Magnetic Properties of Nanoparticle–Polymer Composites Prepared Using Surface Modification and Cross-Linking Reaction

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Polymer composites of magnetic particles are widely used as microwave absorbers. An effective method for obtaining thinner microwave absorbers for device mounting is to increase the volume fraction of magnetic nanoparticles within the composites such that the permeability is enhanced. In this study, composites were prepared using magnetite nanoparticles surface-modified with 4-META (4-methacryloyloxyethyl trimellitate anhydride) and cross-linked with PEG-4SH (pentaerythritol tetra-polyethylene glycol ether with four thiol-modified terminals). These composites have a higher volume fraction of nanoparticles (up to 62 vol%) and higher permeability than conventional epoxy resin composites. In addition, the prepared composites showed good microwave absorption properties ($R.L. < -20$ dB) with a smaller matching thickness ($d = 8.0$ mm) than the epoxy resin composites ($d = 9.0$ mm). [doi:10.2320/matertrans.MAW201020]

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1. Introduction

Recently, the number of communication devices that utilize GHz-range microwave radiation has increased considerably because of the high data transfer rates that can be achieved. However, a consequence of this increase is that disturbance to electrical equipment from the associated electromagnetic interference (EMI) is becoming a serious issue.

To prevent problems arising from EMI, microwave absorbers^{1–3)} using spinel-type ferrite^{4,5)} or metallic magnetic materials^{6–9)} are widely used. As these materials have a strong natural resonance in the high frequency range, microwave absorption is caused by an increase in magnetic loss, μ_r'' . Because of greater flexibility, in practice, microwave absorbers consisting of polymer composites of magnetic powders are preferred over those consisting of sintered bodies.

With the current trend being to miniaturize electrical circuits, thinner microwave absorbers are also required in many devices. To achieve such a decrease in thickness, an effective method is increasing the volume fraction of magnetic powders in composites. This follows from the relationship between the microwave absorber thickness, d , and μ_r'' :

$$d = c/2\pi f\mu_r'', \quad (1)$$

where c is the velocity of light and f is frequency.⁴⁾

However, an aggregation of particles within the composites tends to limit this increase in volume fraction. To address this problem, for practical microwave absorbers, metal flakes with large aspect ratios are fabricated and mixed with resin to form an oriented microstructure.⁷⁾ The drawback to this method is that it involves long and complex processes.

In contrast, it has been reported that covalently modified nanoparticles can be uniformly dispersed within the small length of a polymer of several nanometers,^{10–12)} where only processes for polymer modification and formation of composites are required. This study thus uses polymer modification of nanoparticles to explore the possibility of forming microwave absorbers with a high volume fraction of magnetic particles.

To this end, polymer composites were fabricated using magnetite (Fe_3O_4) nanoparticles, modified with 4-META (4-methacryloyloxyethyl trimellitate anhydride),^{13,14)} and subsequently cross-linked with PEG-4SH (pentaerythritoltetra-polyethylene glycol ether with four thiol-modified terminals). The magnetic properties and microwave absorption properties of these composite were then investigated and compared with epoxy resin composites. From the obtained results, the possibility of using polymer-modified nanoparticles in microwave absorbers is discussed.

2. Experimental Procedure

Fe_3O_4 nanoparticles were prepared by the coprecipitation method as follows. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.011 mol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.021 mol) were dissolved in 20 mL of deionized water, and 150 mL of NaOH (0.45 mol) aqueous solution was then stirred into this solution. For each sample, the reaction temperature was set between 50°C and 100°C. The coprecipitates were firstly washed with deionized water to remove reaction residues and then with ethanol to remove the water. The resulting powder was dried in a glovebox with Ar atmosphere, and the Fe_3O_4 nanoparticles were obtained.

The polymer composites were fabricated by surface modification followed by a cross-linking reaction. Figure 1 shows the chemical structures of 4-META and PEG-4SH, as well as a schematic image of this process. First, 100 mg of Fe_3O_4 nanoparticles were added to a 4-META acetone solution (40 mL, 7.5 g/L, Sun Medical Co., Ltd.). The

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Fig. 1 The chemical structures of (a) 4-META and (b) PEG-4SH, and schematic images of (c) 4-META-modified Fe₃O₄ nanoparticles and (d) Michael addition to 4-META-modified Fe₃O₄ nanoparticles.

product was washed with acetone to remove excess 4-META and dried to afford 4-META-modified nanoparticles.

These 4-META-modified nanoparticles were dispersed in 1.5 mL of PEG-4SH (NOF Corporation) in acetone solution, where the polymerization degree, n , and the molecular weight, MW, of PEG-4SH were 55–57 and 10,000, respectively. With the total weight of 4-META-modified nanoparticles and PEG-4SH powder at 100 mg, the amount of added 4-META-modified nanoparticles, M , was varied from 75 to 95 mass%. The cross-linking reaction was run for 2 h, with sonication of the solution at intervals of 15 min. The cross-linked nanoparticles were then dried and pressed into a toroidal shape ($\phi_{\text{out}} = 7.00$ mm, $\phi_{\text{in}} = 3.04$ mm, $t = 0.5$ – 1.5 mm). Hereinafter, this pressed sample is referred to as the “PEG composite”.

For comparison with microwave absorption properties of the PEG composite, a conventional epoxy resin composite (hereinafter, “ER composite”) was also fabricated. Fe₃O₄ nanoparticles were mixed with epoxy resin (Durofast, Marumoto Struers K.K.), pressed into a toroidal shape and then sintered at 180°C for 20 min in an Ar atmosphere.

To test the samples, a number of techniques were used. The phases present in the samples were characterized by X-ray diffraction (XRD). The microstructure and morphology were observed by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Magnetic properties were measured using a vibrating sample magnetometer (VSM).

From the scattering parameters, S_{11} and S_{21} , measured with the coaxial method using a vector network analyzer in the frequency range of 0.5–20 GHz, the relative complex permeability, μ_r , and permittivity, ϵ_r , were calculated. μ_r , and ϵ_r are then used to calculate the reflection loss ($R.L.$) at

Fig. 2 The relationship between reaction temperature and both the saturation magnetization σ_s (A m² kg⁻¹) and grain size d_s (nm) of Fe₃O₄ nanoparticles prepared using the coprecipitation method.

a frequency, f , and a thickness, d , for each microwave absorber from the following formulae:

$$R.L. = 20 \log |(Z_{\text{in}} - Z_0)/(Z_{\text{in}} + Z_0)| \quad (2)$$

and

$$Z_{\text{in}} = Z_0(\mu_r/\epsilon_r)^{-1/2} \tanh\{2jfd/c(\mu_r\epsilon_r)^{-1/2}\}, \quad (3)$$

where Z_{in} is the input impedance of the microwave absorber and Z_0 is the impedance of air. From the frequency dependence of $R.L.$, the absorption properties of the microwave absorbers were evaluated.

When $R.L.$ is less than -20 dB, the sample exhibits good microwave absorption properties. The thickness of a microwave absorber and the frequency corresponding to the lowest $R.L.$, are defined as the “matching thickness”, d_m , and the “matching frequency”, f_m , respectively. Hence, the product of f_m and d_m (the $f \cdot d$ product) can also be used to evaluate the microwave absorption properties, with a smaller $f \cdot d$ product suggesting a thinner microwave absorber can be used at the same frequency.

3. Results and Discussion

Fe₃O₄ nanoparticles were prepared by the coprecipitation method described in the previous section. Figure 2 shows the saturation magnetization, σ_s (A m² kg⁻¹), of Fe₃O₄ nanoparticles, measured after applying a magnetic field of 0.80 MA m⁻¹, as a function of the reaction temperature of the coprecipitation method. The grain sizes of the samples, calculated from the Scherrer equation, are also shown in this figure.

The saturation magnetization increases as the reaction temperature rises, reaching a maximum of 61.3 A m² kg⁻¹ for the sample prepared at 100°C. Figure 3 presents an XRD pattern and TEM image for this sample prepared at 100°C. The XRD pattern shows a single spinel phase of magnetite, and the grain size of the sample is calculated as 11.7 nm, in agreement with the size observed in the TEM image. From the XRD patterns, the grain sizes for the samples prepared at 50°C and 80°C were calculated as 5.6 and 9.2 nm, respectively. Therefore, by raising the reaction temperature of coprecipitation, the grain size increases, and from the results shown in Figs. 2 and 3, it can be inferred that the saturation

Fig. 3 (a) XRD pattern and (b) TEM image of Fe₃O₄ nanoparticles prepared at 100°C.

magnetization is related to the grain size. Note that the maximum value of the saturation magnetization obtained here, for the sample prepared at 100°C, is lower than the reported value of Fe₃O₄ (92.0 A m² kg⁻¹). This difference is attributed to the superparamagnetic behavior of the small nanoparticles in the sample. However, with the sample prepared at 100°C showing the highest saturation magnetization, the smallest volume fraction of these nanoparticles is required. These nanoparticles were therefore used in the preparation of both the PEG and ER composites.

Figure 4(a) shows the XPS C 1s spectra of Fe₃O₄ nanoparticles with and without surface modification using 4-META. For the sample without surface modification, the two small peaks in the spectrum are considered to be from the solvent residue on the surface of the nanoparticles. This is in contrast to the spectrum of the 4-META-modified nanoparticles, where three carbon components are observed as peaks due to the CH₂, C-O and C=O bonds of 4-META. This suggests that 4-META was present on the surface of the nanoparticles.

Figure 4(b) shows the dependence of the peak intensities on the detection angle for CH₂ and C=O bonds taken from the 4-META-modified nanoparticles, where the intensities were normalized using the integral intensity ratio for each peak after Gaussian fitting. It can be seen from this figure that the intensity of the C=O bond is approximately constant for angles lower than 75°, at which point it begins to increase. Changes at high angles relate to the chemical-bonding state near the surface of the nanoparticles. Hence, Fig. 4(b) indicates that many C=O bonds were present near the nanoparticles' surface. Returning to Fig. 1, which shows the surface modification schematically, it can be seen that a C=O bond exists on the surface of a nanoparticle in the case that

Fig. 4 (a) XPS C 1s spectra of the Fe₃O₄ nanoparticles before and after surface modification, and (b) detection angle dependency of the intensity fractions of CH₂ and C=O bonds measured in the 4-META-modified Fe₃O₄ nanoparticles.

Fe₃O₄ nanoparticles combine with 4-META. Thus, these results signify that covalent bonding has occurred between the 4-META and Fe₃O₄ nanoparticles and is in good agreement with the explanation of 4-META modification of a metal film by Echizenya.¹⁶⁾

Figure 5(a) presents the XPS C 1s spectra of the 4-META-modified nanoparticles before and after the PEG-4SH cross-linking reaction. The three peaks in the sample before cross-linking are those shown in Fig. 4(a). After the cross-linking reaction, the intensity of the C-O bond increases. This is attributed to PEG-4SH on the surface of nanoparticles because PEG-4SH many C-O bonds.

To confirm that Michael addition had occurred, a XPS S 2p spectrum of the cross-linked nanoparticles was compared with that of PEG-4SH powders. The result of this comparison reveals a peak shift from 161.6 to 163.7 eV after the cross-linking reaction (Fig. 5(b)); this shifted peak is thought to be a result of the formation of S-C bonds.^{17,18)} The schematic in Fig. 1 shows how PEG-4SH and 4-META can be combined by an S-C bond. Hence, Fig. 5(b) indicates that the cross-linked nanoparticles were obtained because the thiol groups of PEG-4SH were bound chemically to the 4-META-modified nanoparticles. The PEG composites were fabricated using these cross-linked nanoparticles.

Figure 6(a) shows the relationship between the amount of Fe₃O₄ nanoparticles added to the PEG and ER composites,

Fig. 5 (a) XPS C 1s spectra of the 4-META-modified Fe_3O_4 nanoparticles before and after the cross-linking reaction, and (b) XPS S 2p spectra of the cross-linked nanoparticles in comparison with that of PEG-4SH powders.

M (mass%), and the volume fractions of these nanoparticles, V (vol%), where V is given by

$$V = I_{\text{comp}}/I_{\text{S0}} \times 100. \quad (4)$$

Here, I_{comp} (Wb m^{-2}) and I_{S0} ($= 0.30 \text{ Wb m}^{-2}$) are the saturation magnetizations of each of the composites and the Fe_3O_4 nanoparticles, respectively, and a theoretical density of Fe_3O_4 (5.0 Mg m^{-3}) is used in the calculation of (4). From Fig. 6(a) it can be seen that, in all cases, V is larger for the PEG composite than the ER composite at the same value of M , and V for the PEG composite increases with M until reaching a maximum of 62 vol% at $M = 95$ mass%. Therefore, the volume fraction of magnetic particles in the composites can be increased by using nanoparticles processed with surface modification and cross-linking.

In Fig. 6(b), the maximum value of the imaginary part of the relative permeability, $\mu_r''_{\text{max}}$, in both composites, is shown as a function of V . For each V , the imaginary part of $\mu_r''_{\text{max}}$ is consistently higher in the PEG composites than in the ER composites, and the largest value for the PEG composite is $\mu_r''_{\text{max}} = 1.11$. This is a direct consequence of V being higher for the PEG composites than for the ER composites.

SEM images of (a) PEG and (b) ER composites are shown in Fig. 7 for the each composite showing the maximum V ($V = 62 \text{ vol\%}$ and $V = 48 \text{ vol\%}$, respectively). In the ER

Fig. 6 Comparing the dependence of PEG composites and ER composites on the mass percent ratio M (mass%) of 4-META modified Fe_3O_4 nanoparticles for (a) the volume fraction of Fe_3O_4 nanoparticles, V (vol%), and (b) the maximum values of imaginary relative permeability $\mu_r''_{\text{max}}$.

Fig. 7 SEM images of (a) PEG composite ($V = 62 \text{ vol\%}$) and (b) ER composite ($V = 48 \text{ vol\%}$).

Fig. 8 The relationship between the frequency and (a) the imaginary part of the relative permeability and (b) the reflection loss $R.L.$, for the PEG composite ($V = 62$ vol%) and the ER composite ($V = 48$ vol%).

composite, aggregation of nanoparticles and voids (indicated by white circles in Fig. 7(b)) is observed. This phenomenon is not found in the PEG composite; therefore, PEG composites can be formed without aggregation and voids, leading to an increase in V and μ_r'' max.

Finally, the microwave absorption properties of the PEG and ER composites were evaluated using (2) and (3). In Fig. 8 the dependence of the reflection loss ($R.L.$) on the frequency, f , is shown for both the PEG composite with $V = 62$ vol% and the ER composite with $V = 48$ vol%. Both composites achieve an $R.L.$ of less than -20 dB. This occurs at frequencies of 1.38 GHz and 1.77 GHz for the PEG and ER composites, respectively, with associated matching thicknesses, d_m , of 8.0 mm and 9.0 mm. Furthermore, the $f \cdot d$ product for the PEG composite was lower than that of the ER composite (11.0 GHz·mm compared to 15.9 GHz·mm). Reducing V to 54 and 59 vol% for the PEG composites, the $f \cdot d$ product remains below that of the ER composite, at 11.1 and 12.6 GHz·mm, respectively. Thus PEG composites have the potential to become thinner microwave absorption materials.

4. Conclusions

The PEG composites prepared in this investigation have a higher volume fraction of magnetic particles (62 vol%) than conventional composites prepared using magnetic particles and polymer (40~60 vol%).^{4-6,8,9)} The PEG composites also showed higher permeability and smaller $f \cdot d$ products than ER composites. Therefore, it can be concluded that the process of combining surface modification with cross-linking is an effective method for increasing the volume fraction of magnetic particles in composites and thereby preparing thinner microwave absorbers. However, as Fe_3O_4 nanoparticles were used as magnetic nanoparticles, the μ_r'' max values of the PEG composites prepared in this study were small. Further improvement of μ_r'' max values and $f \cdot d$ products is expected by using nanoparticles of high permeability material, for example, Ni-Zn ferrite and amorphous metal.

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REFERENCES

- 1) Y. Naito: *Electromagnetic Wave Absorber*, (Ohmsha, Tokyo, 1987).
- 2) O. Hashimoto: *Technologies & Applications of Wave Absorber II*, (CMC, Tokyo, 2003).
- 3) O. Hashimoto: *Introduction to Wave Absorber*, (Morikita Publication, Tokyo, 1997).
- 4) Y. Naito and K. Suetake: *IEEE Trans. Microwave Theory Tech.* **19** (1971) 65–72.
- 5) D. Y. Kim, Y. C. Chung, T. W. Kang and H. C. Kim: *IEEE Trans. Magn.* **32** (1996) 555–558.
- 6) M. Matsumoto and Y. Miyata: *J. Magn. Soc. Jpn.* **22** (1998) 885–888.
- 7) S. Yoshida, M. Sato, E. Sugawara and Y. Shimada: *J. Appl. Phys.* **85** (1999) 4636–4638.
- 8) A. Saito, M. Ogawa, K. Tsutsui, H. Endo and S. Yahagi: *Mater. Japan* **38** (1999) 46–48.
- 9) T. Maeda, S. Sugimoto, T. Kagotani, D. Book, K. Inomata, H. Ota and Y. Houjou: *Mater. Trans.* **42** (2001) 446–449.
- 10) Z. Guo, S. Park, S. Wei, T. Pereira, M. Moldovan, A. B. Karki, D. P. Young and H. T. Hahn: *Nanotechnology* **18** (2007) 335704.
- 11) S. Hatamie, S. D. Dhole, J. Ding and S. N. Kale: *J. Magn. Magn. Mater.* **321** (2009) 2135–2138.
- 12) S. Balakrishnan, M. J. Bonder and G. C. Hadjipanayis: *J. Magn. Magn. Mater.* **321** (2009) 117–122.
- 13) N. Morimoto, I. Sato, A. Watanabe, N. Nakabayashi, Y. Iwasaki and K. Ishihara: *Jpn. J. Polymer Sci. Technol.* **59** (2002) 432–437.
- 14) H. Matsumura and N. Nakabayashi: *J. Dent. Res.* **67** (1988) 29–32.
- 15) S. Chikazumi, K. Ohta, K. Adachi, N. Tsuya and Y. Ishikawa: *Handbook of Magnetic Materials*, (Asakura Shoten, Tokyo, 1975).
- 16) T. Echizenya: *Jpn. Soc. Dental Mater. Devices* **11** (1992) 628–641.
- 17) B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling and K. Siegbahn: *Phys. Scripta* **1** (1970) 286–298.
- 18) K. Suzuki, K. Mori, Y. Rongbin and H. Hirahara: *Jpn. J. Polymer Sci. Technol.* **60** (2003) 108–114.