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Porous composites coated with hybrid nano carbon materials perform excellent electromagnetic interference shielding

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ABSTRACT

This work reported preparation of porous composites using a simple dip-coating method, and the fabricated composites containing hybrid carbon nanomaterials performed excellent electromagnetic interference (EMI) shielding properties. A commercial sponge was coated with silver nanoparticles before being dip-coated with graphene (GP)/ink, multi-wall carbon nanotubes (MWCNTs)/ink, or hybrid GP/MWCNTs/ink to form Ag/carbon nanomaterial hybrid composites, and then the composites were subjected to EMI measurements in the frequency range of 0.45–1.5 GHz. For comparison, the sponges without Ag nanoparticle coating were also prepared. Herein, we found an insignificant difference in EMI SE among the porous composites without Ag nanoparticle coating, and the maximum values of approximately 14.4 dB was attained. Interestingly, the hybrid composites with Ag nanoparticle coating exhibited maximum EMI shielding of 24.33 dB. Due to their porous structure, the EMI SE measurements showed that reflection dominates the EMI SE for all the sponge composites studied in this work.

1. Introduction

Carbon materials such as carbon fibers (CF), carbon nanotubes (CNTs), carbon black, and graphite are usually used as fillers for various applications. Beside CF and CNTs, graphene (GP), a novel two-dimensional carbon material with sp^2 planar structure, has attracted significant attention due to its exceptional physical and chemical properties [1]. During the past decade, CNTs have been adopted as fillers for making composites because of their remarkable conductivity, mechanical flexibility, and chemical stability [2], and many articles have investigated CNTs-based polymeric composites for electromagnetic interference (EMI) shielding [3–8]. EMI may be harmful to human health; however, prevention of needless EM wave exposure is suggested and the development of materials with high EMI shielding efficiency (EMI SE) is imperative.

In this study, to develop a light-weight and low-cost EMI shielding material that can be easily produced, commercially available sponges have been used as the skeleton to prepare porous composites. Sponge is a material that consists of randomly interconnected one-dimensional cellulose and/or polyester fibers with high porosity, high surface area, excellent liquid absorbability, light-weight as well as being easily scalable in fabrication. More recently, the use of various sponge materials as frames for making devices or components has been intensively studied [9–12].

In our previous work, we reported a method to fabricate graphene-based commercial melamine sponges with superhydrophobic and superoleophilic properties. The sponges possess good recyclability and excellent absorption capacities, being able to absorb 165 times its own weight [13]. Zhang et al. fabricated the Graphene/PMMA nanocomposites prepared by blending of PMMA with graphene followed by forming the blends using subcritical CO_2 as the agent. The low graphene loading of 1.8 vol% exhibited the EMI SE of 13–19 dB in the frequency range of 8–12 GHz was reported [14]. In a similar topic but with different application, Chen et al. fabricated the flexible graphene foam composites with the EMI SE of 20 and 30 dB in X-band and in the frequency range of 0.03–1.5 GHz, respectively. The foam was prepared using Ni as the starting frame material and subsequently coated with graphene in a chemical vapour deposition (CVD) process using methane as the reactants [15]. However, to the best of our knowledge, no study has been published to investigate the use of a commercial sponge coated with nanoscale carbon fillers for EMI shielding. Herein, we propose an easy method to prepare porous composites with GP/ink, multi-walled CNT (MWCNT)/ink, or GP/MWCNT/ink coatings

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on the surface of inner pores in sponges through a simple dip-coating process to fabricate the EMI shielding materials.

2. Experimental

2.1. Preparation of GP and MWCNTs

Graphite oxide (GO) was prepared by the modified Hummer's method. GP with a thickness of 0.4–1.5 nm was obtained after reduction by $NaBH_4$ (150 mM) at 120 °C for 5 days. The product in the form of slurry was subjected to washing using DI water and subsequent centrifugation, and the processes were repeated until neutralization. The as-synthesized GP was then functionalized by mixing with $KMnO_4$ (in a 1:5 weight ratio) followed by the addition of H_2SO_4 (200 mL). After ultrasonication for 3 h at room temperature, HCl (50 mL) was added to the mixture under stirring. The mixing was continued for 30 min at 70 °C, after which the mixture was filtered and washed using DI water until neutralization. MWCNTs with an average diameter of 25 nm and purity of >95 wt% were purchased from CNT Co., Ltd, Korea. The pristine MWCNTs were acid-treated for functionalization using an acid solution containing HNO_3 and H_2SO_4 (with the volume ratio of 1:3) under stirring for 6 h at 75 °C, and the mixture was filtered and washed with DI water until neutralization.

2.2. Preparations of the sponge composites

To prepare the sponge composites, 1.0 wt% of GP, MWCNT, and GP/MWCNT fillers were individually introduced into an ink (PH-500, H. C. Starck) composed of poly(3,4-ethylenedioxythiophene) (poly(styrenesulfonate) (PEDOT:PSS), dimethyl sulfoxide (DMSO), isopropyl alcohol (IPA), H_2O, and surfactant. The mixture was subjected to ultrasonication for 90 min at room temperature to avoid precipitation of the filler (Fig. 1a). The commercial available melamine sponge was washed and dried, and subsequently immersed into the mixture for 1 min and then dried at 70 °C for 1 h (Fig. 1b). For EMI SE measurements, the sponge composites were cut into hollow cylinders (Fig. 1c). To prevent detachment of the fillers from the skeleton, the sponge composites were dipped into a dilute mixture of polydimethylsiloxane (PDMS, Sylgard 184) in xylene followed by drying at 100 °C for 24 h.

For the preparation of sponge composites coated with Ag particles, the as-purchased melamine sponges were cleaned by immersing the sponge in acetone under ultrasonication for 1 h followed by washing DI water. Next, the sponges were treated sequentially via etching, sensitization, and activation. In the etching process, the sponges were immersed in etchant containing CrO_3 and H_2SO_4 (1:1 volume ratio) for 1 min. For sensitization, the sponge was washed with DI water until achieving neutral pH and then immersed into a solution containing $SnCl_2$ and HCl (1:2.5 volume ratio) for 20 min. Next, the sponge was immersed into the activation solution containing $AgNO_3$ and $NH_3{\cdot}H_2O$ (1:10 weight ratio) for 10 min followed by washing with DI water until neutralization. The coating of the Ag particles was performed by immersing the sponge into $AgNO_3$ (10 mM) for 1 h followed by drying at 70 °C for 1 day. Fig. 2 schematically depicts the coatings of Ag particles and carbon nanomaterial fillers onto the surface of inner pores within sponge. Sponge composites coated with carbon nanomaterial filler only were also prepared for comparison. Specimens with dimensions of 50 × 50 mm were prepared for the microwave oven shielding test.

2.3. Measurements

Atomic force microscopy (AFM, Nanoscope IIIa, Digital Instruments Co.) was used to determine the thickness graphene, which was prepared by spin-coating on a silicon substrate. Field-emission scanning electron microscopy (FESEM, JEOL 6500F) was used for morphology studies of the GP, MWCNTs, and sponge composites. The high-resolution image of GP was recorded using transmission electron microscopy (TEM, JEOL, JEM-2100). Fourier-transform infrared spectroscopy (FTIR, Perkin–Elmer Spectrum RXI) was used to identify the functional groups on the GP and MWCNTs. Raman spectroscopy equipped with a He–Ne laser as the light source (632.8 nm, Raman LabRam-HR 800) was adopted to characterize microstructure of the composites.

The resistance measurement was carried out using a multimeter [DMM-93B]. A network analyzer (Alight Technologies, E 8364 A, PNA series) was used for EMI SE measurements in the frequency range of 0.45–1.5 GHz. Cylindrical specimens with the dimensions of 3.04 mm, 7.0 mm, and 10.0 mm for the inner diameter, outer diameter and length, respectively, were prepared. For the power

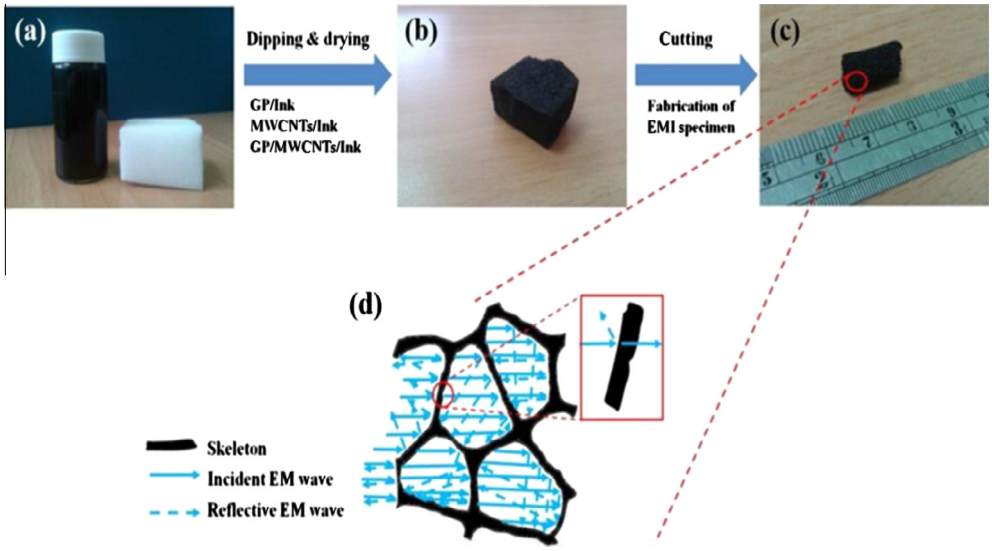

Fig. 1. Fabrication processes of sponge composites for EMI measurement. (a) Preparations of filler/ink solution containing 1.0 wt% of GP/ink, MWCNTs/ink, or hybrid GP/MWCNTs/ink. (b) The pristine sponge was dipped into filler/ink solutions to fabricate conductive networks in the sponge. (c) Appearance of the sponge specimen for EMI SE measurements. (d) Schematic plot of EMI transfer in sponge composites.