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Wear-resistant and electromagnetic absorbing behaviors of oleic acid post-modified ferrite-filled epoxy resin composite coating



Wenjie Wang, Chongguang Zang*, Qingjie Jiao

School of Mechatronical Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China

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ABSTRACT

The post-modified Mn–Zn ferrite was prepared by grafting oleic acid on the surface of Mn–Zn ferrite to inhibit magnetic nanoparticle aggregation. Fourier Transform Infrared (FT-IR) spectroscopy was used to characterize the particle surfaces. The friction and electromagnetic absorbing properties of a thin coating fabricated by dispersing ferrite into epoxy resin (EP) were investigated. The roughness of the coating and water contact angle were measured using the VEECO and water contact angle meter. Friction tests were conducted using a stainless-steel bearing ball and a Rockwell diamond tip, respectively. The complex permittivity and complex permeability of the composite coating were studied in the low frequency (10 MHz–1.5 GHz). Surface modified ferrites are found to improve magnetic particles dispersion in EP resulting in significant compatibility between inorganic and organic materials. Results also indicate that modified ferrite/EP coatings. The enhanced tribological properties of the modified ferrite/EP coatings compared to exhibit better reflection loss compared with the coatings with original ferrite.

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1. Introduction

Ferrite is one of the excellent magnetic materials and has attracted attention owing to its special ferromagnetic property, easy of synthesis and performance stability [1–3]. Therefore, it is tunable to meet the requirements for the applications in electromagnetic shielding and electromagnetic absorbing fields. However, ferrite is subject to strong interparticle magnetic attractive forces between magnetic nanoparticles leading to aggregation of particles. A significant challenge to utilize ferrite particles as electromagnetic absorbers is to overcome aggregation of particles. Surface modification of ferrite particles known as the core-shell structure, is believe to reduce interparticle magnetic forces resulting in uniform dispersion [4–6].

Numerous organic solvents have been developed to be coated on the surface of ferrites, such as oleic acid [4], sodium oleate [7], sodium dodecyl benzene sulfonate [8] and polyethyleneimine [9]. Oleic acid is one kind of long chain fatty acids that were often used as surfactants in the synthesis of magnetic materials. As a result of this modified surface of ferrite, it could exhibit excellent chemical

* Corresponding author. E-mail addresses: zangchongguang@bit.edu.cn, wenjie@bit.edu.cn (C. Zang).

http://dx.doi.org/10.1016/j.jmmm.2014.10.160 0304-8853/© 2014 Elsevier B.V. All rights reserved. stability and homogeneous dispersion, facilitating its application in electromagnetic absorbing field. Wang et al. [7] reported the sodium oleic molecules were linked to the particles through chemical bond. Hyeon et al. [10] synthesized highly crystalline and monodisperse cobalt ferrite nanocrystals using oleic acid as surfactant. Epoxy resin is widely used as electromagnetic absorbing matrix and its advantages, i.e. good mechanical, chemical stability and optical properties [11]. In order to achieve high-quality electromagnetic films or coatings, the surface modified ferrite particles and epoxy resin composites have been developed. Kang et al. [12] demonstrated that the sliding friction and wear as well as the contact angle behaviors of the coatings are highly dependent on the properties of the fillers. Thus, the introduction of surface modified ferrite into the epoxy resin can substantially enhance its mechanical property, dispersion and electromagnetic absorbing property.

In this paper, magnetic Mn–Zn ferrite particles were postmodified by oleic acid, and then mixed with epoxy resin to form composite coatings. The dispersion, contact angle and friction behaviors of as-prepared ferrite/EP coatings were investigated. The complex permittivity, permeability and reflection loss of the fabricated coatings were also characterized and analyzed.

2. Experiment

2.1. Materials

Mn–Zn ferrite was purchased from Nanjing Emperor Nano Material Co. (Nanjing, China). Oleic acid was purchased from Sigma, USA. Isopropanol were obtained from Fisher Scientific. Water was deionized.

2.2. Preparation of ferrite particles coated with oleic acid

Ferrite particles have been modified with oleic acid by a selfassembly process. For the process, 0.6 g of ferrite was suspended in a 60 ml isopropanol solution containing 0.6 vol% of oleic acid for 10 min. The solution was then sonicated for 30 min and stirred for 2 h at 60 °C. Subsequently, the particles were separated from by filtration, washed 3 times with isopropanol, and heated at 90 °C for 3 h.

2.3. Fabrication of ferrite/EP composite coatings

The composite coatings were made by mixing the ferrite particles with epoxy resin (for 10 wt%), followed by stirring, and then adding the curing agent by continuous stirring. The specimens were produced with epoxy-to-hardener ratio of 100:13. Next, one drop of the homogenous liquid was dispensed and coated evenly by spin-coating on a glass slide. Finally, the composites were cured at 90 °C for 90 min.

2.4. Characterization

The chemical structure of original ferrite and post-modified ferrite particles was characterized by Fourier transform infrared spectroscopy (FT-IR). The cross-section of ferrite/EP coating was examined with scanning electron microscope (SEM) operated at 10 kV.

Contact angle was performed using a contact angle instrument. The contact angle of water in air was measured by gently dispensing a drop of water onto the cured composite film. The roughness of the coatings was measured using the VEECO. Friction tests were conducted using a stainless-steel bearing ball and a Rockwell diamond tip, respectively. The loads (F_z) were 300 g, 500 g, and 800 g, and the scanning speed was 0.01 mm/s. Coefficient of friction (COF) is defined as the ratio of the friction force (F_x) over the load.

Complex permittivity and complex permeability of the composite coatings were characterized by an Impedance Analyzer (Agilent E4294A: 10 MHz-1.5 GHz). The sample for the complex permittivity with circular disk was prepared by mixing the ferrite with epoxy resin and curing agent (1:10:1 by weight). The diameter is 20 mm and the thickness is 2 mm according to previous research [3] and testing equipment. The sample was put into the fixture between two polar plates with the same diameter in order to form capacitance during testing process. The equipment can output the value of complex permittivity in accordance with the specific value of capacitance. When it comes to the complex permeability, the sample was fabricated into a ring of 20 mm in external diameter, 5 mm in internal diameter and of 2 mm in thickness. The equipment can output the value of complex permeability by calculating the inductance of the coil sample in the fixture. The reflection loss of the coatings was measured by a Network Analyzer (Agilent E5062A: 10 MHz-1.5 GHz) according to the coaxial transmission method.



Fig. 1. FT-IR of Mn–Zn ferrite particles. (a) The original ferrite particles and (b) oleic acid post-modified ferrite particles.

3. Results and discussion

3.1. FT-IR Mn–Zn ferrite particles

The particle surfaces were characterized by Fourier Transform Infrared (FT-IR) spectroscopy and the result is displayed in Fig. 1(a) the original ferrite and (b) oleic acid post-modified ferrite. The characteristic spinel adsorption at 588 cm⁻¹ confirms the formation of ferrite in each of them [13]. In addition, the peaks at 3435 cm^{-1} and 1626 cm^{-1} are the H₂O characterized absorbing peaks. The particles coated with oleic acid comprised the bands at 2924 cm^{-1} and 2853 cm^{-1} , which were due to $-CH_3$ and $-CH_2$ vibration, respectively [5,7]. The result showed strong C–H peaks at 2924 cm⁻¹, 2853 cm⁻¹, 1046 cm⁻¹, and 795 cm⁻¹. The peak at 795 cm⁻¹ suggests vibrations and out-of-plane bending of the C-H bond [14]. Peaks at 1094 cm⁻¹, 1023 cm⁻¹ and 1415 cm⁻¹ indicate the stretching of C–O bond [15], revealing that the two oxygen atoms in the carboxylate are coordinated on the surface of the particle which confirms the presence of the oleic acid on the surface of the particles.

Fig. 2 shows the possible mechanism for the formation of the oleic acid post-modified ferrite. According to the literature [9,15,16], the oleic acid adsorbed on the surface of the magnetic ferrite particles by the interaction between the metal oxidation and the carboxyl oleic acid. It was a chemical interaction by



Fig. 2. Schematic representation for the grafting of oleic acid on the surface of magnetic ferrite particles.

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