Electromagnetic Properties and Mechanical Properties of $Ni_{0.8}Zn_{0.2}Fe_2O_4$/Polyolefin Elastomer Composites for High-Frequency Applications

Haibo Yang, Ying Lin, Jianfeng Zhu, Fen Wang

Key Laboratory of Auxiliary Chemistry and Technology for Light Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an 710021, China

Received 20 November 2008; accepted 2 June 2009
DOI 10.1002/app.30878
Published online 12 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A low-loss flexible magnetic composite with $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZO) ultrafine particles embedded in a thermoplastic polyolefin elastomer matrix was fabricated with extrusion technology. The electromagnetic and mechanical properties of the as-prepared composites were investigated in detail. The results indicate that as the volume of the ceramic fillers increased, the permittivity, permeability, and dielectric and magnetic loss of the composite all increased. The cutoff frequencies of the composites were all above 1 GHz. Because of the low resistivity of NZO, the dielectric losses of the composites were big and decreased with frequency below 100 MHz. Good frequency stability of the permittivities and permeabilities and low dielectric and magnetic losses within the measurement range were observed. All of the composites showed very good flexibility. With increasing volume of the ceramic filler, the tensile strength and elongation decreased. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3510–3514, 2009

Key words: composites; dielectric properties; mechanical properties

INTRODUCTION

Magnetic materials can be widely used in the making of useful devices, such as inductor cores, circulators, isolators, refrigerator door seals, storage media, and electromagnetic interference shields.[1,2] Polycrystalline ceramic ferrite powders can be incorporated into various elastomer matrices to produce polymer-based ferrite composites.[3–6] Polymer-based composites with high permeability[7–10] have been proposed because of their flexibility, light weight, low loss, compatibility with printed wiring boards, and ability to be molded into complex shapes, which is not easily possible with conventional ceramic magnets. Also, the cutoff frequency of ferrite can be greatly improved when it is incorporated into a polymer matrix. It is known that soft magnets of NiZn ferrites possess a very high permeability and very low magnetic loss below the cutoff frequency. However, their dielectric loss is high, and their cutoff frequency is below 200 MHz, which limits their practical high-frequency application.

In this study, novel low-loss, high-frequency magnetic composites were achieved by the introduction of $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZO) fillers into a thermoplastic polyolefin elastomer (POE) matrix. The electromagnetic properties and mechanical properties of the composites were investigated in detail. Such magnetic composites, possessing very low loss, could be used in high-frequency communications for inductor-integrating devices, such as electromagnetic interference filters and antennas.

EXPERIMENTAL

The POE (density = 0.87 g/cm^3, glass-transition temperature = -55°C, elongation >800%) used was Engage POE 8100 (Dupont Dow Co., USA). The starting materials of NiO (>99%), ZnO (>99%), and Fe_2O_3 (>99%, all from Guo-Yao Co., Ltd., Shanghai, China) were weighed before they were mixed and calcined at 1170°C in air for 2 h to prepare the NZO ceramic, which was ground into powder with a grain size of about 500 nm. The permeability of NZO was 35. To make the powders possess an active surface, they were fully mixed with a 2% oleic acid solution. The surface-modified ceramic filler and the POE were mixed for 12 min in a Rheomix600p system (Rheomix600p, Haake Co., Lippstadt, Germany)

Correspondence to: H.-B. Yang (yanghaibo@sust.edu.cn).
Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50672056, 50432010.
Contract grant sponsor: Educational Fund of Shaanxi Government; contract grant number: 09JK366.

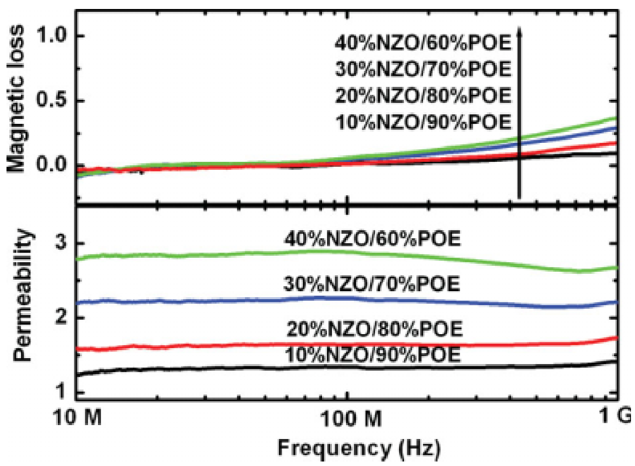

Figure 1 Frequency dependence of the magnetic properties of composites with different volume fractions of NZO. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

operated at 60 rpm and 180°C. Then, the mixture was put into a disk mold and hot-pressed under a stress of 10 MPa at a temperature of 180°C for 5 min. The microstructure was analyzed with scanning electron microscopy (SEM; JEOL JSM-6460, Tokyo, Japan). The stress–strain behavior of the as-prepared composites was measured on a tensile test machine (PT-1036PC, Perfect Instrument Co., Ltd., Taibei, Taiwan) with a deformation speed of 5 mm/min. The dielectric and magnetic measurement were carried out with an HP 4291B impedance analyzer (HP, USA) with an HP 16453A dielectric material test fixture and an HP 16454L magnetic material test fixture, respectively. The frequency ranges were 1 MHz–1 GHz and 10 MHz–1 GHz, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the frequency dependence of the magnetic properties of the composites with different volume fractions of NZO. With increasing NZO, the initial permeability increased. This was because, as the content of NZO increased, the increasing fraction of the ferromagnetic component led to a decrease in the effective magnetic porosity and an increase in the saturation magnetization (M_s). According to Rikukawa,[11] for either domain wall movement or spin rotation, the initial permeability is proportional to M_s^2. Therefore, with increasing NZO content, the initial permeability increased. With increasing frequency, the initial permeabilities of all of the composites nearly remained constant, but the magnetic losses showed frequency dispersion and increased slightly only in the high-frequency range. Also, the cutoff frequencies (i.e., the frequencies where the μ' (real part of permeability) value was reduced by 50%) of all of the composites were above 1 GHz. With decreasing NZO, the cutoff frequency increased. According to Snoek's law,[12] the product of the initial susceptibility and cutoff frequency (f_r) was a constant for a magnetic material:

$$(\mu_i - 1)f_r = \gamma/(2\pi M_s)$$

where γ is the gyromagnetic ratio and μ_i is the initial permeability. The decrease in NZO may have caused the decrease of M_s, and an increase in the cutoff frequency could be expected. Additionally, the magnetic losses of all of the composites were all very low. This was probably due to the insulating polymer matrix wrapping the NZO particles, which drastically increased the resistance and reduced the eddy-current loss[13] of the composites. With increasing NZO, the resistances of the composite decreased, and the magnetic losses increased. For illustration and comparison, calculations using the well-known Maxwell–Garnett (MG) formula, where a fitted percolation threshold is included empirically, are also shown.[14] For the two-phase composite of ferrites and nonmagnetic host matrix, the MG formula for the effective permeability of the composite (μ_e) is

$$\mu_e = 1 + \frac{p}{n_0(1 - p/p_c) + 1/(\mu_i - 1)} \quad (1)$$

where μ_i is the initial permeability of NZO, p is the volume fraction of the NZO particles, p_c is the percolation threshold, and n_0 is the averaged shape factor of the NZO particles. As shown in Figure 2, the solid line is the fitting of the data with eq. (1). The fitting yielded $n_0 = 0.3788$ and $p_c = 0.8093$, which

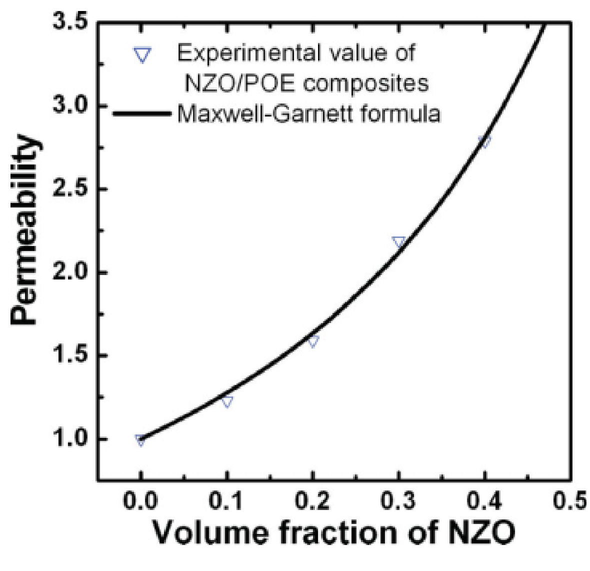

Figure 2 Variation of the experimental and calculated values of composites with the volume fraction of NZO. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

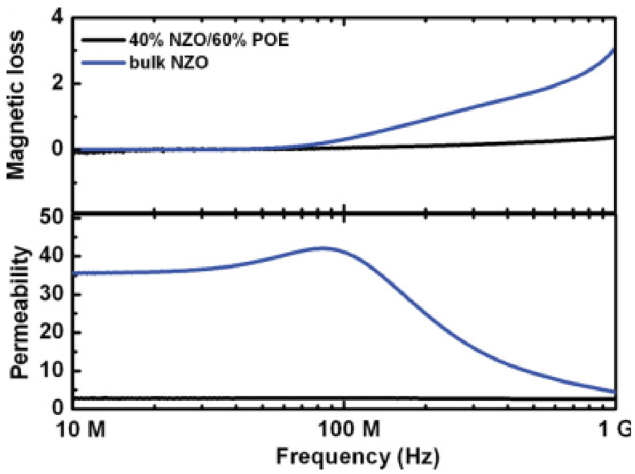

Figure 3 Frequency dependence of the magnetic properties of the 0.4NZO/0.6POE composite and bulk NZO. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

indicated that the shape of NZO particle was nearly ball-like, and the percolation could not occur for the as-prepared composites with an NZO volume fraction of less than 40 vol %.

Figure 3 shows the comparison of magnetic properties for the bulk NZO ceramic and the 0.4NZO/0.6POE composite. The bulk NZO ceramic showed a resonance at about 100 MHz, whereas the resonance frequency of the two-phase composite shifted to a much higher frequency beyond the HP 4291B measurement range, which indicated that the two-phase composite possessed an advantage of a much wider working frequency range.

Figure 4 shows the dielectric properties of the composites with different volume ratios of NZO. The permittivities and dielectric losses of the composites increased with increasing NZO because the permittivity and dielectric loss of NZO were both higher than those of POE. The dielectric losses of all of the composites were very low in the high-frequency range. The permittivities of all of the composites nearly remained constant within the measurement frequency range. Also, the dielectric losses of the composites were relatively high in the low-frequency range. The dielectric losses decreased first and then increased with increasing frequency. This was attributed to the low resistance of NZO and could be explained by the Debye formula.[15] When an alternating electric field is applied, not only polarization loss but also leakage loss is generated. The dielectric loss is divided into two parts:

$$D = D_P + D_G = \frac{(\varepsilon_S - \varepsilon_\infty)\omega\tau}{\varepsilon_S + \varepsilon_\infty\omega^2\tau^2} + \frac{\gamma}{\omega\varepsilon_0}\left(\frac{1}{\varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1+\omega^2\tau^2}}\right) \quad (2)$$

where D is the total dielectric loss tangent, D_P is the polarization loss tangent, D_G is the leakage loss tangent, ε_0 is the permittivity in vacuum, ε_S is the permittivity in the state electric filed, ε_∞ is the permittivity at optical frequency, γ is the conductivity, ω is the angular frequency, and τ is the relaxation time. It can be deduced that at a certain temperature when ω goes to 0, that is, at a static electric field, D_P goes to 0. In such a case, the dielectric loss is almost attributed to the leakage loss. Thus, when the frequency is very low, $\omega \times \tau \ll 1$, the dielectric loss can be described approximately as follows:

$$D \cong \frac{\gamma}{\omega\varepsilon_0\varepsilon_S} \quad (3)$$

Hence, the dielectric loss is inversely proportional to frequency in the low-frequency range. As the frequency increases, D_P gradually increases and becomes predominant, whereas D_G decreased. In the higher frequency range toward the end of the measurement range of HP 4291B, a resonant peak occurred because of the LC resonance in the measurement circuit, which caused the increase in the measured dielectric loss.

The stress–strain curve of the composites with different volume fractions of ceramic filler is shown in Figure 5. The results show that the mechanical properties decreased with increasing volume fraction of filler. The interface between a ceramic filler and the polymer matrix and the dispersion of the filler particles in the matrix plays an important role in determining the properties of a composite.[16,17] The SEM micrographs of NZO/POE composites with different volume fractions of filler are shown in Figure 6. The ceramic fillers were uniformly distributed in the polymer matrix for all of the composites, and the composites were very dense. For the composites with 40 vol % filler, the cross section was very rough, and the NZO particles were bare and floated

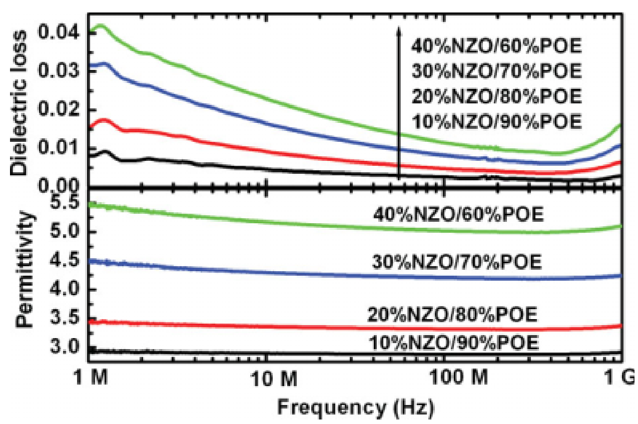

Figure 4 Frequency dependence of the dielectric properties of composites with different volume fractions of NZO. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

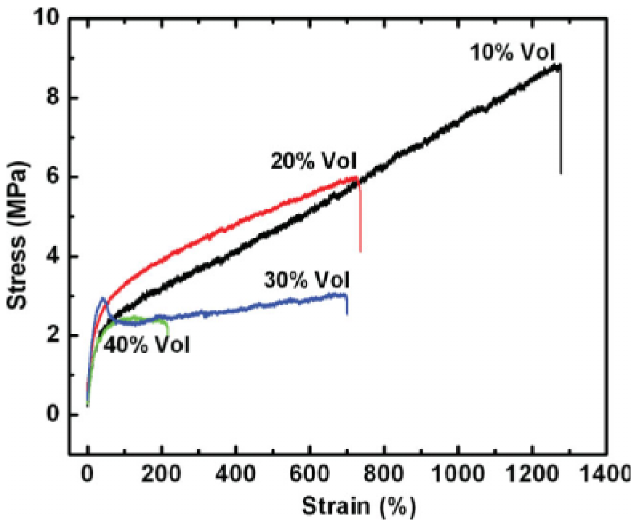

Figure 5 Stress–strain curves of composites with different volume fractions of the ceramic filler. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

on the POE matrix. Hence, nearly all of the fractures happened through the interface between the ceramic filler and the polymer matrix. With decreasing volume of the ceramic fillers, more and more fractures happened through the polymer matrix. For the composites with 10 vol % filler, the cross section was smooth, and the NZO particles were immersed in the POE matrix. It is known that the interface is the vulnerable area of the composite. So with the increase in the volume of filler, the tensile strength of the composites decreases.[18] Because the elongation of the composite is responsible by the flexible polymer matrix, with increasing volume of filler, the elongation of the composites decreases. The composite containing 40 vol % filler had a tensile strength of 2.2 MPa with an elongation at break value of about 200%.

CONCLUSIONS

NZO/POE flexible magnetic composites with various volume fractions of ceramic fillers were prepared with extrusion technology. With increasing volume of NZO, the permittivity, permeability, and dielectric and magnetic loss of the composites all increased. The cutoff frequencies of the composites were all above 1 GHz. The permittivities and permeabilities of all of the composites showed good frequency stability and low dielectric and magnetic losses within the measurement range from 10 MHz to 1 GHz. The mechanical properties of the composites decreased with increasing volume fraction of filler. All of the composites had a very good flexibility. For the 0.3NZO/0.6POE composite, the

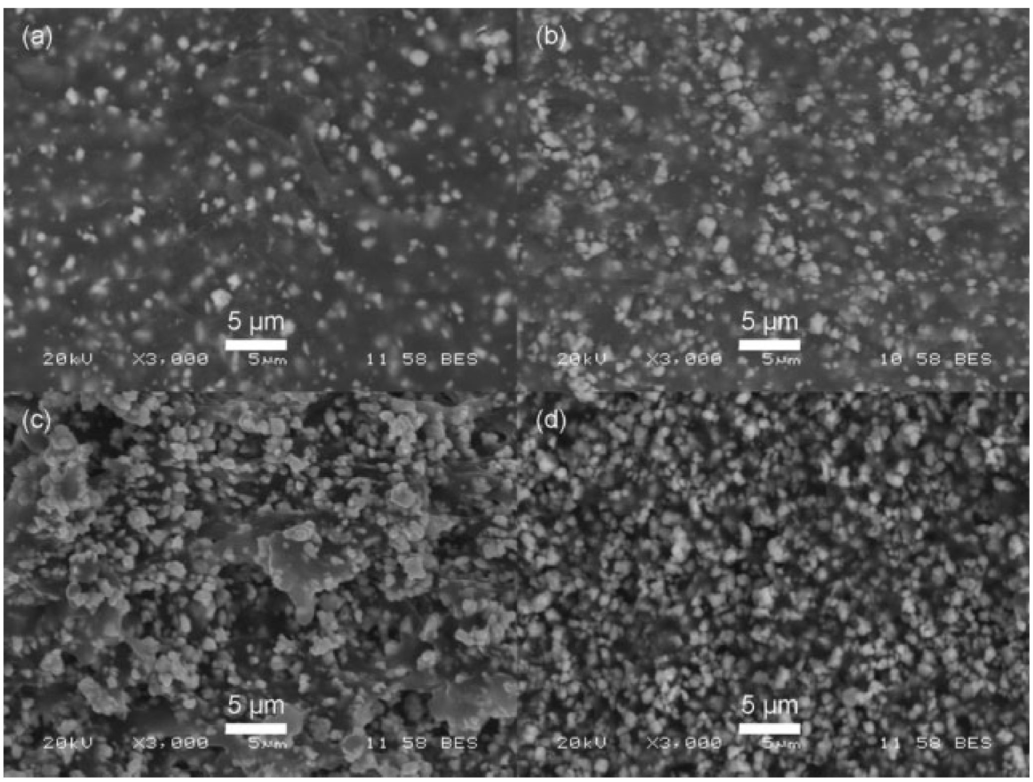

Figure 6 SEM micrographs of NZO/POE composites with different volume fractions of the NZO ceramic filler: (a) 10, (b) 20, (c) 30, and (d) 40 vol %.

permittivity, dielectric loss, permeability, and magnetic loss were 4.3, 0.0018, 2.2, and 0.002 at 100 MHz, respectively. The composite with 40 vol % filler had a tensile strength of 2.2 MPa with an elongation at break value of about 200%. Such magnetic composites are candidates for capacitor–inductor integrating devices, such as electromagnetic interference filters in radio frequency (RF) communications.

References

1. Zhi, Y.; Chen, A. J Mater Sci Mater Electron 2002, 13, 193.
2. Peng, X. L.; Yan, M. Magnetism Base and Magnetic Materials (in Chinese); Zhejiang University Press: Huangzhou, China, 2002; p 15.
3. Phan, M. H.; Peng, H. X.; Yu, S. C.; Wisnom, M. R. J Magn Magn Mater 2007, 316, 253.
4. Malini, K. A.; Mohammed, E. M.; Sindhu, S. J Mater Sci 2001, 36, 5551.
5. Shen, Y.; Yue, Z. X.; Li, M.; Nan, C. W. Adv Funct Mater 2005, 15, 1100.
6. Li, Z. W.; Wu, Y. P.; Lin, G. Q.; Chen, L. F. J Magn Magn Mater 2007, 310, 145.
7. Slama, J.; Dosoudi, R.; Vicern, R.; Giruskova, A.; Olah, V.; Hudec, I.; Usak, E. J Magn Magn Mater 2003, 254, 195.
8. Lebourgeoisa, R.; Berenguerb, S.; Ramiarinjaonab, C.; Waeckerle, T. J Magn Magn Mater 2003, 254, 191.
9. Paterson, J. H.; Devine, R.; Phelps, A. D. R. J Magn Magn Mater 1999, 196, 394.
10. Tsutaoka, T. J Appl Phys 2003, 93, 2789.
11. Rikukawa, H. IEEE Trans Magn 1982, 18, 1535.
12. Snoek, J. L. Physica 1948, 14, 207.
13. Lu, X. G.; Liang, G. Y.; Zhang, Y. M.; Zhang, W. Nanotechnology 2007, 18, 015701.
14. Rozanov, K. N.; Osipov, A. V.; Petrov, D. A.; Starostenko, S. N.; Yelsukov, E. P. J Magn Magn Mater 2009, 321, 738.
15. Sun, M. Z. Dielectric Physics (in Chinese); South China University of Technology Press: Guangzhou, China, 2005; p 114.
16. Huang, C. K.; Chen, S. W.; Wei, W. C. J. J Appl Polym Sci 2006, 102, 6009.
17. Tang, H. G.; Qi, Q.; Wu, Y. P.; Liang, G. H.; Zhang, L. Q.; Ma, J. Macromol Mater Eng 2006, 291, 629.
18. Xiang, F.; Wang, H.; Yang, H. B.; Shen, Z. Y.; Yao, X. J Electrochem 2008, to appear.