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Permeability, Permittivity and EM-wave Absorption Properties of Polymer Composites Filled with MnZn Ferrite and Carbon Black

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Composite materials based on manganese-zinc ferrite (MnZn) and carbon black (CB) as fillers, and natural butadiene rubber (NBR) as a polymeric non-magnetic matrix have been prepared by means of a hot-pressing route. Frequency dispersion of complex (relative) permeability μ and permittivity ε was measured on composite samples using combined impedance/transmission line method and is ascribed to magnetic and dielectric loss in association with domain wall resonance, spin precession resonance, and interfacial polarization. Electromagnetic wave absorption characteristics of composites (such as return loss RL, matching thickness d_m, matching frequency f_m, bandwidth Δf for RL ≤ -20 dB, and the minimum of return loss $\mathrm{RL_{min}}$) were evaluated through numerical simulations depending on the relation between material parameters (μ, ε) and the content of hybrid MnZn/CB filler. The synthesized composites appear to be excellent electromagnetic shields within the frequency interval 300 MHz–2 GHz.

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PACS/topics: composite, ferrite, carbon black, permeability, permittivity, return loss

1. Introduction

Because of the fast expansion of modern electronic wireless communication and information technology systems, and due to an increase of electronic devices in printed circuit boards emitting unwanted electromagnetic noise, the designers and engineers of these systems and circuits are faced a problem of electromagnetic interference (EMI). To solve this problem, magneto-dielectric composite materials consisting of magneto-dielectric fillers (such as soft ferrites) and non-magnetic matrices (such as polymers) have been used. These materials can be good electromagnetic shields if they prevent both incoming and outgoing EMI noise. One can assure that with appropriate frequency dispersion of both the complex permeability and the complex permittivity at a desired frequency range. Permeability dispersion of composite is determined by magnetic filler only, while the permittivity is given by all composite constituents (filler and matrix). Electrical conductivity of constituents also may have a direct impact on the increase in permittivity of composite. The electrically conductive polymers can be used as matrices to enhance permittivity of composites, but these polymers are expensive and therefore less suitable. Probably the best choice is to embed a small amount of conductive filler such as carbon black (CB) into a non-conductive polymer matrix such as rubber. CB nanoparticles have the graphitic crystallite structure resulting in a good electrical conductivity ($\sigma_{DC} \approx 5$–200 S/m), and can also serve as a rubber reinforcement. In addition, the dielectric character of CB may contribute to higher electromagnetic wave (EM-wave) absorbing ability [1, 2]. Herein, MnZn ferrite and carbon black as powder fillers have been added into the natural butadiene rubber (NBR) polymer matrix to fabricate MnZn/CB/NBR composite materials. The magnetic, dielectric and high-frequency EM-wave absorbing performances of composite materials have been investigated as well.

2. Experimental

In this study, MnZn/CB/NBR composite materials based on manganese-zinc (MnZn) ferrite with composition $\approx \mathrm{Mn_{0.68}Zn_{0.24}Fe_{2.08}O_4}$ and carbon black (CB) as fillers, and natural butadiene rubber (NBR) as a polymeric non-magnetic matrix have been synthesized. The compound of rubber batch with the constant content of carbon black (20 phr) and variable content of MnZn ferrite (0–500 phr in steps of 100 phr) was obtained by hot-mixing at 90 °C. Then, the cross-linking of the compound was carried out for the optimum vulcanization time, at 160 °C and a pressure value of 15 MPa using a hydraulic press. The composite samples were cut from final rubber sheets (with size 150 mm ×150 mm)

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into the rings (with an outer diameter of 7 mm, an inner diameter of 3.05 mm and a thickness of 2 mm), and into discs (with an outer diameter of 20 mm and a thickness of 2 mm). The composite samples throughout the text and in figures are designated according to the content of MnZn ferrite, i.e., 500 phr, 400 phr, 300 phr, 200 phr, 100 phr, and 0 phr. The surface morphology and microstructure of composite materials were observed using scanning electron microscope JEOL JSM-7500F. The frequency dependences of complex permeability and permittivity of prepared composite materials have been measured in the range 1–3 GHz by means of a combined impedance/transmission line method using a vector network analyser (Keysight E5063A). The DC electrical conductivity σ_{DC} of fillers (MnZn ferrite and carbon black) was determined using standard two-probe method. Based on frequency responses of material parameters, the monolayer EM-wave absorption characteristics (such as return loss RL, matching thickness d_m, matching frequency f_m, bandwidth Δf for $\mathrm{RL} \le -20$ dB, and the minimum of return loss $\mathrm{RL}_{\mathrm{min}}$) were computed from return loss RL. It is defined as follows:

$$\mathrm{RL} = 20 \log \left| \frac{Z_{\mathrm{in}} - 1}{Z_{\mathrm{in}} + 1} \right|,$$

where

$$Z_{\mathrm{in}} = \sqrt{\frac{\mu}{\varepsilon}} \tanh \left(\mathrm{i} \frac{\omega d}{c} (\mu \varepsilon) \right)$$

is the normalized value of input complex impedance of the absorber, ω is the angular frequency, d is the thickness of the monolayer absorber (backed by a metal sheet), and c is the velocity of light in free space. The composite absorbs the maximum of the energy if $Z_{\mathrm{in}} = 1$ which is reached at a matching thickness $d = d_m$, matching frequency $f = f_m$, and minimum return loss $\mathrm{RL} = \mathrm{RL}_{\mathrm{min}}$.

3. Results and discussion

SEM photographs of MnZn ferrite and carbon black powders can be found in Fig. 1. One may notice that the shape of particles is irregular (polyhedral and/or prismatic). The particle size of MnZn ferrite varies in the range of 0–80 μm, while that of carbon black varies in the interval 20–50 nm.

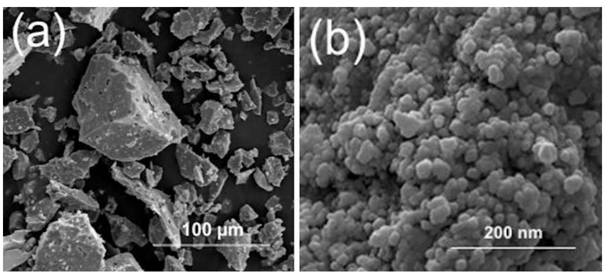

Fig. 1. SEM images of (a) MnZn ferrite and (b) carbon black.

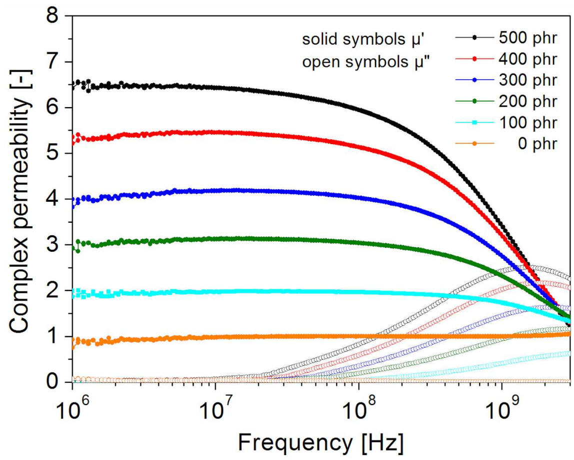

Fig. 2. Frequency dependences of real and imaginary parts of complex (relative) permeability for prepared MnZn/CB/PVC composite materials.

The frequency responses of real μ' and imaginary μ'' parts of complex (relative) permeability $\mu = \mu' - \mathrm{i}\mu''$ as a function of frequency f (Hz) for fabricated MnZn/CB/NBR composites can be found in Fig. 2. The parameter of curves is MnZn ferrite filler content (in "phr" units). The low-frequency value of real part μ' of permeability at $f = 1$ MHz decreases starting from 6.53 (for 500 phr composite sample) to about 0.99 (for 0 phr composite sample). The vertex of imaginary part μ'' goes down, and simultaneously the resonance frequency f_{res}, at which this vertex occurs, shifts towards a higher frequency region with the change of MnZn ferrite filler content in composite samples from 500 to 0 phr. Moreover, the frequency response of real part μ' stagnates up to around 200 MHz, and then reduces to a low value. The highest drop of μ' with frequency behind 200 MHz has been observed in case of 500 phr composite sample. The 0 phr composite sample did not show any frequency response of any part of μ because of its non-magnetic nature. The main mechanisms determining the μ of composites with magnetic filler comprise hysteresis loss, domain wall movement, spin precession, and eddy current effect [3]. In our case, the hysteresis loss due to the irreversible magnetization can be neglected as the composites were tested in Rayleigh region (of low magnetic fields), and at high frequencies. The domain wall movement and the spin precession are usually coupled with resonance phenomena in the permeability spectrum, namely the domain wall and the spin precession (or natural ferromagnetic) resonance. As shown in Fig. 2, the observed peaks in μ''–f dependencies correspond to the spin precession resonance only as the domain walls are unable to keep pace with ac electromagnetic field over about 10^8 Hz. Eddy current effect could also contribute to permeability loss due to high DC electrical conductivity σ_{DC} and low particle size of fillers (MnZn ferrite had $\sigma_{\mathrm{DC}} \approx 0.3$ S/m, while CB had $\sigma_{\mathrm{DC}} \approx 107$ S/m). The eddy currents cause the decrease in effective volume conducing to the μ thanks to the drop of the skin depth

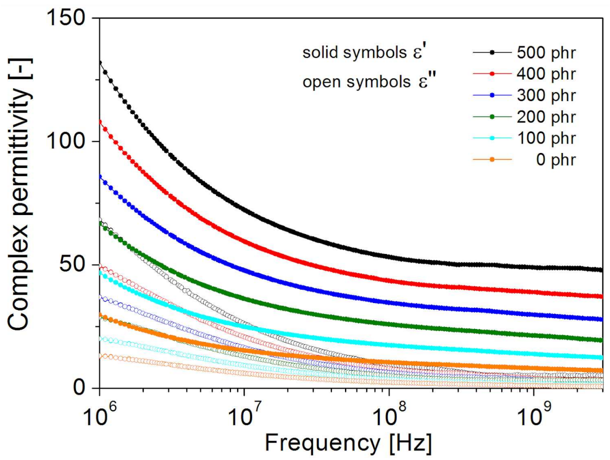

Fig. 3. Frequency dependences of real and imaginary parts of complex (relative) permittivity for prepared MnZn/CB/PVC composite materials.

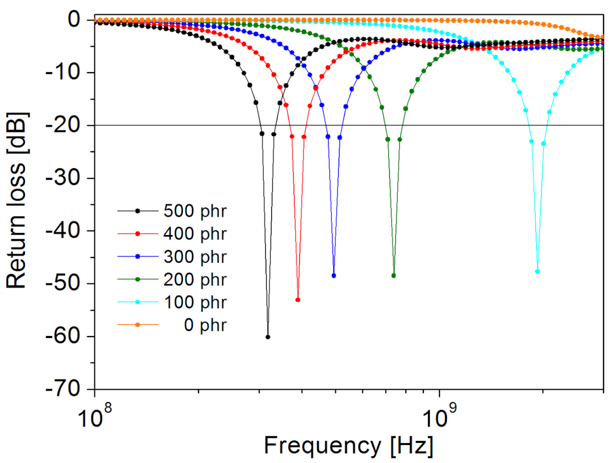

Fig. 4. Frequency dependences of return loss for prepared MnZn/CB/PVC composite materials.

($\delta \approx \sqrt{1/\pi f \sigma_{\mathrm{DC}} \mu_0 \mu'}$ with μ_0 as the permeability of free space). Then the reduction of μ happens behind the frequency, at which δ starts to be smaller than the sample thickness (≈ 2 mm).

Figure 3 depicts the frequency dependences of real ε' and imaginary ε'' parts of complex (relative) permittivity $\varepsilon = \varepsilon' - \mathrm{i}\varepsilon''$ for prepared composite materials. The steeply decrease of ε' is observed at frequencies up to about 10 MHz, and then ε' settles on a constant value. The same trend can be also observed in ε''-f dependencies. This initial decrease of ε' with frequency may be due to semiconducting character of MnZn ferrite and conducting character of CB used as fillers in prepared composites. Note that when the content of MnZn ferrite filler in composites changes, ε' also drops at $f = 1$ MHz: from $\varepsilon' \approx 132$ for 500 phr composite to $\varepsilon' \approx 29$ for 0 phr composite. The observed changes in the frequency responses of complex permittivity may be attributed to various types of polarization mechanisms arising in filler (mainly interfacial polarization brought about by space charge accumulated at boundaries of filler particles dispersed in matrix), as well as polymeric matrix because of their dielectric character [4].

TABLE I

Absorption parameters for prepared MnZn/CB/PVC composites.

MnZn ferrite content in composite [phr]	d_m [mm]	f_m [MHz]	Δf [MHz] for RL ≤ -20 dB	$\mathrm{RL}_{\min}$ [dB]
500	14.27	319	21.3	−60.12
400	14.08	390	42.2	−53.10
300	14.33	495	53.6	−48.50
200	13.38	739	73.1	−48.52
100	8.475	1931	157.5	−47.71
0	–	–	–	–

Figure 4 presents the frequency dependences of return loss RL [dB] for prepared composite materials. Table I summarizes the selected EM-wave absorption parameters: matching thickness d_m of the absorber, matching frequency f_m, bandwidth Δf for RL ≤ -20 dB, and a minimum value of return loss $\mathrm{RL}_{\min}$ at $f = f_m$. With decrease of the content of MnZn ferrite filler in composites from 500 to 100 phr, one can see that the values of f_m, as well as Δf increase in contrast to the values of d_m and $\mathrm{RL}_{\min}$. The obtained results are direct consequence of composite nature: the values of f_m and Δf increase due to the magnetic dilution of composite structure (with the decrease of MnZn ferrite filler content). This, in turns, leaded to the alternation of magnetic (μ) and dielectric (ε) parameters, and therefore also absorption properties (RL, d_m, f_m, Δf, $\mathrm{RL}_{\min}$) of designed absorbers. The computed values of absorption parameters indicate that the prepared composite materials can be thought as suitable candidates for electromagnetic field shielding applications at frequencies above 300 MHz.

4. Conclusions

We have researched the frequency responses of material parameters such as complex permeability and permittivity of polymer-based composited with NBR as matrix, and MnZn ferrite and carbon black as fillers in the frequency range from 1 MHz to 3 GHz. The permeability showed strong while permittivity weak dispersion character. On the basis of material parameters responses we have calculated the return loss and also selected electromagnetic absorption parameters. The absorption peak (the minimum of return loss) shifted towards higher frequencies with the drop of MnZn ferrite in composites. The synthesized composites may be utilized as elastomeric electromagnetic field shields.

Acknowledgments

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References

[1] Y. Pang, Y. Li, J. Wang, M. Yan, S. Qu, S. Xia, Z. Xu, *Carbon* **147**, 112 (2019).

[2] S. Sankaran, K. Deshmukh, M.B. Ahamed, S.K.K. Pasha, *Compos. Part A* **114**, 49 (2018).

[3] R. Dosoudil, M. Ušáková, A. Grusková, J. Sláma, *IEEE Trans. Magn.* **50**, 2800204 (2014).

[4] S.Y. Tong, J.M. Wu, M.J. Tung, W.S. Ko, Y.T. Huang, Y.P. Wang, *J. Alloys Compd.* **525**, 143 (2012).