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High-Frequency Absorbing Performances of Carbonyl Iron/MnZn Ferrite/PVC Polymer Composites

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We have prepared composite materials with a mixture of carbonyl iron (CI) and manganese-zinc ferrite (MnZn) as filler and polyvinylchloride (PVC) as polymer matrix, and then electromagnetic wave absorption properties of CI/MnZn/PVC composites have been studied in the frequency range from 10 MHz to 6.5 GHz. Increasing carbonyl iron loading (to the detriment of MnZn ferrite) results in the rise of permeability and magnetic resonance loss (especially in GHz frequency range) which leads to the shift of absorption peak towards lower frequency and to the decrease of matching thickness. On the contrary, increasing MnZn ferrite loading (to the detriment of carbonyl iron) results in higher absorption bandwidth. The obtained results indicate that the prepared flexible composites may be useful as thin and/or wideband microwave absorbers.

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1. Introduction

With the rapid advances and broad implementation of radio communication and computer technology, and with the ongoing miniaturization of electronic equipments, there is an increased functionality of high-frequency absorbing materials that can provide effective shielding of electromagnetic interferences (EMI), especially in microwave frequency range (over 500 MHz). High-frequency absorbers with defined absorption characteristics have been developed to eliminate EMI, and composites of soft magnetic and insulating materials are particularly focused with much interest in this sphere [1, 2]. CI and MnZn are magnetic materials which exhibit excellent electromagnetic wave absorption properties and many studies on CI or MnZn composites as shielding materials have been published [3–7]. Polymer-based composites have low density and can provide connectivity among the fillers and hence are best suitable for shielding applications. PVC polymer provides flexibility to the composite in addition to its appropriate chemical and dielectric properties and is therefore chosen as the matrix. For the present investigation, the combined CI/MnZn magnetic filler were added into the PVC matrix to prepare CI/MnZn/PVC composite samples with different filler volume fractions and the electromagnetic wave absorption properties of these composites were studied to explore the potential application of these composites.

2. Experimental

The composite samples were prepared by mixing commercially available carbonyl iron — type EN, hard grade, containing 97.5% of iron, 0.9% of carbon, 1.0% of nitrogen and 0.5% of oxygen (BASF company, Germany) and MnZn ferrite with composition $Mn_{0.52}Zn_{0.43}Fe_{2.05}O_4$ (Pramet Šumperk company, Czech Republic) in different filler volume ratios of 1:0, 0.75:0.25, 0.5:0.5, 0.25:0.75, and 0:1 in polyvinylchloride (PVC) polymeric matrix. Then, hot pressing was carried out. Blend of metal/ferrite filler with PVC was plasticized and fired at 135 °C and 5 MPa. Curing time was 30 min. The total volume concentration of combined CI/MnZn filler in composites was kept at 50 vol.%. The pressed composites were prepared in the form of rings with an outer diameter of 7 mm, an inner diameter of 3.05 mm and a height of 2–3 mm.

The microstructural aspects such as surface morphology, particle size and chemical composition of the carbonyl iron and MnZn ferrite powders were estimated using a scanning electron microscope (JEOL JSM-7500F).

Variation of complex (relative) permeability $\mu = \mu' - j\mu''$ versus frequency f in the range from 10 MHz to 6.5 GHz was studied by means of a combined impedance/network analysis method using a vector network analyser (Keysight E5063A). During impedance measurements (carried out in the range 10 MHz–1 GHz), a ring sample was inserted into a coaxial short-circuit sample holder (16454A) and the complex permeability was evaluated from measured complex impedances [8]: $\mu = \mu' - j\mu'' = 1 + (Z - Z_{air})/(jh\mu_0 f \ln(D_1/D_2))$, where Z and Z_{air} are the input complex impedances of the 16454A holder with and without a toroidal sample, respectively, h is the height of the sample, $\mu_0 = 4\pi \times 10^{-7}$ H/m is the permeability of free space, f is the frequency, and D_1 and D_2 are the outer and inner diameters of the sample. Network analysis method was performed in microwave band (100 MHz–6.5 GHz) using standard 7 mm coaxial transmission line holder and the complex permeability was calculated from measured reflection and transmission parameters.

Electromagnetic wave absorption parameters (derived from the frequency dependences of return loss RL) such as the matching thickness d_m, matching frequency f_m,

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bandwidth Δf for RL ≤ -20 dB and the minimum of return loss RL$_{min}$ were obtained by numerical simulations in Mathcad software.

3. Results and discussion

SEM images of carbonyl iron are shown in Fig. 1 (a — surface morphology of particle and b — structure of particle). It can be seen that the carbonyl iron particles have spherical shape with structure similar to onion bulb. The particle size varies in the interval 1–5 μm. SEM image of spinel MnZn ferrite is depicted in Fig. 1c. The MnZn ferrite particles have irregular (polyhedral) shape with the size range of 10–80 μm.

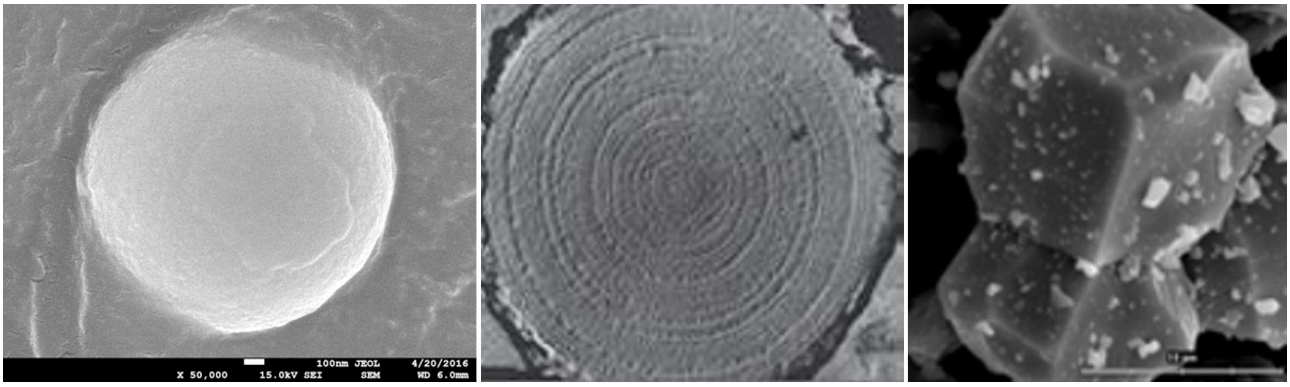

Fig. 1. SEM photographs of (a) carbonyl iron, (b) its microstructure, and (c) MnZn ferrite.

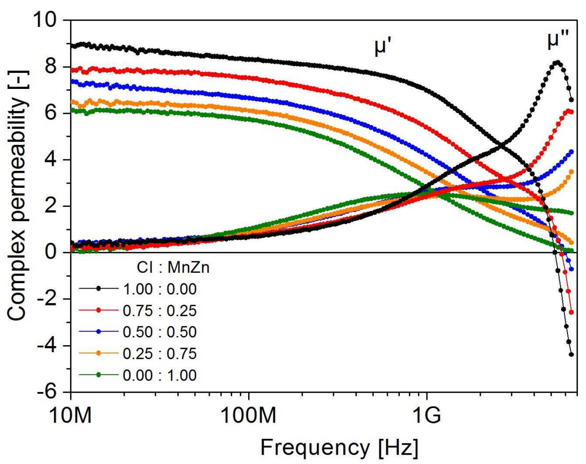

Fig. 2. Frequency dependences of real and imaginary parts of complex (relative) permeability for prepared CI/MnZn/PVC composites with different filler volume ratios.

Figure 2 presents the variation of complex (relative) permeability $\mu = \mu' - j\mu''$ with frequency f for fabricated composite samples. The measured responses showed a dispersive character of $\mu - f$ dependences. The frequency dispersion of complex permeability changed continuously with the change of filler volume ratio between two types of fillers: from relaxation type observed in two-phase MnZn/PVC composite to strong resonance type observed in two-phase CI/PVC sample. The value of μ' increased from about 6 for MnZn/PVC sample to about 9 for CI/PVC one. The obtained frequency dispersion of μ is principally caused by the domain wall resonance (vibrating Bloch's walls due to the force acting on walls in the presence of high frequency external ac electromagnetic field), the natural ferromagnetic and/or ferrimagnetic resonance (also known as the spin precession resonance: the forced precession of magnetization vectors in domains due to the presence of effective magnetic anisotropy), and the relaxation of magnetization [8–10]. Due to a low resistivity of carbonyl iron ($\approx 10^{-7}$ Ωm) and MnZn ferrite (≈ 1 Ωm), also the eddy current effect could influence the measured permeability spectra. For all samples, the real part μ' of μ went down and the imaginary part μ'' of μ increased with growing frequency f. The maximum in μ''-f dependence for MnZn/PVC composite at about 900 MHz is also present for composite samples containing carbonyl iron. On the other hand, the second sharp maximum localised above 5 GHz was observed in samples containing only carbonyl iron. These maxima correspond to critical (resonance) frequency f_r and are caused by mentioned resonance/relaxation phenomena. In addition, the variation of filler volume ratio in composites changed the magnetocrystalline anisotropy and hence also the values of μ and f_r [10].

High-frequency single-layer electromagnetic wave absorption characteristics of fabricated composites were evaluated by numerical calculation of return loss [8, 9]: RL $= 20\log|(\mathrm{j}\mu 2\pi \mathrm{fd/c} - 1)/(\mathrm{j}\mu 2\pi \mathrm{fd/c} + 1)|$, with c the velocity of light, and d the thickness of the single-layer absorber (backed by a metal sheet). The equation for RL meets the condition $d \ll \lambda$, where λ is the wavelength of the incident electromagnetic wave. The absorber (i.e. composite) absorbs the maximum of the energy of the incident electromagnetic wave when $j\mu 2\pi f d/c = 1$. The maximum absorption is then accomplished at a matching thickness $d = d_m = c/[2\pi f_m \mu''(f_m)]$, matching frequency

$f = f_m$, and minimum return loss RL_{min}. Note that $\mu''(f_m)$ indicates the value of μ'' at $f = f_m$.

Figure 3 shows the frequency dependences of return loss RL for fabricated composites. Numerically calculated absorption parameters such as matching thickness d_m, matching frequency f_m, the bandwidth Δf for RL ≤ -20 dB and the minimum of return loss (also known as absorption peak) RL_{min} are summarized in Table I. One may note that with the configuration change from two-phase MnZn/PVC composite sample to CI/PVC one, the matching thickness d_m, the matching frequency f_m and the bandwidth Δf for RL ≤ -20 dB decreased while the minimum of return loss RL_{min} increased. It is evident that increase of carbonyl iron filler loading (to the detriment of MnZn ferrite filler) in composite structure has a major influence on the decrease of matching thickness i.e. the thickness of the absorber. On the other hand, increasing MnZn filler loading (to the detriment of carbonyl iron filler) leads to the rise of absorption bandwidth.

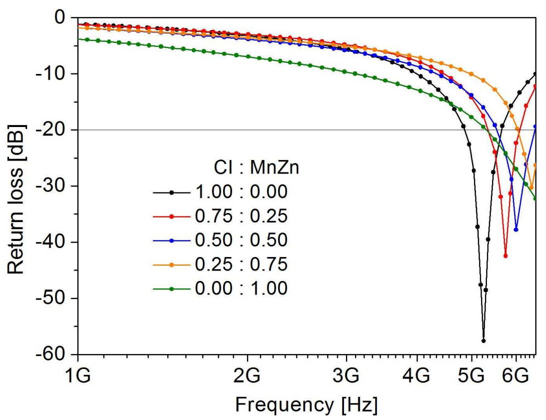

Fig. 3. Frequency dependences of return loss for prepared CI/MnZn/PVC composites with different filler volume ratios.

TABLE I

Absorption parameters for fabricated CI/MnZn/PVC composites of different filler volume ratio CI:MnZn.

Ratio	d_m [mm]	f_m [GHz]	Δf [MHz] (RL≤ -20 dB)	RL_{min} [dB]
1.00:0.00	1.38	5.25	690	−57.61
0.75:0.25	1.44	5.74	750	−42.43
0.50:0.50	1.96	5.99	970	−37.80
0.25:0.75	2.08	6.39	> 1000	−30.28
0.00:1.00	4.32	6.50	> 1000	—

The reason for f_m (and also d_m) variation in three-phase metal/ferrite/polymer composites according to volume ratio of the two-phase metal/ferrite magnetic filler may be found in the basic principles for designing electromagnetic wave absorbers. The relationship between f_m, d_m, and μ', μ'' can be expressed by the following formula [9]: $d_m f_m \approx (\mu\prime)^{-1/2}[4(1 + \tan^2(\mu''/\mu\prime))]^{-1}$. This formula states that $d_m f_m$ value is affected (mainly) by μ' and μ''. The variation of μ' and μ'' with the change of filler volume ratio of two-phase CI/MnZn filler in CI/MnZn/PVC composites has been caused mainly by the modification of magnetocrystalline anisotropy: d_m and f_m decreased with the configuration change from MnZn/PVC composite to CI/PVC one due to the change of f_r. The fabricated composites show strong microwave absorption in a wide frequency range at small thickness.

4. Conclusions

A detailed study was carried out on the electromagnetic wave absorption properties of metal/ferrite/polymer composites with carbonyl iron and manganese-zinc ferrite as two-phase filler and polyvinylchloride as matrix in the broad frequency range (10 MHz–6.5 GHz). The obtained results showed that the high-frequency absorbing properties are influenced by the strong correlation between return loss and complex permeability of the composites. The absorption peak shifted to the low-frequency region and simultaneously the matching thickness decreases with increasing carbonyl iron volume loading. On the other hand, the absorption bandwidth increases with the rise of MnZn ferrite filler in composite. The investigated composite materials make it possible to design thin, broadband and flexible microwave absorbers.

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