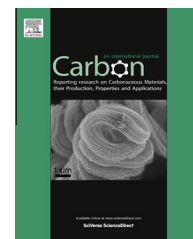


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Flexible electromagnetic interference shields made of silver flakes, carbon nanotubes and nitrile butadiene rubber



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ABSTRACT

The recent advances in portable and flexible electronic devices demand integration of flexibility into future electromagnetic interference shielding materials. Here we synthesized flexible adhesive shields made of microscale silver flakes (Ag flakes), multi-walled carbon nanotubes decorated with nanoscale silver particles (nAg-MWNTs), and nitrile butadiene rubber (NBR). The addition of nAg-MWNTs into the Ag flake–NBR mixture significantly enhanced both conductivity and shielding effectiveness. Long nanotubes electrically linked microscale Ag flakes embedded in the NBR matrix, and nanoscale silver particles further improved the contact interface. There was a logarithmic relationship between the conductivity and shielding effectiveness. The dominant mechanism of electromagnetic interference shielding was reflection. The achieved maximum shielding effectiveness was about ~75 dB at 1 GHz. The flexible adhesive shield printed on a polyimide film was wrapped around a cylindrical rod with a radius of 4 mm. The shielding effectiveness decreased about 20% after 100 wrapping cycles. The conductivity and shielding effectiveness could be adjusted by changing the Ag flake concentration. There was an excellent agreement between the theoretically predicted shielding effectiveness and the experimental data.

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1. Introduction

Electromagnetic interference (EMI) shielding has received considerable attention due to the increased use of highly integrated portable electronic devices [1]. Besides, recent advances in future flexible electronic devices, such as paper-like displays, wearable computers and foldable cellular phones [2–7], demand integration of flexibility into EMI shielding materials. Metal-based shields are currently most widely used, although they are heavy, expensive and subject to potential corrosion [8]. Conductive polymer composites,

consisting of conductive metallic fillers embedded in a polymer matrix, have also been extensively investigated [8,9]. Noble metals such as silver particles were employed as fillers due to the high conductivity and anti-oxidation characteristics. Alternatively, electrically conductive polymers and carbon-based conductive fillers were explored to replace metallic fillers [8,9]. These include polypyrrole, single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs) and graphene [1,10–12].

We previously demonstrated novel conductive composites by using microscale Ag flakes and MWNTs decorated with

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nanoscale silver particles (nAg-MWNTs) [13–15]. A small addition of nAg-MWNTs significantly increased the conductivity of composites. The nanotubes with high aspect ratios constructed effective electrical networks among microscale Ag flakes, and the contact interface was significantly improved by nanoscale silver particles adsorbed onto the side wall of carbon nanotubes [13–15]. This strategy could be successfully applied for epoxy, stretchable polyvinylidene fluoride (PVDF) and flexible nitrile butadiene rubber (NBR) matrices [13–15].

Here, we report flexible adhesive shields (FASs) printed on polyimide (PI) films by a bar-coating method. The microscale Ag flakes and nAg-MWNTs were embedded in NBR to enhance flexibility, conductivity and shielding effectiveness [15,16]. The average film thickness was about 20 μm , and shielding effectiveness was investigated according to ASTM D4935-10. The conductivity and shielding effectiveness of FAS were as high as $18,859.2 \text{ S cm}^{-1}$ and 75 dB at 1 GHz, respectively. The shielding effectiveness decreased about 20% after 100 wrapping cycles around a cylindrical rod with a radius of 4 mm. The adhesion on PI films was good.

2. Experimental

2.1. Materials

Ag flakes with an average size of $\sim 4.3 \mu\text{m}$ (SA-31812; Metalor, Neuchatel, Switzerland) were used as a primary conductive filler. The average outer diameter and length of MWNTs (Hanwha Nanotech Corp.) were 3–5 nm and 10–20 μm , respectively. The optimised synthesis conditions of nAg-MWNTs were previously published [13–15]. Briefly, AgNO_3 in ethanol (Junsei; 0.02 mol l^{-1} , 300 ml) was mixed with benzyl mercaptan solution (0.1 mol l^{-1} , 2.4 ml; Sigma Aldrich, St. Louis, MO, USA) by stirring for 48 h to synthesise Ag nanoparticles functionalised with phenyl rings. In the next step, MWNTs dispersed in 200 ml ethanol were added and additionally sonicated for 8 h (bath sonicator, 200 W). Finally, nAg-MWNTs were obtained by vacuum filtration, rinsing with ethanol and drying in vacuum chamber at room temperature [13–15]. The size of silver nanoparticles adsorbed onto the side wall of nanotubes was 3–5 nm. NBR was selected as a flexible and adhesive polymer matrix [15]. The NBR solution was prepared by dissolving solid NBR (27.5 wt.%) in toluene [15,16]. A commercial EMI shielding paste, composed of flake-type silver particles with an average size of $\sim 300 \text{ nm}$ and thermoplastic resin, was also tested as a control (IDP-01S; Doosung).

2.2. Synthesis of FAS

The schematic of the synthesis of FAS is shown in Fig. 1 following a previously published protocol [15]. First, Ag flakes were dispersed in 4-methyl-2-pentanone (12 ml) by ultrasonication (560 W for 20 min). A magnified scanning electron microscopy (SEM) image of Ag flakes is shown in Fig. 1a. Second, nAg-MWNTs were added and additionally ultrasonicated (560 W for 20 min). A high-resolution transmission electron microscopy (HRTEM) image of nAg-MWNTs is shown in Fig. 1b. In the next step, NBR solution (1 ml) was added and stirred for 1 h. The mixture was applied on a polyimide (PI)

film by a bar-coating method and dried at room temperature for 12 h. The diameter and thickness of the PI film were 13.4 cm and 60 μm , respectively. Finally, the specimen was cured on a hot plate at 170 $^{\circ}\text{C}$ for 45 min. The thickness of FAS on a PI film was in the range between 10 and 27 μm with an average thickness of $\sim 20 \mu\text{m}$ (Fig. 1c). Ag flakes connected by nAg-MWNTs could be observed in a magnified SEM image. As shown in Fig. 1d, the D- and G-mode of MWNTs could be clearly identified in the Raman spectrum of FAS [17]. The area map of the G-mode intensity of FAS shows a relatively uniform distribution of MWNTs in the film. Acronyms and compositions of synthesised specimens are summarised in Table 1. The relative weight ratio of Ag fillers in the commercially obtained thermoplastic resin-based EMI shielding paste (IDP-01S; Doosung) was 83%, which was determined by thermogravimetric analysis. In this study, the relative weight ratio between conductive fillers (Ag flakes and nAg-MWNTs) and NBR was varied in the synthesised specimens. FAS_83%_wo MWNTs were synthesised without nAg-MWNTs, whereas FAS_83% contained both Ag flakes and nAg-MWNTs. The total concentration of Ag flakes and nAg-MWNTs was 83% after curing (FAS_83%). FAS_83%_raw MWNTs contains raw MWNTs instead of nAg-MWNTs.

2.3. Characterisation and measurement set-up

The Raman spectra were obtained at an excitation length of 785 nm (Kaiser Optical Raman Spectrometer, RXN 1). Microscopic images were analysed by SEM (JEOL, Tokyo, Japan; JSM 890) and HRTEM (HRTEM, JEOL 300 kV). The electrical conductivity was measured by a four-point probe in-line method [13–15]. The resistance was measured using a current source (Keithley 6221) and a nanovoltmeter (Keithley 2182A) at a constant current of 20 μA . The probe was made of tungsten, and the distance between probes was 1 mm [13–15]. A schematic diagram of the shielding effectiveness measurement set-up (Korea Testing and Research Institute, Yongin, South Korea) is shown in Fig. 2a. A network analyser (4396B; Agilent Technologies, Inc., Santa Clara, CA, USA) and an S-parameter test set (Agilent; 85046A) were employed. The frequency range was between 30 MHz and 1.5 GHz. A coaxial sample holder was designed according to ASTM D4935-10. Reflectivity and transmissivity were also measured using a different set-up (Agilent, E5071C; Gumi Electronics & Information Technology Research Institute, Gumi, South Korea). Schematic diagrams of the reference and load specimens are shown in Fig. 2a. The diameter of the load specimen was 13.4 cm.

3. Results and discussion

3.1. Electrical conductivity and shielding effectiveness

The electrical conductivity and shielding effectiveness of specimens are shown in Table 1 and Fig. 2b, respectively. The conductivity of FAS_83%_wo MWNTs was negligible, although the concentration of Ag flakes was 83%. NBR has high flexibility and adhesion, but it is an insulating material [15]. It is possible that the Ag flakes were well surrounded by the NBR matrix leading to a negligible conductivity of

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