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

Kazuaki Shimba*1, Kiyotaka Furuta*1, Nobuyuki Morimoto, Nobuki Tezuka and Satoshi Sugimoto*2

Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

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-methacryloylloxyethyl 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). 

Keywords: magnetic nanoparticles, magnetite, surface modification, cross-linking, microwave absorbers

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 absorbers1–3 using spinel-type ferrite4,5 or metallic magnetic materials6–9 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, $\mu_r''$. 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 $\mu_r''$:

$$d = c/2\pi f \mu_r'',$$

(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$_3$O$_4$) nanoparticles, modified with 4-META (4-methacryloylloxyethyl trimellitate anhydride),13,14) and subsequently cross-linked with PEG–4SH (pentaerythritol tetrapolyethylene 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$_3$O$_4$ nanoparticles were prepared by the coprecipitation method as follows. FeCl$_2$·4H$_2$O (0.011 mol) and FeCl$_3$·6H$_2$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$_3$O$_4$ 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$_3$O$_4$ nanoparticles were added to a 4-META acetone solution (40 mL, 7.5 g/L, Sun Medical Co., Ltd.). The
The PEG composite, a conventional epoxy resin composite as the ‘PEG composite’. Marumoto Struers K.K.), pressed into a toroidal shape and nanoparticles were mixed with epoxy resin (Durofast, 0.80 MA m⁻³), 1.5 mL of PEG-4SH (NOF Corporation) in acetone solution, and dried to afford 4-META-modified nanoparticles. The 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 (\( \phi_{\text{out}} = 7.00 \text{ mm}, \phi_{\text{in}} = 3.04 \text{ mm}, t = 0.5–1.5 \text{ mm} \)). 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, \( \mu_r \), and permittivity, \( \varepsilon_r \), were calculated. \( \mu_r \) and \( \varepsilon_r \) are then used to calculate the reflection loss (RL) at a frequency, \( f \), and a thickness, \( d \), for each microwave absorber from the following formulae:

\[
RL = 20 \log \left| \frac{Z_{\text{in}} - Z_0}{Z_{\text{in}} + Z_0} \right|
\]

and

\[
Z_{\text{in}} = Z_0 (\mu_r/\varepsilon_r)^{-1/2} \tanh(2jf/\varepsilon_r \mu_r)^{-1/2},
\]

where \( Z_{\text{in}} \) 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 \( -20 \text{ dB} \), 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”, \( d_{\text{in}} \), and the “matching frequency”, \( f_{\text{in}} \), respectively. Hence, the product of \( f_{\text{in}} \) and \( d_{\text{in}} \) (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, \( \sigma_0 \) (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 Scherer 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
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 Fe$_3$O$_4$ (92.0 A m$^2$ 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 Fe$_3$O$_4$ 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 CH$_2$, 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 CH$_2$ and C=O bonds taken from the 4-META-modified Fe$_3$O$_4$ nanoparticles. Where three carbon components are observed as peaks due to the CH$_2$, C-O and C=O bonds of 4-META. This suggests that 4-META was present on the surface of the nanoparticles.

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. 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 Fe$_3$O$_4$ nanoparticles added to the PEG and ER composites.
(mass%), and the volume fractions of these nanoparticles, \( V \) (vol%), where \( V \) is given by

\[
V = \frac{I_{\text{comp}}}{I_{S0}} \times 100.
\]  

Here, \( I_{\text{comp}} \) (Wb m\(^{-2}\)) and \( I_{S0} \) (= 0.30 Wb m\(^{-2}\)) are the saturation magnetizations of each of the composites and the \( \text{Fe}_3\text{O}_4 \) nanoparticles, respectively, and a theoretical density of \( \text{Fe}_3\text{O}_4 \) (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, \( \mu''_{\text{max}} \), in both composites, is shown as a function of \( V \). For each \( V \), the imaginary part of \( \mu''_{\text{max}} \) is consistently higher in the PEG composites than in the ER composites, and the largest value for the PEG composite is \( \mu''_{\text{max}} = 1.11 \). 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 \( V \) (\( V = 62 \) vol% and \( V = 48 \) vol%, respectively). In the ER composite, the volume fraction of magnetic particles in the composites can be increased by using nanoparticles processed with surface modification and cross-linking.
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 $V_{22}$.

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 ($40 \sim 60$ vol%). 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$_3$O$_4$ nanoparticles were used as magnetic nanoparticles, the $\mu''_{\text{max}}$ values of the PEG composites prepared in this study were small. Further improvement of $\mu''_{\text{max}}$ values and $f \cdot d$ products is expected by using nanoparticles of high permeability material, for example, Ni-Zn ferrite and amorphous metal.

Acknowledgements

The authors would like to thank Mr. N. Akao and Ms. Y. Ohira of Tohoku University for their help in performing XPS measurements.

REFERENCES