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# Synthesis and microwave absorption characteristics of polyaniline/NiZn ferrite composites in 2–40 GHz

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ABSTRACT

NiZn ferrite coated with polyaniline, forming a composite structure, were synthesized by *in situ* polymerization at different aniline/NiZn ferrite weight ratio (Ani/NiZn ferrite = 1/1, 2/1, 3/1) and introduced into epoxy resin to be a microwave absorber. The spectroscopic characterizations of the formation processes of polyaniline/NiZn ferrite composites were studied using Fourier transform infrared, ultraviolet–visible spectrophotometer, X-ray diffraction, scanning electron microscopy, transmission electron microscopy and electron spin resonance. Microwave absorbing performances were investigated by reflectivity in 2–18 and 18–40 GHz using arch method. The results showed that a wider absorption frequency range could be obtained by adding different polyaniline content in NiZn ferrite.



## 1. Introduction

Microwaves are electromagnetic waves with a frequency range in the electromagnetic spectrum of 300 MHz to 300 GHz. However, most applications of microwave technology make use of frequencies in the range of 1–40 GHz. Many problems have occurred along with it, which are a misoperation of precise electronic equipment and leak of secret information occurred by a leakage of electromagnetic wave. Thus, the electromagnetic compatibility (EMC) and electromagnetic interference (EMI) are becoming a serious problem, and much attention has been paid towards finding suitable microwave absorber to solve this problem. Extensive studies have been carried out to develop new and high efficient absorbents, and various absorbers (such as conductive metal powder, ferrites, carbon products, chiral materials, synthetic organic fibers, etc.) have been singled out or synthesized [1–4].

Due to its high conductivity, environmental stability and rather simple synthesis, polyaniline (PANI) became the focus of attention for preparation of new materials for the fabrication of industrial devices [5–8]. In addition, the PANI not only reflects but also absorbs electromagnetic wave, and may attain high levels of shielding performance [9,10]. Ferrites serve as better electromagnetic interference (EMI) suppressors compared to their dielectric counterparts on account of their excellent magnetic properties. Ferrite materials exhibit various electrical and magnetic properties of which the complex permeability and the complex permittivity, in particular, are important in determining their high frequency characteristics. The NiZn ferrites are found to be the most versatile technological materials especially suited to high frequency applications on account of their high resistivity [11]. If NiZn ferrite can be coated with PANI, both the physiochemical properties and the electromagnetic shielding performance are expected to be improved.

In this article, we present a novel approach to synthesizing composite structural PANI/NiZn ferrite composites. The influence of the PANI content with respect to the electromagnetic properties of PANI/NiZn ferrite composites has been investigated. The origin of their electromagnetic properties is also discussed on the basis of the structural characterization; including Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The ultraviolet–visible spectrophotometer (UV–Vis), four probe method and electron spin resonance (ESR) have been used for investigating the electrical conductivity. Microwave absorbing properties of the NiZn ferrite and PANI/NiZn ferrite reinforced epoxy resin composites were tested at 2–18 and 18–40 GHz using arch method, which was chosen to validate the absorbing efficiency of microwave absorbing material [12]. The NRL (Naval Research Laboratory) arch free-space measurement method was chosen to validate the absorbing efficiency of microwave absorbing material. The NRL arch was widely used initially by the U.S. Navy for research testing purposes, and is a microwave measurement system that can measure the free space radar reflection coefficient.

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## 2. Experimental

### 2.1. Preparation of NiZn ferrite, PANI/NiZn ferrite, epoxy-NiZn ferrite and epoxy-PANI/NiZn ferrite composites

The NiZn ferrite magnetic particles were prepared by the sol–gel autocombustion method at room temperature, as reported elsewhere [13]. The powders were calcined at 900 °C for 2 h to obtain the spinel phase. The powder from the composite of PANI-dodecylbenzene sulfonic acid (DBSA) and the NiZn ferrite (aniline: NiZn ferrite = 1:1, 2:1 and 3:1) was prepared by the emulsion polymerization method. Ten grams of NiZn ferrite were added to 300 mL of deionized water and vigorously stirred at room temperature for 3 h, producing a fine aqueous dispersion. The subsequent addition of aniline and DBSA (molar ratio aniline: DBSA was 1:3), and deionized water (200 mL) into the NiZn ferrite–water dispersion was done at ambient temperature. The composite ratios of NiZn ferrite and aniline in weight were 1:1 (PANI/NiZn ferrite-1), 2:1 (PANI/NiZn ferrite-2) and 3:1 (PANI/NiZn ferrite-3), respectively. The monomer–NiZn ferrite–water dispersion was stirred for 3 h, and cooled to ~0 °C with stirring. An aqueous solution of $(NH_4)_2S_2O_8$ was added dropwise to initiate the polymerization. The concentration of the $(NH_4)_2S_2O_8$ solution was adjusted to have an aniline:$(NH_4)_2S_2O_8$ molar ratio of 1:1.5. The polymerization was carried out at ~0 °C for 12 h, with stirring. The polymerization was terminated by pouring acetone into the mixture, and then the PANI/NiZn ferrite composites were obtained. This material was isolated by filtration, washed with acetone and deionized water and dried under vacuum at 40 °C for 24 h.

The absorbing composite materials were prepared by molding and curing the mixture of NiZn ferrite and PANI/NiZn ferrite powders and a thermal-plastic epoxy resin. The mixing ratio of specimen powders to epoxy resin was 2:1 by weight. Molding was carried out in a hydraulic press at 5 MPa pressure and 100 °C for 1.5 h, obtaining specimens of 180 mm × 180 mm with thickness of 2 mm for reflectivity measurements.

### 2.2. Experimental techniques

The FTIR and UV–Vis spectra of the samples were recorded on a Tensor 27 (Bruker) and UV-3000 spectrophotometer. The phase identification of the samples was performed with X-ray diffraction with Cu Kα radiation. The particle morphology was observed with a JEOL JEM-200CX scanning electron microscope as well as a Philips CM-200 transmission electron microscope. The ESR spectra of the samples were recorded on a Bruker EMX-10 electron spin resonance spectrometer operating at the X-band ($\nu$ = 9.6 GHz) with 100-kHz field modulations. Diphenyl picrylic hydrazole (DPPH) ($g$ = 2.0036) was used as a field marker.

The performance test of radar absorbing was evaluated by reflectivity using Arch method. Reflectivity $R$ is ratio of radar-absorbing material (RAM) reflective power to metallic plate reflective power, which can be expressed as:

$$R = \frac{P_a}{P_m} \tag{1}$$

Where $P_a$ is the reflective power of the sample and $P_m$ is the reflective power of metallic plate.

In practice, we surveyed the ratio of the reflective power of the sample and the reflective power of metallic plate to the same reference signal that was in direct proportion to transmit, respectively.

$$R_m = \frac{P_m}{P_i}, \quad R_a = \frac{P_a}{P_i} \tag{2}$$

where $P_i$ is the reference signal. So

$$R = \frac{P_a}{P_m} = \frac{P_a/p_i}{P_m/p_i} = \frac{R_a}{R_m} \tag{3}$$

The reflectivity was finally expressed with db as:

$$R_{db} = 10 \log R_a - 10 \log R_m \tag{4}$$

The reflectivity measurement of the experimental setup was shown in Fig. 1. The reflectivity of the samples was measured and compared with that from a plane metallic plate. Measurement was carried out using an HP8722ES network analyzer in the swept frequency range of 2–18 and 18–40 GHz. All samples were made 180 mm × 180 mm with thickness of 2 mm in order to cover the metallic plate for reflectivity measurements.

## 3. Results and discussion

### 3.1. Structure characterization

The FTIR spectra of the NiZn ferrite and PANI/NiZn ferrite composites are shown in Fig. 2. The bands at 590 (tetrahedral) and 390 $cm^{-1}$ (octahedral) are the characteristic bands of NiZn ferrite ($Fe^{3+}$–$O^{2-}$). The characteristic absorption bands of PANI are at 1550 and 1450 (C=N and C=C stretching), 1390 (C–N stretching), 1296 (N–H bending), 1236 (asymmetric C–N stretching of the benzenoid ring), 1120 (a vibration mode of N=Q=N) and 800 $cm^{-1}$ (out-of-plane stretching vibration of C–H) [14]. As shown in Fig. 2, with an increase in the PANI content, the intensity of the bands at 1550, 1450 and 1390 $cm^{-1}$ corresponding to PANI characteristics increases distinctively, and the band at 390 and 590 $cm^{-1}$ corresponding to NiZn ferrite was greatly diminished. These results indicate that there is well wrapping of NiZn ferrite particles with PANI in the PANI/NiZn ferrite composites.

**Fig. 1.** Reflectivity measurement setup of arch method.

Fig. 3 shows the XRD patterns of the NiZn ferrite particles and the PANI/NiZn ferrite composites. The main peaks in the XRD patterns of the PANI-DBSA composites, which were characteristic of the broad amorphous halo over the range $2\theta$: 10–25°, appeared in the positions of approximately 13 and 24.5° [15,16]. Both the pure NiZn ferrite and composite powders are a single-phase NiZn ferrite with a spinel structure. This agrees well with the results obtained for NiZn ferrite prepared by sol–gel synthesis [13,17]. Therefore, we can estimate the size of the NiZn ferrite grain ($2\theta$ = 36°) with Scherrer's formula, $D = 0.9\lambda/\beta \cos\theta$, where $D$ is the crystallite size (nm), $\lambda$ is the radiation wavelength (0.154056 nm for Cu Kα), $\beta$ is the bandwidth at half-height, and $\theta$ is the diffraction peak angle [18]. The calculated crystallite sizes of the NiZn ferrite particles range from 0.2 to 0.5 μm.

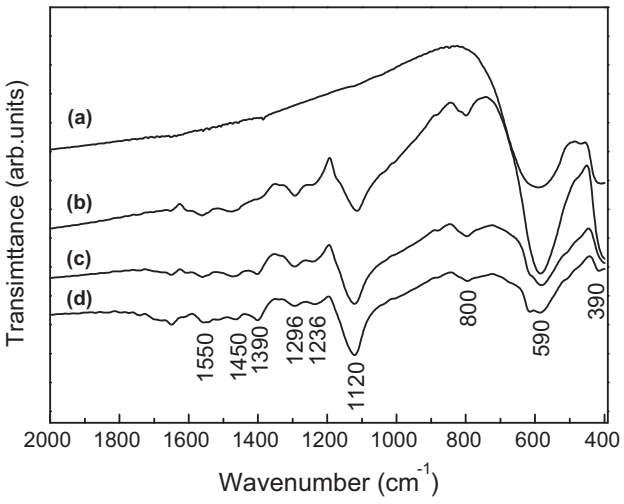


**Fig. 2.** FTIR spectra of (a) NiZn ferrite, (b) PANI/NiZn ferrite-1, (c) PANI/NiZn ferrite-2 and (d) PANI/NiZn ferrite-3 composites.