Preparation of Fe-Co metallic fibers reinforced composites and their electromagnetic properties

Sang-Bok Lee[1], Jin-woo Yi[1], Sang-Kwan Lee[1], Jin-Bong Kim[1], and Ki-Hyeon Kim[2]

[1] Composite Materials Research Group, Korea Institute of Materials Science, 797 Changwondae-ro, Changwon, Gyeongnam 641-010, South Korea
[2] Department of Physics, Yeungnam University, 214-1 Dae-dong, Gyeonsan, Gyeongbuk 712-749, South Korea

Introduction

Recently, a technology of EM absorbing at high frequency ranges has received an increasing attention. To develop high performance EM wave absorbing materials, fillers with high permeability and permittivity at GHz frequency ranges are indispensable for the development of thin, light, and high-performance absorbers with broad BWs. Conventional spherical magnetic particles have some drawbacks such as low permittivity and low permeability as well as high density at GHz frequency range [1-2]. Magnetic metal fiber with high aspect ratio, however, can lead to high permittivity and permeability at GHz frequency ranges due to their forming ability of bigger electric and magnetic dipoles, conductive networks, and the effect of nano-sized dimension to eliminate the eddy current loss [3-4].
In this paper, two different methods, electrospinning process (ESP) and electroless plating, were studied to prepare Fe-Co nano-fibers and Hollow Fe-Co fibers. The morphology and phase evolution in synthetic processes were analyzed with scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD). The permittivity and permeability of the composites were also measured using a network analyzer to assess their EM characteristics.

Experiment

Fabrication of Fe-Co nanofibers
Polyvinylpyrrolidone, anhydrous ethanol, Iron (III) nitrate, and cobalt nitrate were used as the precursor for Fe-Co nanofibers. The prepared solution was loaded into a plastic syringe that was connected to multi nozzles (50 series nozzles) with needle-like structure (inner diameter of 0.15 mm). A copper pin connected to a high-voltage generator was placed in the solution. The ESP was conducted facing upward to prevent the solution from dripping.
Based on the TG-DTA results, PVP/Fe salt nanofibers were calcined under air condition at 600°C for 1 hr, and were reduced in the high-purity H_2 atmosphere (flow rate of 5 ml/sec) at 500°C for 300 min, respectively.

Fabrication of hollow Fe-Co fibers
The Islands-in-the-Sea polyester fiber (70% PET/30% COPET), SESIL, provided by SAEHAN Company was used as a substrate. Before the hydrolysis, neat Islands-in-the-Sea polyester fibers were cleaned by a surfactant. Cleaned Islands-in-the-Sea polyester fibers were hydrolyzed in the solution of 8.5 g/L NaOH at 120℃ for 50 min.
Ni-P plating was carried out by Pd activation solution and phosphorous type reducing agent. The Ni-P plating solution contained the mixture of $NiSO_4 \cdot 6H_2O$, $KNaC_4H_4O_6 \cdot 4H_2O$, $NaPH_2O_2 \cdot H_2O$, $NH_3 \cdot Cl$ and deionized water. Electroless Ni-P plating was carried out at 90 °C for 8 min. Fe-P plating was performed on the surface of Ni-P coated fibers. The plating process was similar to Ni-P. $FeSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$, $KNaC_4H_4O6 \cdot 4H_2O$, $NaPH_2O_2 \cdot H_2O$, NaOH and deionized water constituted the Fe plating solution. In order to remove polymer substrates heat treatment resulting in the hollow structure was conducted at 500°C for 3 hr under the Ar atmosphere.

Fabrication of composites
Composites containing electrospun Fe-Co nanofibers and hollow Fe-Co fibers were fabricated with epoxy matrix by shear mixing method. The mixtures of epoxy resin and grinded Fe nanofibers were stirred using homogenizer (HMZ-20Dn, Global lab) for 20 min, degassed for 20 min, and then cured at 120°C for 2 hrs. The microstructures of the composites were observed using SEM. To analyze the EM wave characteristic of the composites, they were cut into cylindrical shapes (inner and outer diameters of 3.0 and 7.0 mm, respectively). The complex permittivity and permeability of the composites were measured in the 2~18 GHz frequency range using a network analyzer (Agilent N5230A).

Results and Discussion

Figure 1 illustrates SEM micrographs of electrospun PVP/Fe-Co salt nanofibers and as-reduced Fe-Co fibers at optimal ESP condition (applied voltage of 32 kV and feed rate of 5 ml/hr). There is a decreasing trend in the average diameters and standard deviations with applied voltage. The average diameters of electrospun PVP/Fe-Co salt nanofibers and as-reduced nanofibers were approximately 470 nm and 400 nm. From the XRD result, metallic nanofibers with Fe-Co phase were successfully fabricated by ESP and heat treatment. Amorphous phase of PVP/Fe-Co salt nanofibers transformed into $CoFe_2O_4$ phase and Fe_2Co phase during the calcination and the reduction processes.

Figure 2 illustrates SEM micrographs of electroless plating Ni/Fe-Co fiber and hollow Ni/Fe-Co fiber. Iron and cobalt alloy was coated on the surface of Ni-coated micron-sized fibers by electroless plating. From the SEM and XRD results, hollow Ni/Fe-Co fibers were also successfully fabricated by electroless plating and heat treatment. The plating thicknesses of Ni layer and Fe-Co layer were approximately 200 nm and 700 nm.

Figure 3 shows the complex permittivity and permeability of the epoxy composites containing 30 wt% of Fe-Co nanofibers. From the EM properties of Fe-Co nanofibers composites and hollow Ni/Fe-Co compoisites, it is concluded that metallic fiber of high aspect ratio also improves the permittivity and permeability compared to simple metallic spheres or particles of low aspect ratio.

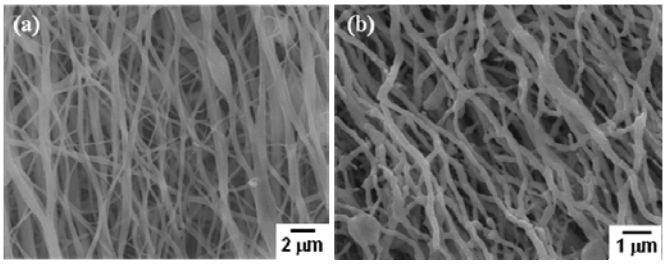

Fig. 1 SEM morphologies of (a) electrospun PVP/Fe-Co salt nanofibers and (b) as-reduced Fe-Co nanofibers

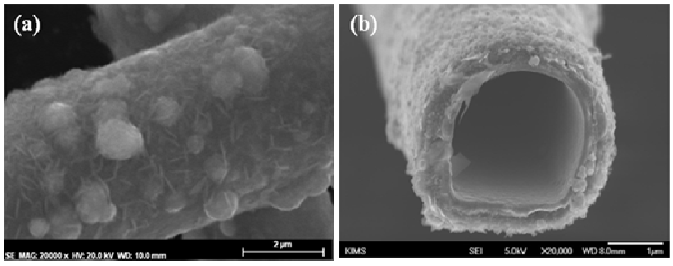

Fig. 2 SEM morphologies of (a) electroless plating Ni/Fe-Co fiber and (b) hollow Ni/Fe-Co fiber

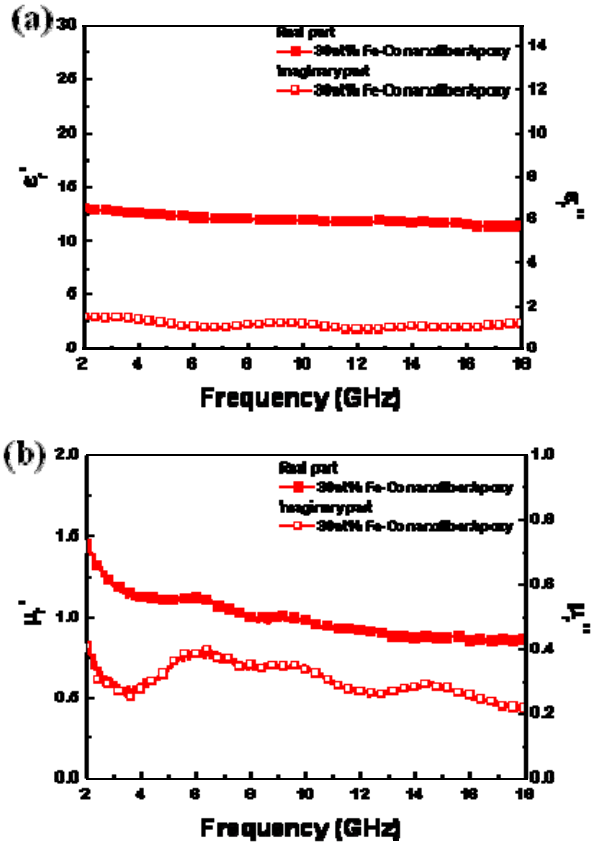

Fig. 3 EM properties of the epoxy composites containing 30 wt% of Fe-Co nanofibers: (a) permittivity and (b) permeability, respectively

Summary

In order to increase the EM wave absorbing properties in GHz frequency region, Fe-Co nanofibers and Ni/Fe-Co hollow fibers have been successfully synthesized by ESP and electroless plating. The high aspect ratio Fe-Co nanofibers have the excellent EM properties compared to spherical magnetic particles.

References

1. Martha P. *J. Magn. Magn. Mater.* **215-216** (2000) 171-183.
2. Kim SS, Kim ST, Ahn JM, Kim KH. *J. Magn. Magn. Mater.* **271** (2004) 39-45.
3. Kim M.S., Min E.H., and Koh J.G., *J. Magn. Magn. Mater.* **321** (2009) 581-585.
4. Itoh M., Liu J.R., Horikawa T., and Machida K., *J. Alloys Compo.* **408-412** (2006) 1400-1403.