

Preparation and Microwave Absorbing Properties of BaFe₁₂O₁₉ / Unsaturated Polyester Nanocomposites

Chang Sun, Kang-ning Sun, Peng-fei Chui

*Key Laboratory for Liquid-Solid Structure Evolution and Processing of Materials (Ministry of Education)
Shandong University
Jinan, China
sunkangning@sdu.edu.cn*

Chang Sun, Kang-ning Sun, Peng-fei Chui

*Engineering Ceramics Key Laboratory of Shandong Province
Shandong University
Jinan, China
sunchang@sdu.edu.cn*

Chang Sun

*Shandong Supervision and Inspection Institute for Product Quality
Jinan, China*

Abstract: The BaFe₁₂O₁₉/unsaturated polyester nanocomposites have been prepared. The complex permeability and permittivity of the BaFe₁₂O₁₉/unsaturated polyester nanocomposites were measured by the transmission/reflection coaxial line method in the range of 0.5 to 5.0 GHz. Based on the theoretical calculation of reflection loss, the microwave absorption properties of BaFe₁₂O₁₉/unsaturated polyester nanocomposites have been made in the frequency range from 0.5 to 5.0GHz. A maximum reflection loss value of - 52.7 dB has been obtained for absorber thickness of 11.2 mm at 4.4 GHz. The result indicates that the nanocomposites have significant potential for electromagnetic wave absorption application or electro-magnetic shields in the future.

Keywords: barium ferrite; unsaturated polyester nanocomposites; microwave absorption

1. Introduction

The integration of magnetic materials and organic materials has attracted an increased interest. Such composite materials exhibit not only magnetic property but also useful electrical or optical properties[1, 2], offering potential applications in numerous areas such as carriers for controlled drug delivery[3], magnetic refrigeration[4], information storage and electro-magnetic shields and microwave absorbing materials[5, 6]. Recently, as the number of communication devices using 0.5-5 GHz range of radiation, such as mobile phones and LAN systems, has greatly increased, serious electromagnetic interference (EMI) problems have become more apparent. Shield of components from unwanted radio frequency (RF) signals in a communication device is important in order to improve the accuracy and performance of the system. Ferrite serve as better EMI suppressors compared to their dielectric counterparts on account of their excellent magnetic properties. For microwave application, there is an increasing interest in using ferrite films rather

than bulk ferrites. Films possess several advantage, such as lower cost, low density, size reduction and enhanced compatibility, compared with bulk ferrites. In our present work, therefore, BaFe₁₂O₁₉/unsaturated polyester thick films have been prepared. Unsaturated polyester has been used as the polymer because of its high electrical resistivity and low dielectric constant. Although some work on ferrite-polymer composites has been reported in recent years, there seem to be less reports on the microwave absorbing properties of BaFe₁₂O₁₉/ unsaturated polyester composites in the frequency range from 0.5-5.0 GHz[7-9]. Consequently, the complex permittivity and complex permeability and microwave absorption properties of BaFe₁₂O₁₉/unsaturated polyester nanocomposites were measured by the transmission/ reflection coaxial line method in the range of 0.5 - 5.0 GHz.

2. Experimental

An unsaturated polyester resin (UPR 191[#]) used in this study contains 35% styrene and 65% unsaturated polyester prepolymer by weight. Cobalt octoate (CoOct, a mineral spirit solution containing 6.0 wt% active cobalt) was employed as the promoter to decompose the initiator at low temperatures. The initiators used in this study

Sponsors: the Natural Science Foundation of the People's Republic of China (Grant No. 30870610), China Postdoctoral Science Foundation (No. 200804401138) and Shandong Province Postdoctoral Innovation Foundation (No. 200902030).

were methyl ethyl ketone peroxide (a single component initiator). Unsaturated polyester resin, its curing agent and the promoter are purchased commercial reagents. $\text{Ba}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used to incorporate metal ions needed for preparation of BaM-type hexagonal ferrite $\text{BaFe}_{12}\text{O}_{19}$ by sol-gol method. All materials were used as received without further purification in order to mimic the industrial applications.

The synthesis procedure of $\text{BaFe}_{12}\text{O}_{19}$ was as follows. A stoichiometric amount of $\text{Ba}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in a citric acid aqueous solution under stirring. The molar ratio of nitrates to citric acid was 1:1. A homogenous transparent solution was achieved within a few minutes. An appropriate amount of ammonia hydroxide solution was added to the solution to adjust the pH value to about 7. During this process, the solution was continuously stirred using a magnetic agitator. After the precursor mixture was heated by water bath at 80°C and stirred for 3 h, the gel formed. Then, the gel was put into drying cabinet at 120°C , and dried gel was got after 1-2 days. Then the dry gel was milled in a mortar. In order to remove the organic substance, the dried gel was calcined at 210°C in silicon carbide furnace. It sharply burnt and give out bright flame. Finally, it was calcined at 800°C and the $\text{BaFe}_{12}\text{O}_{19}$ powder was obtained. The average particle size of the ferrite powders was about 43 nm.

$\text{BaFe}_{12}\text{O}_{19}$ / unsaturated polyester composites were prepared by mixing the above prepared ferrite powder with unsaturated polyester. A weighed amount of $\text{BaFe}_{12}\text{O}_{19}$ powder and Cobalt octoate were added into a weighed amount of UPR to form a viscous mixture under stirring. The weighed ratio between PUR, $\text{BaFe}_{12}\text{O}_{19}$, Cobalt octoate and methyl ethyl ketone peroxide used was 100:10:5:2. After stirring the mixture with a high shear mixer, methyl ethyl ketone peroxide initiator was added just before molding and mixed. Then the mixture was directly poured into cylindrical shaped compacts. These compacts were cured to be formed into toroidally shaped samples ($\phi_{\text{out}}=16.00$, $\phi_{\text{in}}=9.00$, $d=10.00\text{mm}$) to fit tightly into 16mm coaxial measurement cell. The scattering parameters of the toroidal sample corresponding to reflection (S11) and transmission (S21) of a transverse electric and magnetic (TEM) wave were measured by the coaxial method using a Hewlett-Packard HP8753ES S-parameter network analyzer in the frequency range of 0.5–5.0 GHz. The real and imaginary components of the complex magnetic permittivity, $\epsilon = \epsilon' - \epsilon''$, and permeability, $\mu = \mu' - \mu''$, were determined from the relative complex scattering. A full two-port calibration was initially performed on the test setup to remove errors due to directivity, load match, isolation and frequency response in both the forward and reverse measurements. The reflection loss (RL) at a thickness was determined by the complex permittivity, $\epsilon = \epsilon' - \epsilon''$, and permeability, $\mu = \mu' - \mu''$.

3. Results and discussion

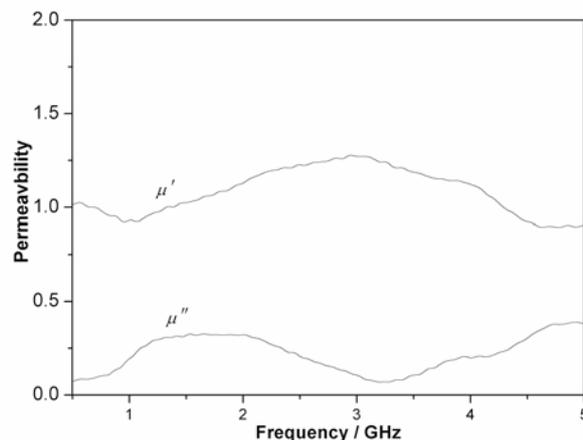


Figure 1. The permeability spectra of the $\text{BaFe}_{12}\text{O}_{19}$ /unsaturated polyester nanocomposites

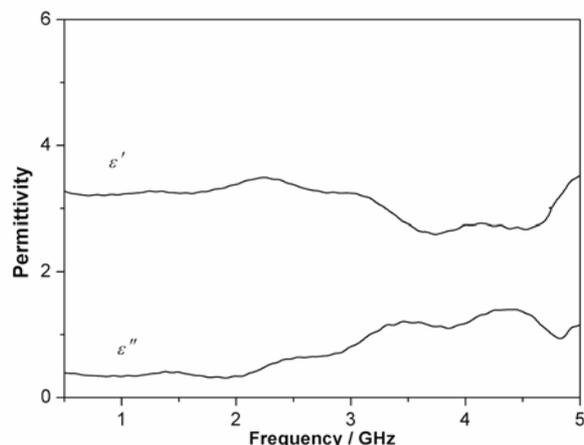


Figure 2. The permittivity spectra of the $\text{BaFe}_{12}\text{O}_{19}$ /unsaturated polyester nanocomposites

Fig. 1 and Fig. 2 illustrate the frequency dependence of the complex permeability (μ' and μ'') and permittivity (ϵ' and ϵ'') for the $\text{BaFe}_{12}\text{O}_{19}$ /unsaturated polyester sample in the range of 0.5 to 5.0 GHz. It can be observed that the value of real part of permeability (μ') shows a peak at about 3.0 GHz. This can be ascribed the demagnetizing field produced by magnetic poles in the surface of ferrite particles in the composites, which lead to the increase of resonance frequency compared to sintered ferrite[10]. Then the value of μ' slightly decreases. This is favorable for electromagnetic wave surface impedance match because the wavelength in microwave absorber decreases as the frequency increases. The magnetic spectra of the image part of permeability (μ'') shows a weak frequency dispersion phenomenon in Fig.1. The mechanism of natural magnetic field and domain wall turning resulted in the frequency dispersion of $\text{BaFe}_{12}\text{O}_{19}$ /unsaturated polyester nanocomposites. In the weak alternative mag-

netic field, the dominant magnetization process fundamentally belongs to mechanism of domain wall turning. Moreover, the crystal grains of ferrite are enveloped by non-magnetic coating of polyester which enhances the effective reluctance of the composites, thus resulting in the weak dispersion phenomenon in the spectra of μ'' [11]. On the other hand, Fig. 2 shows the frequency dependence of complex permeability (ϵ' and ϵ'') of the BaFe₁₂O₁₉/unsaturated polyester sample. The value of the real part of complex permittivity decreases in the range of 0.5-3.6 GHz with the frequency and then increases, but the image part of complex permittivity increases with frequency and presents a peak in 4.5 GHz, then decreases [12].

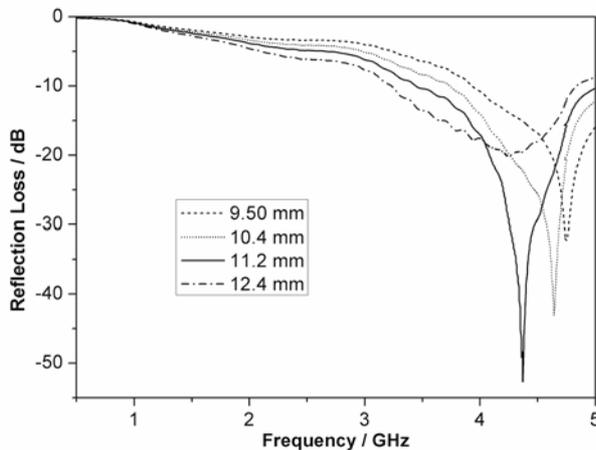


Figure 2. The calculated reflection loss value of the BaFe₁₂O₁₉/unsaturated polyester nanocomposites

For a microwave absorbing layer backed metal plate, the normalized input impedance (Z_{in}) at the absorber surface is given by

$$Z_{in} = Z_0 \sqrt{\mu/\epsilon} \tanh\{j(2\pi f d/c)\sqrt{\mu\epsilon}\} \quad (1)$$

where ϵ is the complex permittivity ($\epsilon = \epsilon' - j\epsilon''$), μ the complex permeability ($\mu = \mu' - j\mu''$), Z_0 is the impedance of air, c is the velocity of electromagnetic waves in free space, f is the frequency, and d is the thickness of the absorber. According to transmission line theory, the reflection loss (RL) is a function of the normalized input impedance (Z_{in}), which can be expressed as shown below:

$$RL = 20 \log |(Z_{in} - Z_0)/(Z_{in} + Z_0)| \quad (2)$$

The reflection loss for the BaFe₁₂O₁₉/unsaturated polyester sample can be calculation using Eqs. (1) and (2). Obviously, the reflection loss is negative, and the lower the reflection loss, the higher is the absorption. Fig. 3 shows the calculated the reflection loss as a function of frequency for the thick of 9.5, 10.4, 11.2, and 12.4 mm. The calculation uses the actual values of μ and ϵ as shown in fig. 1 and fig. 2. It can be seen that the value of reflection loss less than 20 dB in the range of 4.0-4.9 GHz (matching frequency, f_m). In particular, a minimum reflection loss value of -52.7 dB is obtained at 4.4 GHz with a

matching thick of 11.2 mm, and the minimum d_m value of 9.5 mm is obtained at 4.7 GHz. The reflection less is found to depend sensitively on the absorber thickness. The attenuation peak shifts to low frequency when the thickness of composite materials increases. This shows that attenuation peak frequency of the BaFe₁₂O₁₉/unsaturated polyester composites can be manipulated easily by changing the thickness of materials.

4. Conclusions

In this research, the BaFe₁₂O₁₉/unsaturated polyester nanocomposites have been synthesized. Microwave absorbing characterization shows that the composites obtain a reflection loss below -10dB over 1GHz and the maximum reflection loss of -52.7dB for absorber thickness of 11.2mm at 4.4GHz. The BaFe₁₂O₁₉/unsaturated polyester nanocomposites exhibited a good electromagnetic wave absorption properties in the rang of 3-5 GHz.

4. Acknowledgements

We would like to thank Mr. C. Li, and Mr. T. Zhao at Engineering Ceramics Key Laboratory For their technical support. This research was supported by the Natural Science Foundation of the People's Republic of China (Grant No. 30870610), China Postdoctoral Science Foundation (No. 200804401138) and Shandong Province Postdoctoral Innovation Foundation (No. 200902030).

References

- [1] Jianguo Deng, Yuxing Peng, Chuanlan He, Xingping Long, Pei Li, and Albert S C Chan, "Magnetic and conducting Fe₃O₄-polypyrrole nanoparticles with core-shell structure," *Polymer International*, vol. 52, pp. 1182-1187, July 2003.
- [2] Y. A. Barnakov, B. L. Scott, V. Golub, L. Kelly, V. Reddy, and K. L. Stokes, "Spectral dependence of Faraday rotation in magnetite-polymer nanocomposites," *Journal of Physics and Chemistry of Solids*, vol. 65, pp. 1005-1010, May 2004.
- [3] Y. Wu, J. Guo, W. Yang, C. Wang, and S. Fu, "Preparation and characterization of chitosan-poly(acrylic acid) polymer magnetic microspheres," *Polymer*, vol. 47, pp. 5287-5294, July 2006.
- [4] K. A. Gschneidner, Jr and V. K. Pecharsky, "Magnetic Refrigeration Materials," *Journal of Applied Physics*, vol. 85, pp. 5365-5368, April 1999.
- [5] P. Gomez-Romero, "Hybrid Organic-Inorganic Materials-In Search of Synergic Activity," *Advanced Materials*, vol. 13, pp. 163-174, February, 2001.
- [6] K. Sunderland, P. Brunetti, L. Spinu, J. Fang, Z. Wang, and W. Lu, "Synthesis of γ -Fe₂O₃/polypyrrole nanocomposite materials," *Materials Letters*, vol. 58 pp. 3136-3140, October 2004.
- [7] R. Dosoudil, M. Usakova, J. Franek, J. Slama, and V. Olah, "RF electromagnetic wave absorbing properties of ferrite polymer composite materials," *Journal of Magnetism and Magnetic Materials*, pp. 304 pp. e755-e757, September 2006.
- [8] S. M. Abbas, A. K. Dixit, R. Chatterjee, and T. C. Goel, "Complex permittivity, complex permeability and microwave absorption properties of ferrite-polymer composites," *Journal of Magnetism and Magnetic Materials*, vol. 309, pp. 20-24, February 2007.

- [9] A. Verma, A. K. Saxena, and D. C. Dube, "Microwave permittivity and permeability of ferrite-polymer thick films," *Journal of Magnetism and Magnetic Materials*, vol. 263, pp. 228-234, July 2003.
- [10] T. Tsutaoka, M. Ueshima, T. Tokunaga, T. Nakamura, and K. Hatakeyama, "Frequency dispersion and temperature variation of complex permeability of Ni - Zn ferrite composite materials," *Journal of Applied Physics* vol. 78, pp. 3983-3991, September 1995.
- [11] P. Singh, V. K. Babbar, A. Razdan, S. L. Srivastava, and T. C. Goel, "Microwave absorption studies of Ca-NiTi hexaferrite composites in X-band," *Materials Science and Engineering B*, vol. 78, pp. 70-74, December 2000.
- [12] Y. Yang, B. Zhang, W. Xu, Y. Shi, N. Zhou, and H. Lu, "Microwave absorption studies of W-hexaferrite prepared by co-precipitation/mechanical milling," *Journal of Magnetism and Magnetic Materials*, vol. 265, pp. 119-122, September 2003.