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Plating of Metal (Co, Ag) Thin Films on Hollow Microspheres of Low Density and Its Application to Lightweight Microwave Absorbers

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Conductive (Ag) and magnetic (Co) thin films are plated on hollow silica microspheres of low average density (about 0.2 g/cc) for the application to lightweight microwave absorbers. The metal plating was carried out in a two-step electroless plating process (pre-treatment of sensitizing and subsequent plating). Grain morphology and uniformity of the coated films were observed by SEM. Complex permeability and permittivity, and microwave absorbance were determined in the rubber composites containing the metal-coated microspheres. For Ag-coated particles, high dielectric constant (due to space charge polarization between the conductive particles) and considerable conduction loss are observed. For Co-coated particles, additional loss due to ferromagnetic resonance is identified in microwave frequency range. Due to these high-frequency electromagnetic properties, the composite specimens (in particular, containing the Co-coated microspheres with magnetic loss) show high absorption rate (more than 20 dB) for electromagnetic radiation in X-band frequencies with a small thickness (2 mm) and a low density (about 1.0 g/cc).

Key words: microwave, absorber, lightweight, thin film, microsphere

1. INTRODUCTION

Electromagnetic interference (EMI), a specific kind of environmental pollution, is drawing more attention due to the rapid growth in the utilization of telecommunication and electronic devices in the residential and industrial applications. A number of materials have been described in the prior arts, which are capable of absorbing electromagnetic radiation. However, the conventional absorptive materials such as iron powders and ferrites are quite heavy, which restricts their usefulness in applications requiring lightweight mass [1, 2]. Plastic foams containing carbon particles, metal powders and ferrites require a considerable thickness and are physically too weak for many applications [3]. Resonant absorbers based on resistive material quarter wavelength from a reflector are only effective at a very narrow frequency band [4].

As one of the ways to overcome this problem, the use of metal thin films coated on the microspheres of low density has been suggested. Gindrup [5] proposed an electromagnetic radiation absorptive composition, which comprises hollow microspheres having a low density (below 0.5 g/cc) and a thin coating of metals on the microsphere surface. However, since the coating on microsphere is confined to only single layer of silver (which has only conduction loss), the microwave absorption was inferior to conventional absorptive materials.

The present study proposes a magnetic (Co) thin film as the coating layer on the hollow microspheres and investigates its magnetic loss contribution to the microwave absorbing properties. As the reference data with a pure conduction loss, the experimental result on Ag-coated microspheres is also provided.

2. EXPERIMENTAL

Commercially available hollow microspheres were obtained from PQ Cooperation, USA. The microspheres have a hollow ceramic (silicate) shell and thus having a low average density (0.2 g/cc). Metal (Ag, Co) plating was carried out in a two-step operation in which the surface of microspheres is first sensitized by treatment with salts of metal ($SnCl_2$ for Ag plating, $PdCl_2$-$SnCl_2$ for Co plating), followed by chemically reducing salts of metals ($AgNO_3$ and $CoSO_4$) using a mild reducing agent (fructose for Ag plating and $NaPH_2O_2{\cdot}H_2O$ for Co plating).

Uniform coating of metals on microspheres can be identified by two methods: one is by measuring the apparent electrical resistance and the other is by direct observation using SEM. Apparent electrical resistance was measured in the compacts of metal-coated microspheres (with a fixed weight of 0.05 g) in insulated cylinder mold of 10 mm inner diameter.

The complex permeability and permittivity was determined by reflection/transmission technique in the composite specimens of the metal-coated microspheres dispersed silicone rubber matrix. The mixing ratio of particles to rubber was 1:1 by weight. Reflection loss was determined by measuring the reflection coefficient after the rear face of sample was terminated by metal.

3. RESULTS AND DISCUSSION

3.1 Ag-coated microspheres

The electrical conductivity of Ag films on microspheres was controlled by $AgNO_3$ concentration in the plating solution. A highly conductive film (with apparent resistance below 10 Ω) was obtained with sufficient supply of Ag ions (high concentration of $AgNO_3$ in plating solution), because of large surface area of the microspheres. The result is confirmed with microstructures. In the surface of highly resistive microspheres (6 kΩ), island structure of Ag grains (separated with each other) was observed (Fig. 1). On the while, highly conductive microspheres (0.13 Ω) have the uniform coating with connected grain structure as shown in Fig. 2.

Fig. 3 shows the real and imaginary part of complex permittivity ($\varepsilon_r=\varepsilon_r'-j\varepsilon_r''$) determined in the composites containing the Ag-coated microspheres. In the case of non-coated microspheres, very low value of $\varepsilon_r'=2.6$ and $\varepsilon_r''\approx0$ were determined. Both ε_r' and ε_r'' increase with decrease of resistance. $\varepsilon_r'=15$ and $\varepsilon_r''\geq0.5$ were determined in the conductive microspheres of 0.13 Ω, which is due to the space charge polarization between the Ag-coated particles and the conduction loss along the film surface.

Fig. 4 shows the reflection loss determined in the composites containing the Ag-coated microspheres.

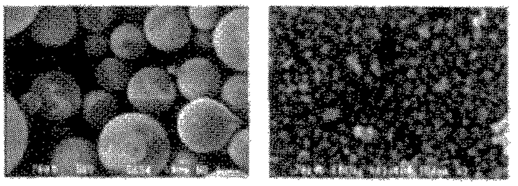

Fig. 1. SEM observation of Ag-coated microspheres (6 kΩ).

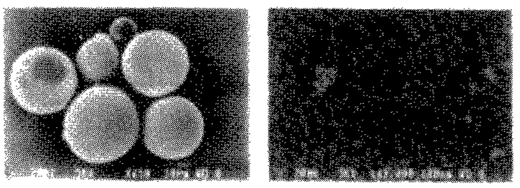

Fig. 2. SEM observation of Ag-coated microspheres (0.13 Ω).

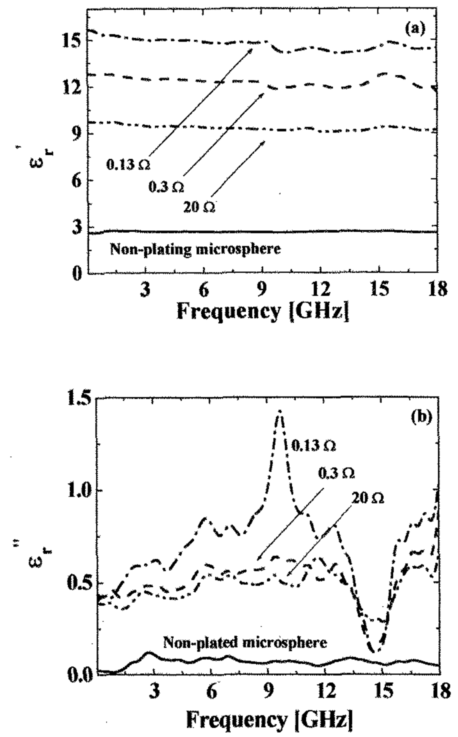

Fig. 3. Real (a) and imaginary (b) part of complex permittivity determined in the rubber composites containing Ag-coated microspheres.

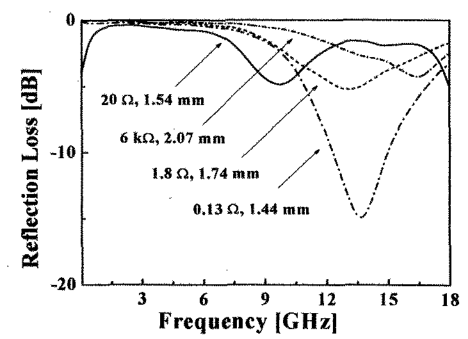

Fig. 4. Reflection loss determined in the rubber composites containing Ag-coated microspheres

The microwave absorbance increases with decrease of resistance. For the microspheres of 0.13 Ω (with a thickness 1.44 mm), the reflection loss was reduced to −15 dB at 13.5 GHz.

3.2 Co-coated microspheres

The microstructure of Co-coated microspheres is shown in Fig. 5. Uniform, but relatively thick film (approximately 2 μm estimated by SEM) was observed. Due to this uniform film morphology, the apparent resistance was measured to be very small (0.12 Ω).

Fig. 6 shows the complex permeability and complex permittivity determined in the rubber composites containing the Co-coated microspheres. Magnetic loss (μ_r'') appears in the microwave frquencies. Because of uniaxial anisotropy field of Co, magnetic loss spectrum shows the increasing behavior with frequency up to 18 GHz. Nearly constant and high value of dielectric constant ($\varepsilon_r' \cong 16$) is also observed, but the dielectric loss is very small ($\varepsilon_r'' \leq 1$).

Fig. 7 shows the reflection loss determined in the rubber composite specimens containing the Co-coated microspheres. The frequency of minimum reflection decreases with increase of thickness. The lowest reflection loss was predicted at 9 GHz with a thickness of 2 mm. The matching thickness is small compared with conventional ferrites composite absorber (about 3 mm at 9 GHz). Moreover, the density of the Co-coated mirospheres is very low (approximately 0.84 g/cc estimated from weight gain after plating), which makes it possible to produce lightweight microwave absorbers.

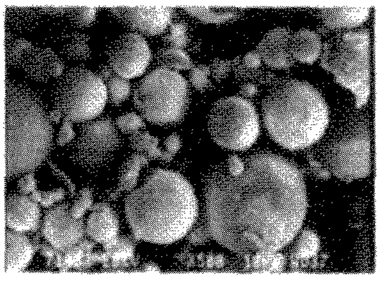

Fig. 5. SEM morphology of Co-coated microspheres.

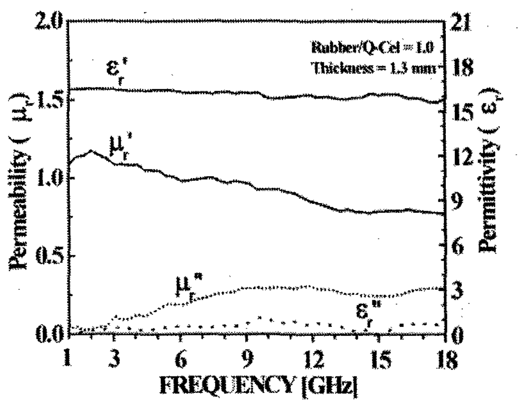

Fig. 6. Complex permeability and permittivity determined in the rubber composite containing Co-coated microspheres.

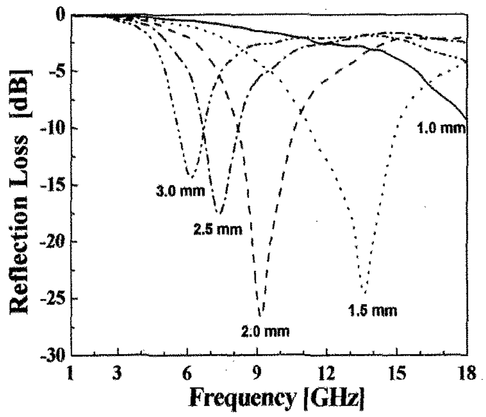

Fig. 7. Reflection loss determined in the rubber composites containing Co-coated microspheres.

4. CONCLUSION

Lightweight microwave absorbers using the metal-coated hollow microspheres were demonstrated. Highly conductive (Ag-coated) and magnetic (Co-coated) microspheres could be prepared by electroless plating. Due to their conduction loss (Ag film) and magnetic loss (Co film), microwave attenuation was predicted in the rubber composites containing the microspheres. However, the Co-coated microspheres have a better microwave absorbance than the silver-coated ones, which is due to magnetic loss in addition to conduction loss. Reflection loss was found to be –20 dB in X-band frequencies with a small thickness (2 mm) and a low density (about 1.0 g/cc).

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