MEASUREMENT OF ELECTROMAGNETIC PROPERTIES FOR POLYMERIC COMPOSITES CONTAINING METAL-COATED SUBMICRON POLYSTYRENE PARTICLES

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Abstract

As substrates for electroless metal plating, submicron polystyrene spheres were synthesized by dispersion polymerization. These metal-coated polymer particles were designed for light and high efficient electromagnetic wave absorbing materials. SEM, TEM and EDS confirmed the surface morphology and coating thickness of Ni and Fe. Polymeric composites containing metal-coated PS particles were prepared to compare electromagnetic properties. Complex EM properties showed the tendency to increase with the net concentrations of Fe. The composite of 30 wt% Fe shows the higher complex permeabilities compared to the BF-contained composite (35 wt%) despite its lower density

1 Introduction

For a long time, magnetic particles have been of some interests simply because of their magnetism [1]. However, they have attracted attention considerably because of the potential for the electromagnetic (EM) interference and absorbing materials nowadays [2]. But there are also a few drawbacks, for instance, the diversity of particle shape/size that probably make inhomogeneity in the polymer composite system. The high density (4~8 g/cm^3) problem of magnetic particles may give birth to increasing weight of composites related to EM applications. Accordingly it is necessary by all means to improve those points of magnetic particles.

To prepare light/homogeneous EM absorbing materials containing originally heavy magnetic particles, the combination of technologies to make light polymer substrate particles (around 1 g/cm^3 density) and coat magnetic portion on the surface is required

Several techniques have been developed to prepare micro or submicron polymer particles. The polymerization method such emulsion [3], suspension [4] and dispersion polymerization [5] is a typical way which has been applied to the manufacturing of commercial products. Especially, when size control in submicron dimension can be possible, these polymeric particles may give a variety of applications in the field of analytical chemistry, biomaterials, information technology and coating, etc.

Dispersion polymerization with vinyl monomer, initiator and stabilizer is one of the most effective methods in preparing polymer particles. It can make particles directly by means of the solubility difference for polymerization media between monomer and polymer. Moreover, particle size, size distribution and morphology can be easily regulated through the change in contents of agents and reaction conditions.

In this article, we have performed dispersion polymerization in order to synthesize polymer particles of submicron size and metallic coating on the surface of particles. For metallic coating, electroless plating [6] which so far has been well established was used. In addition, we have fabricated polymer composites reinforced with metal-coated polymer particles and evaluated the degree of coating followed by measuring their EM properties such as permittivity and permeability.

2 Experimentals

2.1 Materials

Styrene and divinyl benzene (DVB) were purified under the reduced pressure to remove an inhibitor. Purified 2,2-azobis(isobutyronitrile) (AIBN) and poly(vinyl pyrrolidone) (PVP) were used as an initiator and stabilizer respectively. Pure

methanol was used as a polymerization medium without further purification. Barium ferrite (BF, Aldrich, 325 mesh) was used as received.

Electroless Ni-P plating [7-8] process was achieved by commercial activation solution and plating bath. The Fe plating bath was formulated.

2.2 Polymerization

The dispersion polymerization of styrene was conducted in methanol with DVB, AIBN and PVP. The polymerization was carried out in a 500 ml vessel under nitrogen atmosphere with mechanical stirring at 400 rpm. 40 g of methanol was first poured into a 4-necked flask and 4 g styrene, 0.4 g DVB, 0.4 g PVP, 0.1 g AIBN were next charged. Reaction was kept in the temperature of 60℃ and for 6 hours. After polymerization was completed, the filtered result was cleaned off with the excess of methanol/ distilled water and then dried in a vacuum oven at 60℃ for 16 hours.

2.3 Electroless plating

Ni-P plating was carried out by Pd activation solution and phosphorous type reducing agent in comply with the commercial instruction. Plating process is divided into five steps; dispersion, sensitization, activation and acceleration followed by deposition. Ni-P coated particles were heat-treated at 400 ℃ for 4 hours under the Argon atmosphere to induce the magnetism.

Fe plating process is similar to Ni-P. The plating solution consists of $FeSO_4 \cdot 7H_2O$, $KNaC_4H_4O_6 \cdot 4H_2O$, $NaH_2PO_2 \cdot H_2O$ and distilled water adjusted to pH 11.

2.4 Fabrication of composites

Composites containing metal-coated particles were fabricated with the different concentrations of fillers. At first, the mixtures of particles and resin with net concentrations of 13, 22, 30 wt% Fe and 20 wt% Ni were ultra-sonicated for well dispersion. And then they were cured at high temperature.

3 Characterization

SEM was used for the observation of surface morphologies of polystyrene particles and metal-coated particles. The layer thickness of metals on the polymer particles was observed by SEM/TEM technology and EDS showed the element composition of coated particles.

In order to measure the complex permittivity and permeability at the microwave frequency band, Agilent N5230A (PNA-L Vector Network Analyzer) and 7 mm coaxial airline with Agilent N3696A (Electrical Calibration Module) were used. Composite specimens used for the measurements were machined out of plates so that the specimen could be inserted into the coaxial airline. Complex EM property data were obtained using Agilent 85071E (Material Measurement Software), in which the Nicolson-Ross-Weir method is implicated, from scattering parameters for reflected and transmitted microwaves over 0.5 GHz ~ 18 GHz. [9]

4 Results and Discussion

4.1 Submicron Polystyrene (PS) particles

PS submicron particles were prepared by dispersion polymerization using AIBN as a radical initiator and PVP as a dispersion stabilizer. DVB was incorporated to enable PS particles to retain the resistance to organic solvents which would be contained in matrix resins. Particle sizes ranged practically from 0.8 to 1.0 ㎛. It has been well known that they have some difficulties in obtaining a narrow size distribution of PS particles when the simple combination of AIBN and PVP is made through the dispersion polymerization [5]. The morphology of particles was not a perfect spherical shape because of the usage of DVB [10].

4.2 Ni-coated particles

Figure 2 shows the morphology of Ni-P coated particles by the electroless plating method. Particle sizes slightly increased due to the surface-coated layer of Ni-P around 1.1 ㎛. In order to confirm the layer and composition of Ni-P, EDS analysis was carried out. EDS peaks in Figure 3 show the approximate layer composition of 94 wt% Ni and 6 wt% phosphorus.

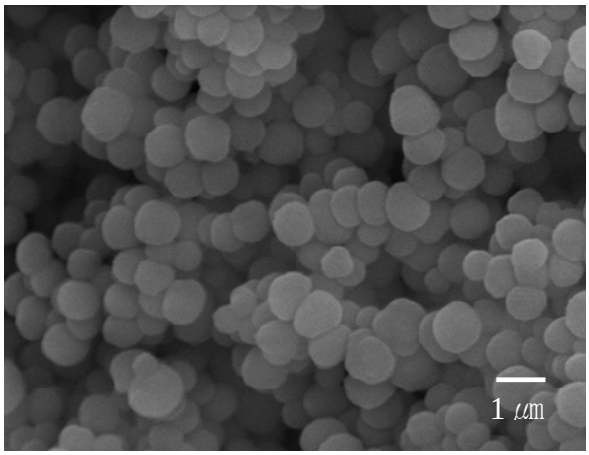

Fig. 1. SEM micrograph of PS submicron spheres

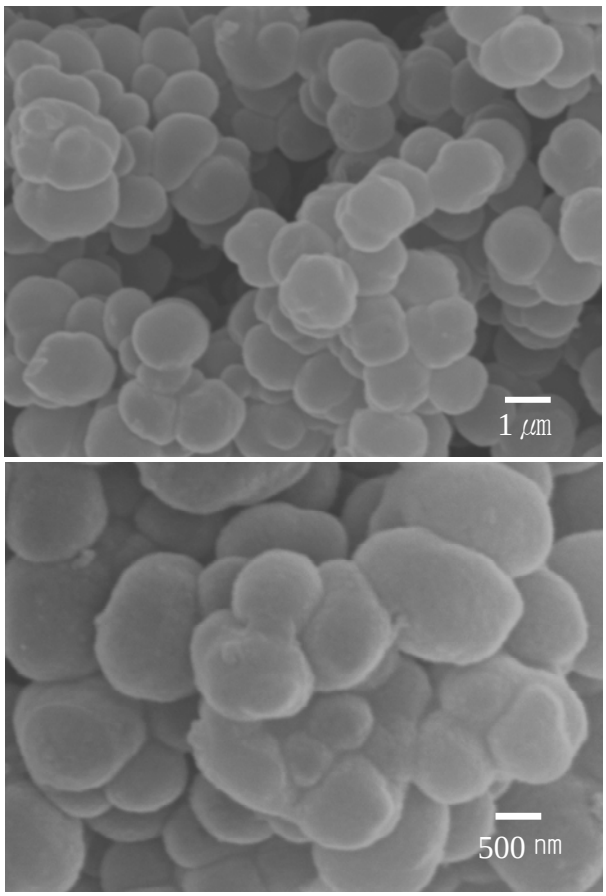

Fig. 2. SEM micrograph of Ni-coated PS particles

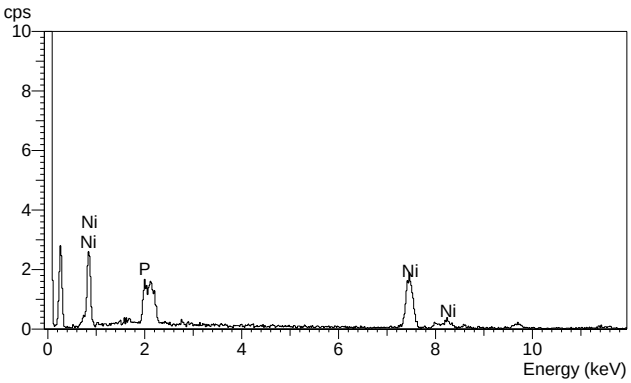

Fig. 3. EDS peaks of surface of Ni-P coated particles

To verify the thickness of coated layer of Ni on the PS surface, we embedded those particles in epoxy resin and polished. A SEM micrograph in figure 4 shows the sectional area of those particles embedded in epoxy resin. The thickness was approximately about 100 nm [8].

4.3 Fe-coated particles

Through the similar analytic processes as Ni-P case, surface morphology and diameter of Fe-plated particles were also verified. The slight increase in particle size was observed by the image of figure 5.a). Diameters were around ~ 1.1 μm. Figure 5.b) shows the morphology of Fe-coated particles after heat treatment by TGA. During heat treatment, polymeric portion underwent thermal degradation and then we could clearly see the exact plating shape.

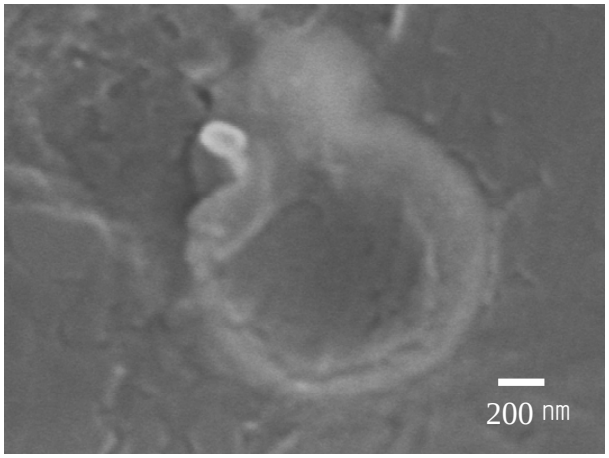

Fig. 4. Cross section of a metal-coated particle

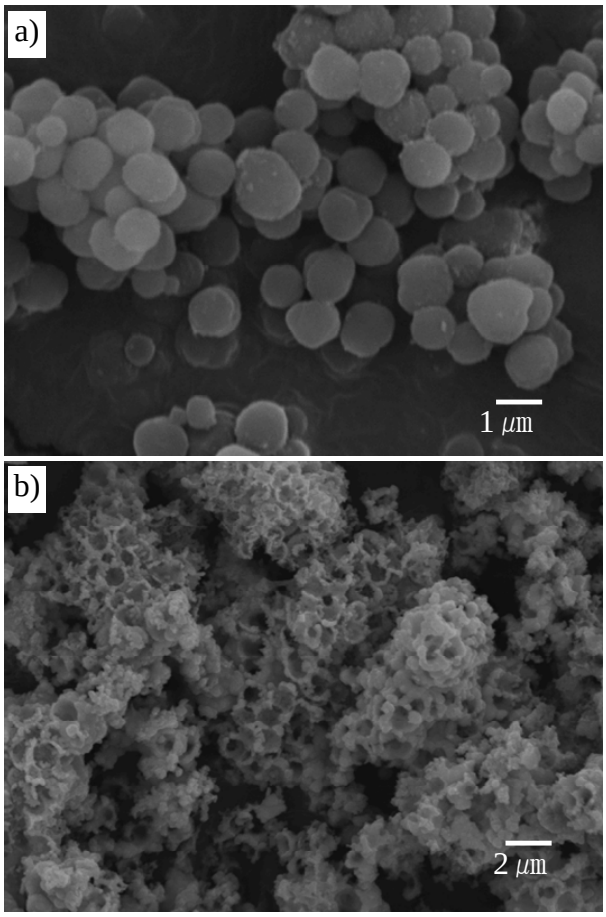

Fig. 5. SEM micrograph of Fe-coated PS particles
a) before heat treatment b) after heat treatment

According to that image, Fe portion did not completely cover the surface area of PS particles. It is apparent that outward surface at any points where several tens of particles themselves aggregated was only coated. We can expect that if some efforts to disperse PS particles better before electroless plating are made, it is possible for Fe portion to cover total surface of PS particles. Fe-coated particles contain 43.2 wt% of Fe in average. (Fig. 6) EDS analysis was also performed to demonstrate Fe coating. (Fig. 7)

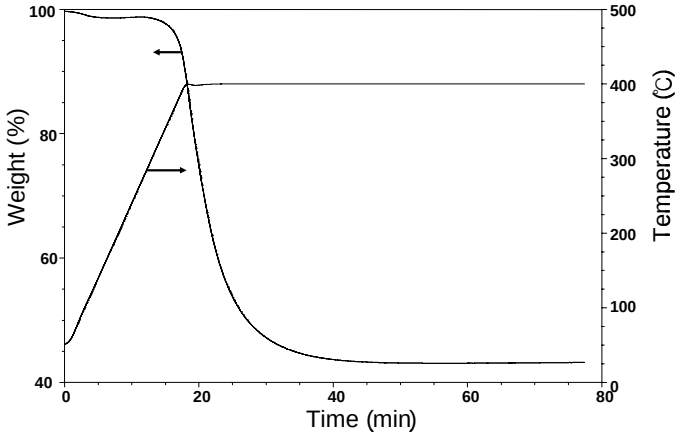

Fig. 6. TGA analysis of Fe-coated PS particles

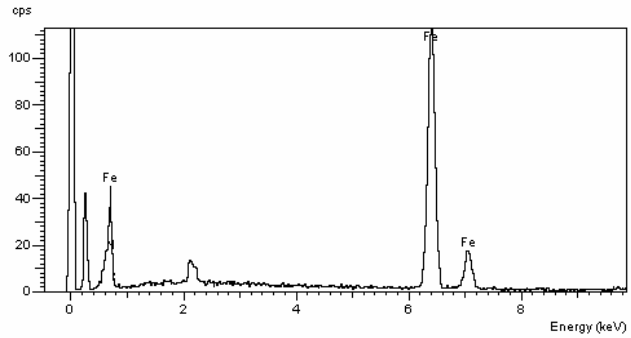

Fig. 7. EDS peaks of Fe coated particles

It is necessary to verify the thickness of Fe-coated layer as well. In case of Fe coating, we were able to measure the thickness easily and precisely by means of TEM technology (Fig. 8) resulting in 80 ~ 90 ㎚.

4.4 Composites containing metal-coated particles

We fabricated polymer composites containing metal-coated particles to measure electromagnetic characteristics, especially complex permeability. In addition, a BF composite was also prepared to compare the properties. Figure 9. a) and b) shows the real and imaginary parts of complex permittivity

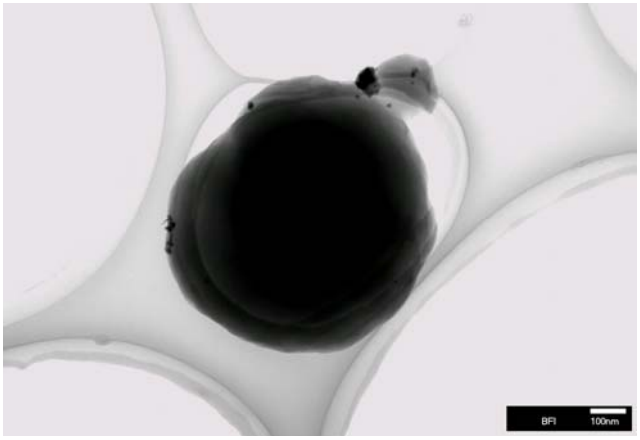

Fig. 8. TEM micrograph of a Fe coated particle

respectively. In case of Fe-coated particles, both real and imaginary permittivities of these composites increase as the net Fe concentrations increase. The composite containing 20 wt% of Ni-P has higher

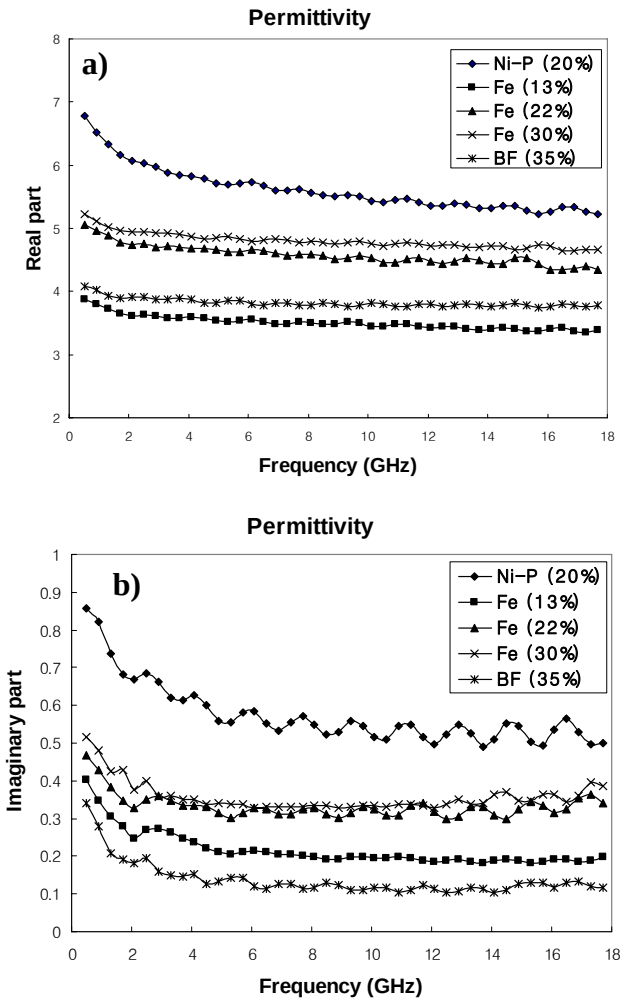

Fig. 9. The complex permittivity of composites a) real part b) imaginary part

permittivity values than those of the corresponding composite that contains 22 wt% and even 30 wt% of Fe. This phenomenon can be explained by the effect of heat treatment. Heat treatment of Ni-P must be needed to induce the magnetic properties. In general, after heat treatment Ni-P becomes denser resulting in, for instance, crystalline structure. Even if original conductivity values of Fe and Ni are nearly equivalent, heat-treated Ni is likely to show higher conductivity. Higher conductivity of heat-treated probably has a great effect on the permittivity.

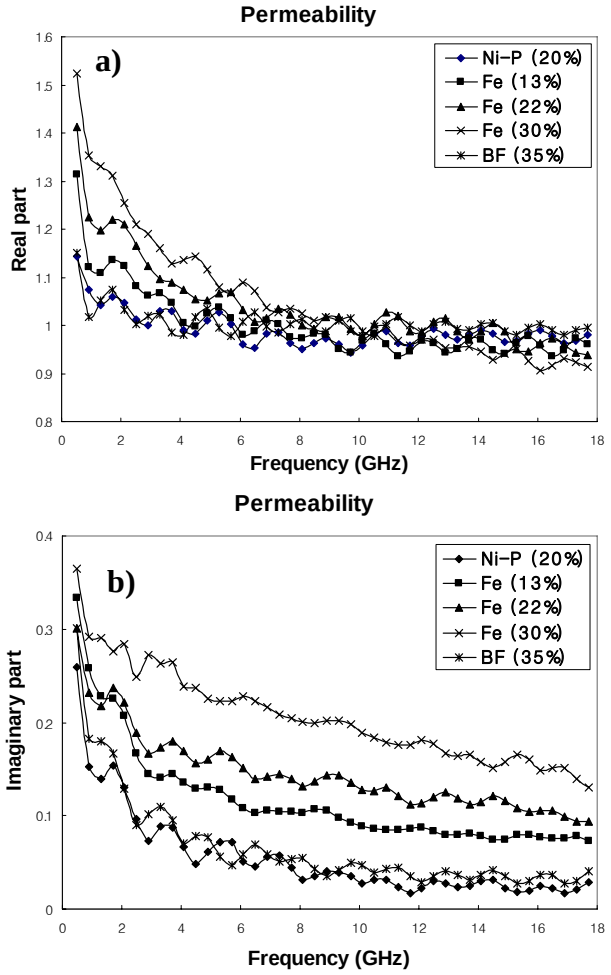

Fig. 10. The complex permeability of composites a) real part b) imaginary part

Figure 10. a) and b) shows the real and imaginary parts of complex permeability results on which were focused in this paper. Permeability values of Fe-contained composites tend to increase certainly as these magnetic filler concentrations increase. It was observed that the imaginary part increase more rapidly compared to the real part over all frequency. The composite containing 30 wt% of Fe displays much higher permeability values than that of the BF-contained composite even though it has a smaller density (Table 1). Composite density is one of the key factors in producing an efficient EM wave absorber. BF is a typical magnetic material widely used to make magnets.

Table 1. Density of composites in variation of net concentrations

Notation	Coated metal	Net concentration (wt%)	Density (g/cm^3)
Ni-P (20 wt%)	Ni-P	20	1.41
Fe (13 wt%)	Fe	13	1.25
Fe (22 wt%)	Fe	22	1.35
Fe (30 wt%)	Fe	30	1.44
BF (35 wt%)	-	35	1.64

5 Conclusions

Polystyrene spheres with the submicron size around 0.8 ~ 1.0 ㎛ were produced by dispersion polymerization using an initiator, AIBN and a stabilizer, PVP. On the surface of these PS spheres, Ni and Fe were coated by the electroless plating method. EDS peaks confirmed the surface coating layer of Ni and Fe and analyses of SEM and TEM indicated that coating thickness was around 80 ~100 ㎚ and however further study on the particle dispersion and electroless plating was needed to fully control the surface morphology of metal-coated layer. We also prepared polymeric composites containing metal-coated PS particles to measure electric and magnetic properties. Depending on the coated metal types, real/imaginary parts of permittivity and permeability were different. The order of net Fe concentrations in the composites no doubt influenced the increasing tendency of each EM property. The composite of 30 wt% Fe shows the higher complex permeabilities compared to the BF-contained composite (35 wt%) despite its lower density.

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