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Highly anisotropic Cu oblate ellipsoids incorporated polymer composites with excellent performance for broadband electromagnetic interference shielding

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ABSTRACT

In this study, highly anisotropic Cu oblate ellipsoids incorporated polymer composites were prepared that revealed excellent broadband electromagnetic shielding effectiveness of 80.0 to 62.1 dB at a frequency region between 300.0 KHz and 12.0 GHz, at low Cu contents. Cu-coated hollow polymer beads were fabricated through electroless plating of Cu on the polymer hollow beads. The hollow polymer beads were prepared through thermal expansion of acrylonitrile-based polymer beads containing a blowing agent. These beads were capable of incorporating highly anisotropic 2-dimensional (2D) Cu oblate ellipsoids into polymer composite through simple compression molding process. The resulting broadband electromagnetic shielding performance attributes to a low percolation behavior of the composites due to high anisotropy of the conductive Cu filler and their multilayered structure in the composites.

1. Introduction

Recent advances in telecommunication and electronic technologies have brought innovative prosperity in the ubiquitous life of human beings. Despite these advances, however, the unwanted electromagnetic (EM) signal interference produced through the excessive use of electronic devices has led to deterioration in performance of neighboring electronic gadgets, also causing invisible hazards to the health of humans [1–4].

Metals have excellent electrical conductivity among the materials; therefore, they are the most promising materials for electromagnetic interference (EMI) shielding because this characteristic is proportional to their excellent electrical conductivity [5,6]. However, metals have several disadvantages, including corrosion, large density, and relatively high cost. To mitigate these disadvantages, many carbon-filled polymer composite systems were explored for EMI shielding applications. Carbon filler-coated polymer composites were researched to get 20.2 dB at extremely low loading of MWCNT and graphite nanoplatelets [7] and 45.1 dB at 3.47 vol% of reduced graphene oxides [3]. However, the EMI shielding efficiency was required to be further improved. Recently, metal-filled polymer composites also received a great attention. But, to obtain a sufficient EMI shielding performance, large amount of particulate metallic fillers were incorporated in the polymer matrix to exceed the percolation limit [8–13]. The high percolation not only increases the density and cost but also decreases the processability and mechanical reliability of the product [12–15].

Recently, the incorporation of anisotropic metallic fillers, such as 1-dimensional (1D) metal nanowire [16,17] and 2-dimensional (2D) metal flakes [18] has gained tremendous interest to reduce the percolation threshold concentration. Arjmand et al. [16] and Al-Saleh et al. [17] reported that 1D Ag nanowire/PS (Ag nanowire 2.5 vol%) and 1D Cu nanowire/PS composites (Cu nanowire 2.1 vol

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%), due to the huge shape anisotropy of 1D nanowire fillers, showed low percolation and resultant high EMI shielding effectiveness (SE) values of 31.8 dB and 35.0 dB in X-band, respectively. However, the synthesis cost of 1D fillers, such as Cu and Ag nanowires is much higher than the common particular fillers and therefore, the use of 1D nanowire fillers are not economically viable to use in practical applications where high EMI shielding >50 dB is required. Li et al. [18] fabricated electrically conductive polyethersulphone (PES) composites containing 2D Al flakes (30 vol%) and an EMI SE value of above 50 dB was obtained at 1 GHz. EMI shielding performance of 2D flakes is better than isotropic particular filler systems [14,15], but it need to be improved compared with the 1D fillers.

Meanwhile, EMI shielding materials that cover a broadband frequency region are inevitably required to be developed for many arising future applications, such as satellite communications for GPS and navigation applications (3.0–30.0 MHz), aerospace communications (1.0–1.2 GHz), cellular devices (mobile phones and global positioning systems) (0.3–6.0 GHz), wireless LAN (2.4–5.0 GHz), and radar systems for self-driving car that can work in further expanded range of frequency (3.0–30.0 GHz). However, so far, most of the researches on EMI shielding materials have been focused on a limited frequency range, notably the X-band.

This study demonstrates that highly anisotropic Cu incorporated polymer composites, fabricated via a simple electroless plating of Cu onto the expanded polymer hollow beads followed by compression molding, provided excellent EMI shielding ability at a very broad frequency range.

2. Experimental section

2.1. Materials

Expandable polymer beads (Expancel 461 DU 40, Akzo Nobel, Sweden) were made of an acrylonitrile-based copolymer as shell and isobutane as blowing agent in core with diameter of 1–15 μm. Polystyrene (PS) and dimethylformamide (DMF) were purchased from Daejung Chemicals & Metals, Republic of Korea. All electroless plating reagents, including conditioner, sensitizer, activator, accelerator and electroless Cu plating solution were purchased from PI Tech, Republic of Korea. Cu solid beads were purchased from Sigma Aldrich.

2.2. Preparation of Cu coated expanded polymer beads (CuEBs)

Expanded polymer beads (EBs) were prepared through the thermal treatment of the expandable beads in oven at 130 °C for 5 min. The prepared EBs had the diameter of 20–40 μm. For the Cu coating on the surface of EBs, they were initially rinsed in 1 M NaOH solution for 5 min followed by neutralizing with the HCl solution. Then, the EBs were treated with tin and palladium catalyst and were stirred in the plating solution containing $CuSO_4$ for 30 min at 60 °C to perform the electroless Cu plating. The resulting Cu-coated EBs (CuEBs) were rinsed with distilled water and dried in oven at 70 °C for 18 h.

2.3. Preparation of CuEB/PS composites

PS was dissolved in DMF (10.0 mg mL^{-1}) under sonication for 30 min. The CuEBs were mixed with the PS solution in DMF while stirring for 30 min. CuEB/PS composites were precipitated in excessive methanol and the precipitate was dried in an oven overnight at 70 °C. The products were put into a stainless steel mold with a toroidal shape ($\phi_{out} = 7.0$ mm, $\phi_{in} = 3.0$ mm) and pressed under 5.0 MPa at 95 °C using a compression molding machine (Auto series, Carver Inc., U.S.A), (Fig. S1). Cu solid beads incorporated Cu/PS composites were compared as a control system. Isotropic Cu solid beads had the diameter of 40 μm.

2.4. Characterizations

The morphologies of CuEBs and CuEB/PS composites were examined using optical microscopy (DM2500P, Leica, Germany) and field-emission scanning electron microscopy (FE-SEM, Inspect F50, FEI Company, USA) techniques. Electrical conductivity of composites was examined using a four-pin probe (MCP-TP06P PSP) method with a low resistivity Loresta GP meter (MCP-T610, Mitsubishi Chemical, Japan). EMI SE of the samples was examined using a vector network analyzer (ENA5071, Keysight Technologies, USA) with a coaxial air line sample holder. Toroidal-shaped composite specimen ($\phi_{out} = 7.0$ mm, $\phi_{in} = 3.0$ mm) were prepared for EMI measurements [19,20].

3. Results and discussion

The fabrication process of CuEB/PS composites with highly anisotropic Cu oblate ellipsoids is exhibited in Fig. 1a. Optical microscopic images of polymer beads before (Fig. 1b) and after (Fig. 1c) expansion, and Cu-coated expanded polymer beads (Fig. 1d) are also shown. The expandable polymer beads were consisted of acrylonitrile-based copolymer shell and volatile isobutane blowing agent core. The expandable polymer beads with diameter of 1–15 μm were gradually foamed into expanded beads (EBs) with diameter of 20–40 μm through evaporation and escaping of blowing agent out of the polymer beads at 130 °C. The resulting EBs had completely spherical shape and an extremely low density of approximately 0.02 g cm^{-3}. CuEBs were prepared through uniform Cu coating on the surface of EBs through electroless plating method [21,22]. The EBs with inner empty space play as a template for the fabricating of Cu hollow beads. Average thickness of Cu shell was about 1 μm, which was confirmed by SEM analysis (inset of Fig. 1e). Cu coating layers formed very smooth surface on the EBs and exhibited high crystallinity without the formation of oxidation layer, as shown in Fig. S2. The CuEB/PS composites with highly anisotropic Cu oblate ellipsoids were successfully fabricated through compression molding of CuEB and PS blend under high pressure. Spherical CuEB beads were simultaneously deformed into highly anisotropic oblate ellipsoids, as shown in Fig. 1e and f. The Cu oblate ellipsoid morphology was examined through the observation of disc-shape morphology in a top view and squeezed ring shape morphology in a cross-sectional view. The Cu oblate ellipsoids were well distributed in the CuEB/PS composite and there were not found any voids between ellipsoids and matrix, indicating that there is no any interfacial debonding between Cu fillers and matrix polymer after compression molding process. Due to the highly anisotropy of Cu ellipsoid, CuEB/PS composites formed a percolative structure even at 7.0 vol% CuEBs. Additionally, it is worth noting that CuEB/PS composite revealed much larger compressive modulus and compressive strength than neat PS, as shown in Fig. S3. These are attributed not only to good dispersion quality of Cu ellipsoid dispersions in a matrix polymer, but also to larger modulus of Cu filler than PS matrix.

PS is an insulating polymer with an electrical conductivity of less than 10^{-16} S cm^{-1}. The electrical conductivities of CuEB/PS composites increased with the increase in CuEB content and exhibited the values of 1.1×10^{-7}, 7.8×10^{2} and 4.2×10^{3} S cm^{-1} at 2.7, 7.0 and 15.0 vol% of CuEBs, respectively (Fig. 2). Isotropic Cu solid beads with a diameter of 40 μm were used as a control system. The Cu/PS composite with 15.0 vol% isotropic Cu solid bead revealed very low electrical conductivity of 5×10^{-5} S cm^{-1}, which is much smaller than that of CuEB/PS composite at the same Cu