40 standard cubic centimeter per minute (sccm), respectively. Table 1 shows the detailed reaction conditions for the deposition of CNCs and CMCs. For CNT deposition, commercial multi-walled CNTs (Carbon Nanotech., Korea) with diameters of 5–20 nm were used. The detailed morphologies of the as-grown carbon coils and CNTs were investigated using field-emission scanning electron microscopy (FESEM; S-4300, Hitachi, Japan).

To prepare the different composites of CNMs in PU, namely CNC@PU, CMC@PU, CNT@PU, CNC + CMC@PU, and CNC + CNT@PU, the CNCs, CMCs, CNTs, CNCs + CMCs, and CNCs + CNTs were dispersed with added dimethylformamide (DMF) in PU (Songwon Ltd., Korea) using an ultrasonic system. After 120 min of on/off ultrasonic treatment at 500 W and 20 kHz, paste-type CNC–PU–DMF, CMC–PU–DMF, CNT–PU–DMF, CNC–CMC–PU–DMF, and CNC–CNT–PU–DMF mixtures were obtained. We prepared five kinds of samples (samples A, B, C, D, and E) with different CNMs in PU mixtures, as shown in Table 2. Each sample was then coated onto a circular glass plate measuring 133 mm in diameter, where about 20 mL of the paste-type sample was poured onto the glass plate, and the sample coatings were dried naturally in a fume hood for about 24 h at room temperature. The thickness of the sample coatings was measured using vernier calipers, and the measured values were calibrated by comparing with the cross-sectional FESEM images of certain points of the samples.

Table 2
Composition of paste-type mixtures of five kinds of samples (A, B, C, D, and E) consisting of different carbon materials (CNCs, CMCs, CNTs, both CNCs and CMCs, or both CNCs and CNTs), PU, and DMF.

Sample	Composition by weight (%)				
	CNC	CMC	CNT	PU	Type of composite
A	~22	–	–	~78	CNC@PU
B	–	~12	–	~88	CMC@PU
C	–	–	~12	~88	CNT@PU
D	~11	~11	–	~78	CNC + CMC@PU
E	~11	–	~11	~78	CNC + CNT@PU

For the electrical-resistivity measurements, we prepared rectangular sheets of CNM–PU mixtures on glass sheets with dimensions of 40 (length) × 35 (width) mm. For the coatings, about 2 mL of the paste-type sample mixtures were poured onto the glass sheets, and the coated sheets were naturally dried in the fume hood for 24 h. The volume resistivity (Ω cm) of the sheets was measured by a four-point probe (labsysstc-400, Nextron, Korea) using Ohm's law and a correction factor at room temperature [11].

The shielding effectiveness (SE) of the CNM–PU composite mixtures was analyzed using a network analyzer (SynthNV2_3b, Windfreak Tech., USA) in accordance with ASTM D4935-99. The setup, the coaxial sample holder, and the coaxial transmission test specimen were set as previously reported [9,10]. The performance measurements of the SE for the CNM–PU composite mixtures were made in the range of 250 MHz to 4.0 GHz.

3. Results and discussion

To obtain dominant formation of CNCs and CMCs, we used the thermal chemical vapor deposition system and controlled the temperature during the reaction. Indeed, as shown in Fig. 1, we could obtain mostly well-structured single-helix-type CNCs with a twisted-rope-type morphology on the surface of the substrate at

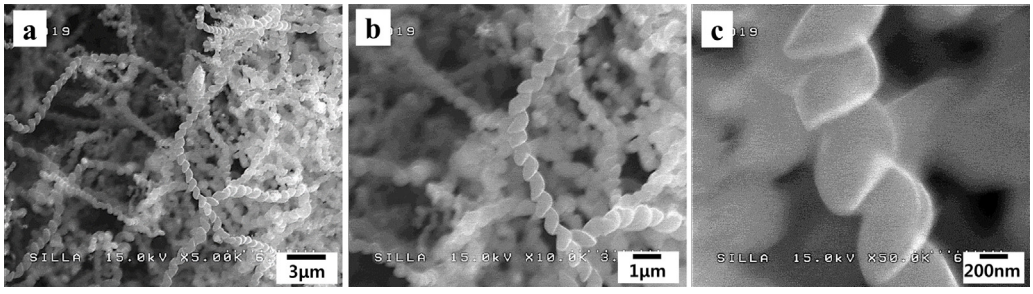

Fig. 1. Representative FESEM images of substrate surface morphologies obtained at a relatively low reaction temperature (550 °C). (a) Formation of single-helix-type CNCs with a twisted-rope-type morphology on the entire surface of the sample. (b) Magnified (×10k) image of (a). (c) Highly-magnified (×50k) image of (b).

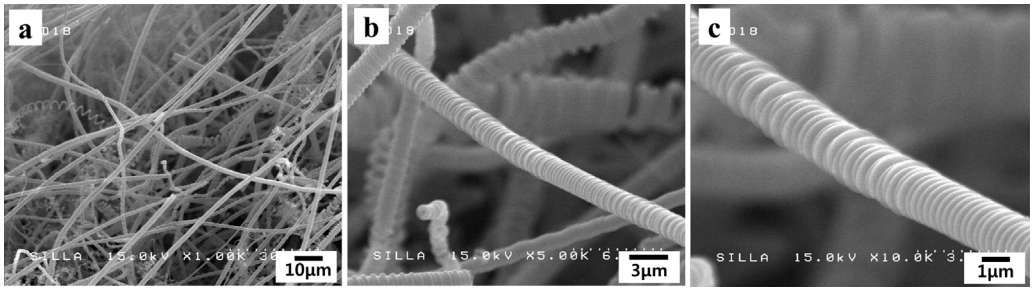

Fig. 2. Representative FESEM images of the substrate surface morphologies obtained at a relatively high reaction temperature (750 °C). (a) Dominant formation of double-helix-type CMCs with a DNA-like morphology on the entire surface of the sample. (b) Magnified (×5k) image of (a). (c) Highly-magnified (×10k) image of (b).

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