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Effects of titanate coupling agent on the dielectric properties of NiZn ferrite powders–epoxy resin coatings

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Abstract

During ferrite powder–polymer resin slurry preparation, the ferrite particles tend to hold together, forming agglomerates, which lead to the formation of micro-structural defects in the ferrite powder–polymer coatings. These defects affect the quality of magnetic devices. In this study, the titanate coupling agent effects on the NiZn ferrites powder dispersion in an epoxy resin and solvent system and the electromagnetic properties of NiZn ferrite powders–epoxy resin composite coatings are investigated. It was observed that the dispersion of NiZn ferrite powders and the affinity of NiZn ferrites and epoxy resin can be substantially enhanced by coating a titanate coupling agent onto the ferrite powder surfaces. This coating promotes mixing homogeneity and increases the dielectric constants at low frequencies (below 100 Hz) due to the increase in phase boundary between the NiZn ferrite powders and epoxy resin.

Keywords: C. Dielectric properties; NiZn ferrites; Epoxy resin; Titanate coupling agent

1. Introduction

Ferrite powder–polymer composites have been used extensively in the suppression of electromagnetic noise due to their superior electromagnetic properties [1–3]. In general, the composites are prepared by mixing 20–50 vol% ferrite powders with polymer. The electromagnetic and mechanical properties of the composites are determined by the ferrite properties and also by the interaction between the ferrite particles and polymer [4,5]. During ferrite powder–polymer resin slurry preparation the ferrite particles tend to hold together. The particles form agglomerates because of the strong magnetic interactions between the ferrite particles. Moreover, the NiZn ferrite particles are hydrophilic and cannot be dispersed homogeneously in organic resins. The agglomerates and inhomogeneous ferrite powder mixing in organic resins generally leads to the formation of micro-structural defects in the ferrite powder–polymer coatings. These defects affect the quality of magnetic devices. The surface modification of ferrite powders with a coupling agent in epoxy resin formulations can offer superior performance, such as improved dispersibility, increased compatibility between the ferrites and epoxy resin and adhesion strength between the ferrite particles and polymer matrix because the coupling agent grafts onto the ferrite powder surface. Hsiang and Tsai [6] investigated the titanate coupling agent effects on nonaqueous Co_2Z ferrite suspensions dispersion and observed that the Ti–O–Fe covalent bond was formed through the interaction of the Ti–O bond in the titanate coupling agent and FeOH onto the surface of ferrite powders. The investigations of the dielectric and magnetic properties of ferrite powder–polymer most focused on the ferrites content, particle size and distribution effects [7–10]. However, the effects of dispersion of ferrite powders on the microstructure, magnetic and dielectric properties have rarely been reported. In this study, a titanate coupling agent was used to modify the surfaces of NiZn ferrite powders to prevent agglomeration and enhance the mixing homogeneity in epoxy resins. The titanate coupling agent effects on the surface property, dispersion and dielectric properties of NiZn ferrite powder–polymer coatings were investigated using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and LCR meter.

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2. Experimental procedure

2.1. Materials

The $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite powders were prepared from reagent-grade NiO, ZnO and Fe_2O_3, which were mixed and then calcined at 1100 °C for 6 h. The calcined powder was used as the raw material and milled for 6 h using Y-TZP balls using ethanol as the medium. The specific surface area (BET) value of the ball-milled $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite powder was about 1.24 m^2/g. The Titanate coupling agent, tri(dioctyl) pyrophosphato titanate-Lica 38 (Kenrich Petrochemicals Inc., USA) was used without further purification. The epoxy resin used was brominated epichloro hydrin-bisphenol A (NPEB450A80, Nan Ya Plastics Co., Taiwan), with a weight per epoxy equivalent of 425–455 g. Dicyanodiamide (DICY) and 2-methyl imidazole (2-MI), purchased from Acros Chemical (Geel, Belgium), were used as the hardener and accelerator, respectively. The carboxyl-terminated butadiene-acrylonitrile liquid rubber (CTBN) (Hypro 1300x13, Emerald Performance Materials LLC, USA) was used to improve the toughness of the epoxy resin. Aceton, toluene and dimethyl fumarate (DMF) were used as solvents without further purification. Aceton and toluene were used as the solvent and prepared in a 75:25 ratio before use.

2.2. Experimental procedure

Prior to surface modification, the NiZn ferrite powders were dried in an oven to remove moisture. The NiZn ferrite powders with the addition of Lica 38 and aceton were ball-mixed in polyethylene bottles for 6 h. The titanate-coupling agent concentration varied from 0 to 2.5% with a step of 0.5% of the solid weight. After ball-mixing, the surface modified NiZn ferrite powders were subsequently washed 3 times with aceton to remove the non-adsorbed Lica 38. The slurry was then dried at 80 °C for 24 h. Suspensions were prepared by mixing 50 g surface modified NiZn ferrite powders with 50 ml aceton. To breakdown the agglomerates, the suspensions were sonicated for 15 min using a high-energy ultra-sonicator. The suspensions were then allowed to stand undisturbed at room temperature for 200 h to achieve complete settling prior to the sedimentation studies. The sediment height was recorded and used as an indicator for NiZn ferrite powder dispersion. The chemical characteristics of NiZn ferrite powders with various amounts of added Lica 38 were determined using Fourier transform infrared spectroscopy (EQUINO 55, Brucker, Germany).

NiZn ferrite powder–epoxy resin composite coatings were prepared as follows. Firstly, 15 phr CTBN was mixed with epoxy resin and a proper amount of acetone. Thirty or fifty percent weight surface modified Ni–Zn ferrite powder was added to the above CTBN-epoxy resin mixture, diluted with a proper amount of acetone/toluene (75/25) binary solvent. The appropriate amount of DICY and 2-MI dissolved in DMF were then added quantitatively to the NiZn ferrite powder–epoxy resin slurry. The mixture was then stirred using a rotary evaporator under reduced pressure to remove the excess solvent and obtain a suspension with a proper viscosity for casting. The wet coatings (about 50 μm) were prepared from the suspension onto transparent PET films. Coated samples were aged under ambient conditions for 24 h and then baked at 160 °C for 1 h.

Scanning electron microscopy (SEM) was used to observe the NiZn ferrite powder–epoxy resin composite film microstructure. The dielectric properties of the NiZn ferrite powder–epoxy resin composites were measured over the range of 20 Hz to 1 MHz using a HP 4284A impedance analyzer at room

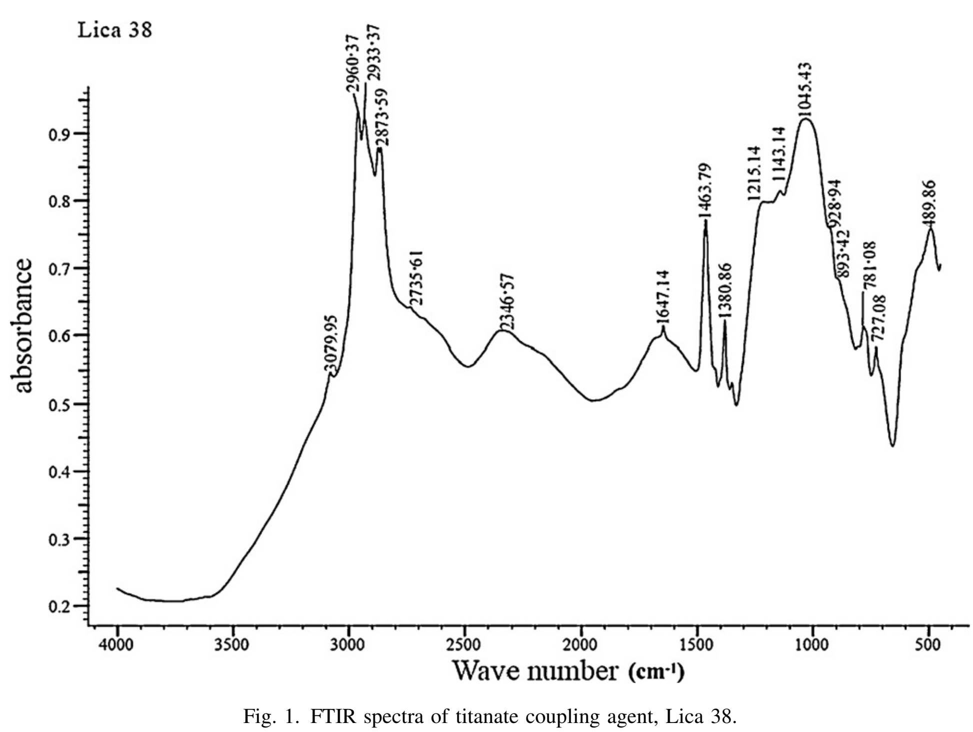

Fig. 1. FTIR spectra of titanate coupling agent, Lica 38.

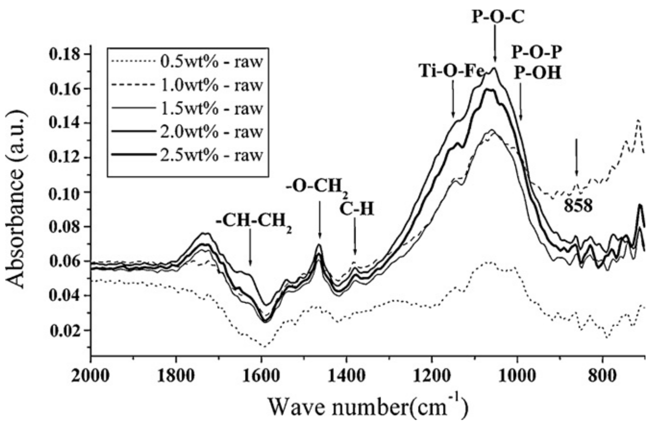

Fig. 2. FTIR spectra of NiZn ferrite powders treated with various Lica 38 content in the region 800–2000 cm^{-1}.

Table 1
Integrated infrared intensities of Ti–O–Fe bonding around 1150 cm^{-1} (A_{1150}), the absorption peak belonging to ferrite powders at 858 cm^{-1} (A_{858}), and the ratio of A_{1150} to A_{858}.

Lica 38 amount	A_{858}	A_{1150}	A_{1150}/A_{858}
0.5	0.118	0.022	0.186
1	0.075	0.015	0.200
1.5	0.090	0.019	0.211
2	0.061	0.014	0.226
2.5	0.124	0.027	0.218

temperature. The magnetic properties of the NiZn ferrite powder–epoxy resin composites were measured over the range of 1 MHz to 1.8 GHz using a HP 4291B material analyzer at room temperature.

3. Results and discussion

Fig. 1 shows the FTIR spectra of Lica 38. The main absorption bands at 1215, 1143, 1045, and 928 cm^{-1} are attributed to the P=O, Ti–O, P–O–C, P–O–P, and P–OH groups, respectively. The FTIR spectra of NiZn ferrite powders treated with various Lica 38 content in the region 800–2000 cm^{-1} are shown in Fig. 2. A new peak at about 1150 cm^{-1} is observed, which may be attributed to the Ti–O–Fe linkage formed by breaking Ti–O–C and bonding with FeOH [6]. The relative integrated intensities of Ti–O–Fe bonding around 1150 cm^{-1} with respect to the absorption peak belonging to ferrite powders at 858 cm^{-1} (A_{1150}/A_{858}) obtained from the Lica 38-treated ferrite powders plotted against the Lica 38 amounts are shown in Fig. 3. The A_{1150}/A_{858} value can be used as an indicator for Lica 38 adsorption onto the ferrite powder surface. The evaluation of A_{1150} and A_{858} was conducted by using the Bruker FTIR software. Before integration, the IR curves were subtracted by the data with 0 wt% Lica 38 addition. Then, A_{1150} and A_{858} were integrated from the subtracted curves. The values of A_{1150} and A_{858} are listed in Table 1. The percentage of Lica 38 adsorbed onto the surface of the ferrite powders increased with increasing Lica 38 addition and reached a maximum at about 2.0 wt% and then declined.

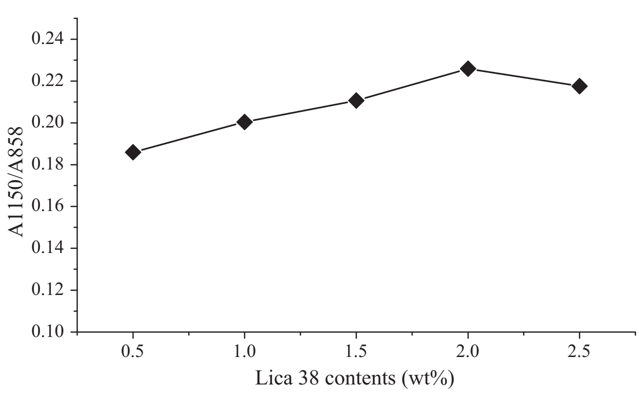

Fig. 3. Relative integrated intensities of Ti–O–Fe bonding around 1150 cm^{-1} with respect to the absorption peak belonging to ferrite powders at 858 cm^{-1} (A_{1150}/A_{858}) obtained from the Lica 38-treated ferrite powders plotted against the Lica 38 amounts.

The effect of Lica 38 addition on the sedimentation heights of the suspensions with Lica 38 treated ferrite powders is shown in Fig. 4. The sedimentation height decreased with increasing Lica 38 addition, reaching a minimum at about 2.0 wt%, indicating that coating Lica 38 onto the ferrite powders can provide a surface coverage on the particle surface and effectively prevent the particles from agglomerating due to magnetic interaction.

Fig. 5 shows the SEM micrographs of the NiZn ferrite powder–epoxy resin coatings with different concentrations of Lica 38. For the sample without surface modification, the agglomeration easily occurred for NiZn ferrites due to the strong magnetic attraction between particles. This led to the NiZn ferrite powders not being dispersed uniformly in the epoxy resin. With the increase in Lica 38 concentration, the mixing homogeneities of NiZn ferrite powders and epoxy resin were gradually improved. This indicates that Lica 38 coated onto the surface of NiZn ferrite powders can change the ferrite powder surface from hydrophilic into hydrophobic and hence enhance the ferrite powder affinity to epoxy resin, making the ferrite powder and epoxy resin mix homogeneously.

The initial permeabilities of samples with various amount of added Lica 38 are shown in Fig. 6. The initial permeabilities are all about 1.7–1.8 in the frequency range of 100 MHz to 1 GHz with no obvious differences in the initial permeability observed for the NiZn ferrites powder–epoxy resin composite coatings treated with different amounts of added Lica 38. The initial permeabilities of samples with ferrite loadings of 30 and 50 wt% are shown in Fig. 7. The initial permeability remained almost unchanged below 1 GHz, and increased from 1.35 to 1.75 as the ferrite loading was increased from 30 to 50 wt%. The porosity will affect the permeability and dielectric constant. However, the porosities of all samples were nearly same due to the wet-coating process. These suggest that the magnetic property is mainly dependent on the ferrite content. The variations in dielectric constant and dielectric loss (tan δ) for samples with various amount of Lica 38 addition as a function of the frequency are shown in Fig. 8. For all samples, the dielectric constant and tan δ decreased rapidly with

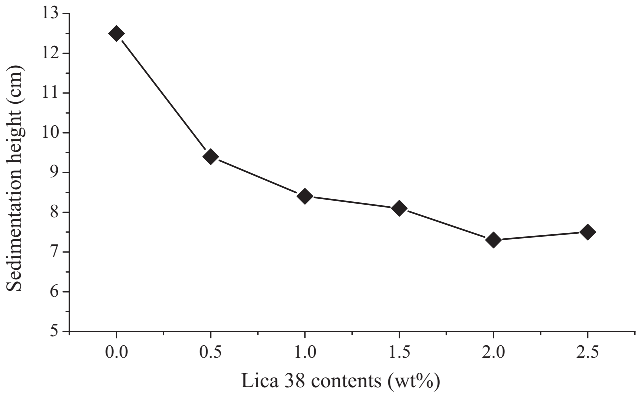

Fig. 4. Effect of Lica 38 addition on the sedimentation heights of the suspensions with Lica 38 treated ferrite powders.

increasing frequency up to 10 kHz and beyond that remained constant. A barrier-layer structure with semiconducting areas encircled by insulating layers can be used to explain the large dielectric constant of ferrite powder–epoxy resin composites at low frequency. This behavior is characterized by the space charge polarization arising from differences between the conductivity of the various phases present. At low frequency electron hopping may occur between Fe^{3+} and Fe^{2+} on the octahedral sites for NiZn ferrites [11]. The electrons reach the phase boundary between NiZn ferrites and epoxy resin through hopping and are piled up at the phase boundaries, which results in the interfacial polarization. However, as the frequency is increased, the probability of electrons reaching the phase boundary decreases, which results in a decrease in the interfacial polarization. Therefore, the dielectric constant decreases with increasing frequency.

Note that the relative dielectric constant at low frequency (below 100 Hz) increased with increasing Lica 38 concentration and passed through a maximum at a concentration of

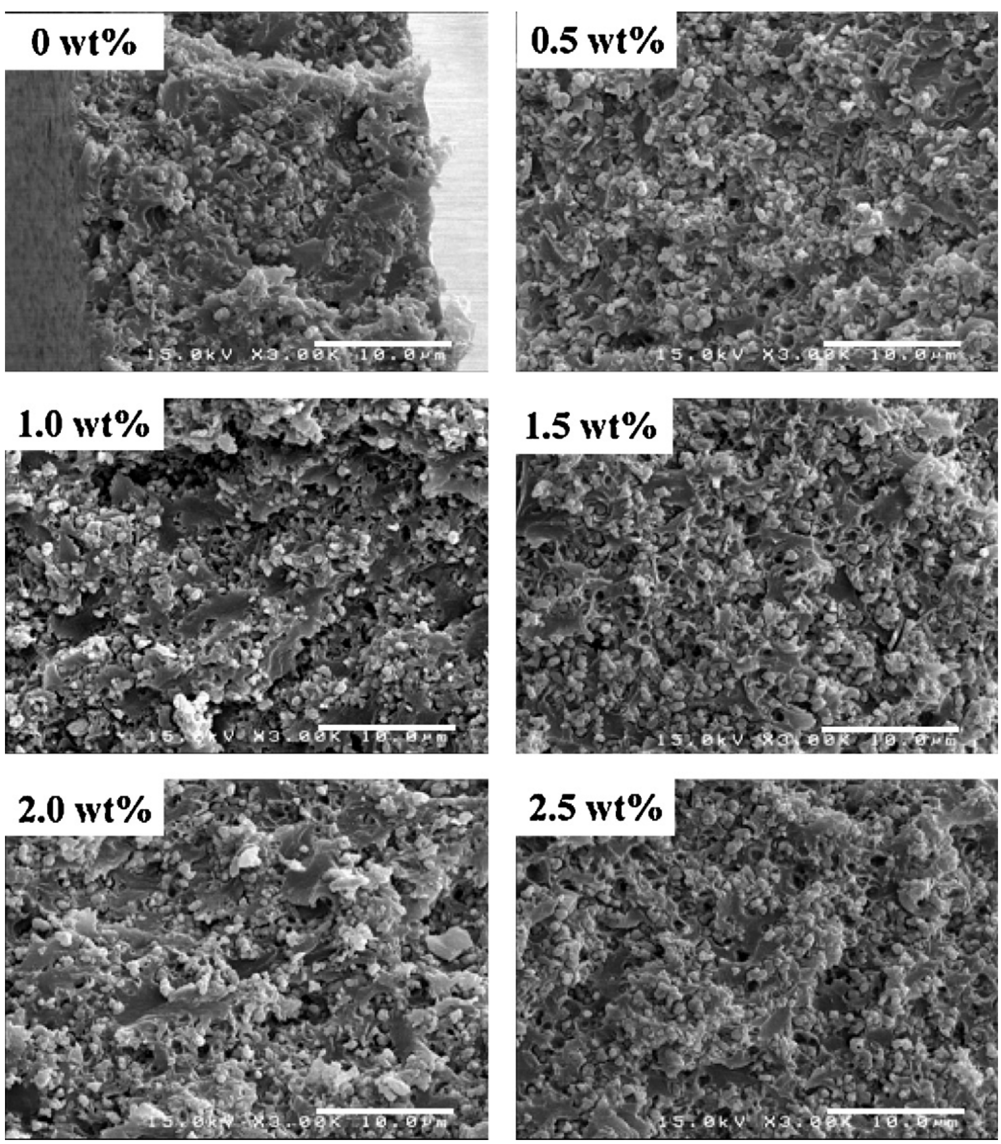

Fig. 5. SEM micrographs of the NiZn ferrite powder–epoxy resin coatings with different concentrations of Lica 38.

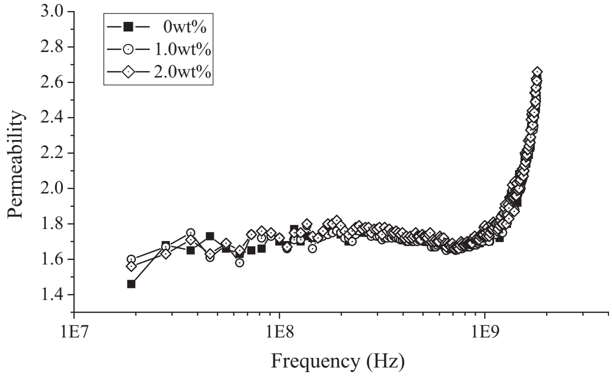

Fig. 6. Initial permeabilities of samples with various amount of added Lica 38.

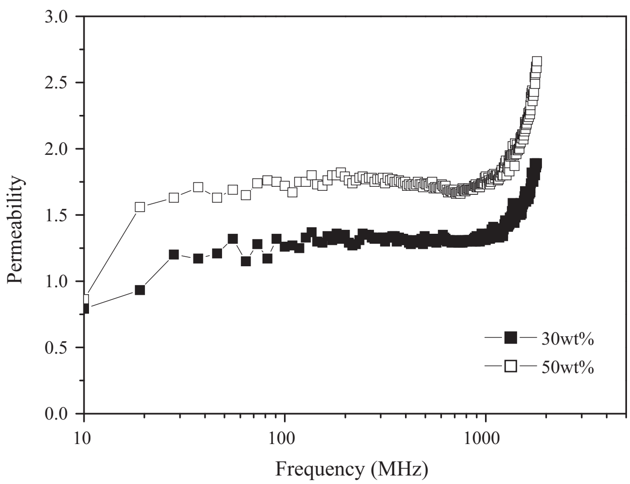

Fig. 7. Initial permeabilities of samples with ferrite loads of 30 and 50 wt%.

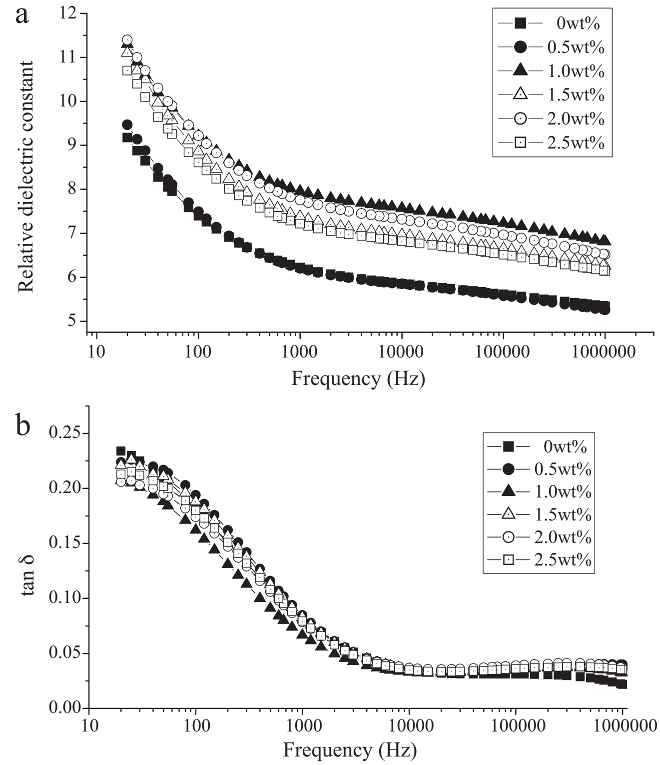

Fig. 8. Variations in (a) dielectric constant and (b) tan δ for samples with various amount of Lica 38 addition as a function of the frequency.

1–2 wt%, with no obvious difference in the dielectric loss for all samples. This is due to the dispersion of NiZn ferrite powders and the affinity of NiZn ferrites and epoxy resin was substantially enhanced by coating Lica 38 onto the ferrite powder surfaces. This Lica 38 coating promotes homogeneous mixing and increases the phase boundary between NiZn ferrite powders and epoxy resin. However, as the coupling agent concentration increased above 2.5 wt%, the relative dielectric constant decreased, which may be due to excess titanate coupling agent, resulting in polymer bridging and decreased phase boundary between the NiZn ferrite and epoxy resin.

4. Conclusion

The effects of a titanate coupling agent, Lica 38, on the dispersion of NiZn ferrite powders in the epoxy resin and solvent system and the electromagnetic properties of NiZn ferrite powder–epoxy resin composite coatings were investigated. Lica 38 coated onto the surface of NiZn ferrite powders can change the ferrite powder surface from hydrophilic into hydrophobic and hence enhance the affinity between ferrite powders and epoxy resin. This affinity makes ferrite powder and epoxy resin mix homogeneously. The maximum dielectric constant at low frequency (below 100 Hz) can be obtained due to the increase in phase boundary between NiZn ferrite powders and epoxy resin for ferrite powder samples treated with 2 wt% Lica 38. However, the magnetic property was mainly dependent on the ferrite content and no obvious difference in the magnetic permeability was observed for the NiZn ferrite powder–epoxy resin composite coatings surface treated with different amounts of added Lica 38.

Acknowledgments

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