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Electromagnetic wave absorption properties of composites with ultrafine hollow magnetic fibers

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ABSTRACT

Ultrafine hollow magnetic fibers were prepared by electroless plating using hydrolyzed polyester fiber as a sacrificial substrate. These hollow fibers can be served for lightweight and efficient electromagnetic (EM) absorbing materials. As observed from SEM and EDS analysis, hollow structures consisting of Ni inner layer and Fe or Fe–Co outer layer were obtained. By introducing Co onto Fe, oxidation of the Fe layer was successfully prevented making it possible to enhance the complex permeability compared to a case in which only Fe was used. Polymeric composites containing the hollow fibers with different weight fractions and fiber lengths were prepared by a simple mixing process. The electromagnetic wave properties of the composites were measured by a vector network analyzer and it was found that the hollow magnetic fibers show a clear resonance peak of the complex permittivity around the X-band range (8–12 GHz) and the resonance frequency strongly depends on the fiber concentration and length. A possible explanation for the unique resonance is that the hollow fibers possess relatively low electrical conductivity and a long mean free path due to their oxidized phase and hollow structure. The calculated EM wave absorption with the measured EM wave properties showed that the composite containing 30 wt% hollow Ni/Fe–Co (7:3) fibers in length of 180 μm exhibited multiple absorbance peaks resulting in a broad absorption bandwidth of 4.2 GHz. It is obvious that this multiple absorbance is attributed to the resonance characteristic of the composite.

1. Introduction

Many studies of magnetic materials have been carried out over time, and the results of many have been realized in various fields of industry owing to the simple magnetism of the materials. In recent years, there has also been a dramatic proliferation of research concerned with the potentials of electromagnetic (EM) wave absorbers [1–5]. Although several types of magnetic particles, such as spheres, flakes and fibers, have been comprehensively studied [6–12], there are still a few drawbacks associated with conventional magnetic particles when applying them in EM-absorbing applications. Because, in particular, spherical and flaky particles generally have low permittivity, they show some limitations in engineering thin EM wave absorbers in the range of GHz frequency, at which many of the newest equipment for military and electronic applications is operated. Even though these particles are contained at a very high volume, the weight of absorbers increases but the permittivity improvement is marginal due to the low aspect ratio.

Several studies of the fabrication of fibrous magnetic particles have also been reported [13,14]. The high aspect ratio of the particles can enhance the permittivity of the composite absorbers containing them compared to the same volume fraction of conventional particles with a low aspect ratio. However, the diameters of most of the fibers are too large to make thin composite absorbers. Even in the case of nano-size magnetic fibers, it was noted that they can easily aggregate and connect with physical or chemical linkages [15–17]. In addition, the density of the fibers as well as other types of particles is generally very high (4–8 g/cm^3); consequently when conventional magnetic particles and fibers are added, the composite absorbers inevitably become heavy.

In order to fabricate lightweight EM absorbers including heavy magnetic fillers, the fillers with a hollow structure can be more efficient than those with a solid structure. Hollow particles at a certain weight fraction can occupy a greater volume in the matrix.

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Moreover, it is predicted that the permittivity and permeability of composites with fine fibrous particles can be enhanced while leaving the intrinsic properties unchanged. Regarding this point, in our previous research, we proposed an approach to produce ultrafine hollow magnetic fibers using island-in-the-sea fibers as a substrate for an electroless plating method and then reported the results of the preparation of ultrafine hollow Ni/Fe fibers and the dispersion state of their composites [18]. However, the outer layer thickness of the hollow fibers should be precisely controlled at less than 700 nm, as the Fe layer is subject to becoming oxidized under ambient conditions. To minimize the oxidation, we introduced cobalt (Co) onto the Fe layer. Furthermore, we expect that less oxidative Co can improve the permeability of composites within the GHz frequency. Therefore, in this work, we additionally prepared hollow Ni/Fe–Co fibers to study the effect of Co element on the complex permittivity and permeability of composites. From these results, we investigated the EM absorption behaviors of these hollow Ni/Fe or Ni/Fe–Co fibers at the GHz frequency.

2. Experiment

2.1. Fabrication of hollow magnetic fibers and their composites

As a substrate for the metal deposition, island-in-the-sea polyester fibers, SESIL (SAEHAN, Korea) were used. The fibers consisting of 36 fibrils and a soluble part were cut into pieces about 500 μm in length and were then hydrolyzed in a solution of 8.5 g/L NaOH maintained at 120 °C for 50 min. During the hydrolysis process, the soluble part was dissolved away from the original fibers and completely removed by washing with an excess amount of water. The average diameter of the remaining fibrils was about 2 μm.

Before the nickel (Ni) plating step, the hydrolyzed fibers were sensitized by a $SnCl_2$ solution and subsequently activated by a $PdCl_2$ solution. The activated fibers were accelerated by a concentrated aqueous H_2SO_4 solution. Ni was coated onto the surface of the pre-treated fibers. Iron (Fe) and cobalt (Co) were simultaneously deposited on the surface of the Ni-coated fibers resulting in an Fe layer and an Fe–Co alloy layer. The plating solution included the two metal salts of $FeSO_4 \cdot 7H_2O$ and $CoSO_4 \cdot 7H_2O$. $NaBH_4$ and NaOH were used as a reducing agent and a pH-controlling agent, respectively. The added weight ratio of the Fe salt and the Co salt was 5:5. The specific compositions of the ingredients and the plating conditions for the metal plating process are shown in Table 1.

Table 1
Chemical compositions and plating conditions for the Ni and Fe–Co plating.

	Ni plating	Fe–Co plating	
		Weight ratio of Fe salt 10:0	Weight ratio of Co salt 5:5
Chemicals (g/L)			
$NiSO_4 \cdot 6H_2O$	30	–	
$FeSO_4 \cdot 7H_2O$	–	25	12.5
$CoSO_4 \cdot 7H_2O$	180	120	12.5
$KNaC_4H_4O_6 \cdot 4H_2O$	70	–	120
NH_3Cl	60	–	–
$NaPH_2O_2 \cdot H_2O$	–	20	–
$NaBH_4$			20
Conditions			
pH	9.1	12.9	
Temperature (°C)	89	45	
Plating time (min)	8	60	

To remove the polymer substrates, a heat treatment was conducted at 500 °C for 3 h under an argon atmosphere resulting in the hollow structure. Composites containing the hollow magnetic fibers were fabricated with different concentrations. Mixtures of epoxy resin and the hollow magnetic fibers at concentrations of 10, 20, 30 wt% were homogenized at 60 °C so that they would be well dispersed. After these mixtures were degassed under a vacuum at 60 °C for 50 min, they were cured at 120 °C for 3 h.

2.2. Characterizations

SEM was used for the observation of the morphology and layer thickness of the fibers. The element compositions, particularly, the Co atomic fractions, were measured by EDS. X-ray diffraction (XRD) patterns of the hollow fibers were obtained using Cu Kα radiation with a voltage of 40 kV and a generator current of 40 mA (Rigaku, D/max 2200). The scanning rate and interval were 5°/min and 0.02°, respectively.

To measure the complex permittivity and permeability of the composites at the microwave frequency band, an Agilent N5230A analyzer (PNA-L Vector Network Analyzer) and a 7 mm coaxial airline with an Agilent N3696A module (Electrical Calibration Module) were used. The composite specimens were machined and trimmed into a toroidal shape with an outer diameter of 7 mm and an inner diameter of 3 mm. Silver paste was applied to the edges of the specimens, and they were inserted closely into the coaxial airline. The dimensionless permittivity and permeability were obtained from scattering parameters for reflected and transmitted microwaves over 0.5–18 GHz using an Agilent 85071E (Material Measurement Software) which adopted the Nicolson–Ross–Weir method [19].

3. Results and discussion

3.1. Morphology and phase analysis of the hollow magnetic fibers

Typical morphologies of metal-coated polymeric fibers and the corresponding heat-treated fibers are shown in Fig. 1. SEM examinations revealed that most of the fibers were well separated from each other, with a precise hollow structure with an inner layer (Ni) thickness of 100–200 nm and an outer layer thickness (Fe or Fe–Co) of 500–700 nm. The average diameter of the hollow fibers was measured at ~3.5 μm. From the results of the EDS analysis (Table 2), we also confirmed the elemental compositions of the Ni/Fe and Ni/Fe–Co fibers. As expected, the fibers are mainly composed of Ni, Fe and Co elements, and the composition of the fibers can be controlled without significant differences by varying the initial amount of the metal salts in the plating solution.

Fig. 2 shows XRD patterns of the hollow fibers. As the heat treatment led to crystallization of the coated magnetic layers, different sharp peaks were seen. Diffraction peaks of elemental Fe or Co which are generally considered indistinguishable [20], correspond to 44.5°, 65.2° and 82.5° at 2θ values, and new alloy formations of NiFe or NiFeCo were observed at 43.5°, 50.7° and 74.6° indicating that the Ni element around the interlayer region had slightly diffused into the Fe or Fe–Co layer during the heat treatment. One noticeable feature was that unlike Ni/Fe fibers, the peaks of the oxidized phase (Fe_3O_4) of the Ni/Fe–Co fibers were considered to be negligible due to the very low intensity. It is probable that their high resistance to the oxidation is attributed to the addition of Co into the Fe layers. Therefore, by alloying with the Co element, more stable hollow fibers against ambient conditions can be fabricated.