

Physical Characterization of Nano-ferrites Modified Epoxy Resins

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Ferrites are generally used to obtain soft magnets for domestic or industrial applications but their use in this direction had generated an increasing interest in modifying the polymer properties by dispersing in their volume certain amounts of these ceramic compounds. Of course one issue of each researcher is to find a way or a technique to orientate the ferrites particles inside the polymer matrix to obtain structures able to respond to application of an external magnetic field. The use of ferrites nano-sized particles is facilitating their uniform distribution inside the polymer and, because of the viscous properties of pre-polymer mixture, is avoiding their aggregation. One way to create oriented distributions of the nano-particles is to use external magnetic fields during polymerization such as, at the end of process, they will be kept in fixed position inside the polymer network. The current study is about electrical properties induced by the presence of nano-sized strontium ferrite and barium ferrite in an epoxy matrix. Three types of epoxy resins had been used with 5% weight ratio of each type of ferrite and 10% weight ratio when both ferrites were used to modify the properties of the same polymer matrix. Electric conductivity had been studied by two methods – one on steady-state regime and one in variable regime. Using the variable measurement of electromagnetic properties the dielectric permittivity and the magnetic permeability were also determined.

KEY WORDS: epoxy resin, nano-sized ferrites, electromagnetic properties

A composite material is made by combining two or more materials – often having very different properties. Both constituents have to be present in reasonable proportions, say greater than 5% [1]. The two materials work together to give the composite unique properties [2], [3]. Most composites in industrial use are based on polymeric matrices, both thermosets and thermoplastics. In this regard the use of thermoset polymer (especially epoxy resins) is much easier due to their way of forming namely by mixing two liquids (in determined ratios) that will transform into a gel and then into a solid. Generally the polymerization of the resin is determined by the presence of the hardener and this fact is offering the greatest advantage of using this polymers – the possibility of dispersing a powder into the resin prior of the hardener adding. Ferrites have high dielectric constants which makes them very useful for microwave applications. They remain the best magnetic material and cannot be replaced by any other magnetic elements because they are inexpensive, more stable and have a wide range of technological applications in transformer cores, high quality filters, radio wave circuits and operating devices [4]. The electrical conductivity and dielectric behavior of ferrites markedly depend on the sintering time and

temperature, chemical composition, preparation conditions, and the quantity and type of additives [5].

Strontium ferrite ($\text{SrFe}_{12}\text{O}_{19}$), as an important member of hexa-ferrites, has higher saturation magnetization, coercivity and the Curie temperature because of high magneto-crystalline anisotropy compared to barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) [6-8].

The electric and dielectric properties of ferrites have been studied extensively, but the strontium ferrite and barium ferrite in an epoxy matrix have rarely been treated in the literature.

Experimental part

Three epoxy systems were chosen mostly because of their different bisphenol A content namely (E) Epiphen RE4020-DE 4020 (Bostik), (C) Epoxy Resin C (R&G GmbH Waldenbuch), and (H) Epoxy Resin HT-2 (R&G GmbH Waldenbuch). Ferrites used in this study are commercially available ferrite: Strontium ferrite ($\text{SrFe}_{12}\text{O}_{19}$) and barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$). The structural characteristics of ferromagnetic additives are given in table 1. Ferrites have been considered as highly important electronic materials for more than half a century [9].

Table 1
THE STRUCTURAL CHARACTERISTICS OF FERROMAGNETIC ADDITIVES

Characteristics	Strontium ferrite	Barium ferrite
Chemical formula	($\text{SrFe}_{12}\text{O}_{19}$)	($\text{BaFe}_{12}\text{O}_{19}$)
Colour	Brown - Black	Brown - Black
Purity [%]	99,8	97
Form	Powder	Powder
Crystalline network	Hexagonal	Hexagonal
Particle size [nm]	< 100	< 100
Melting point [°C]	> 450	> 450
Density [g/mL] at 25°C	5,18	5,11
Specific weight [g/mol]	1,1111.46	1,111.46

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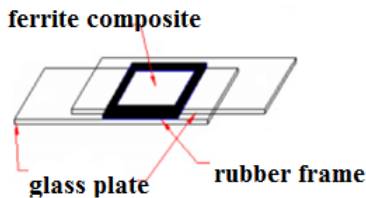


Fig.1. Forming technique

Ferrite composite materials were made by the following process: (1) mold preparation; (2) mixing ferrite particles with resin; (3) casting the mixture into the mold. Materials were poured in plates and cylindrical specimens. For casting into plates, two glass plates of 170 x 170 mm, spaced with a rubber frame of 5 mm (fig.1) were used. The same arrangement was used to form materials in external magnetic field by placing permanent magnets (Neodymium) on two parallel edges of the glass mould. In the case of casting into cylindrical specimens polypropylene tubes with a diameter of 8 mm and a length of 200 mm were used.

In order to determine the electromagnetic properties of composite materials, an RLC meter Protek9216A type was used. Values of working frequency were processed and used to determine the electromagnetic properties of evaluated composites. The measurements were carried out on plates, in five different points, both on the surface of the material (when the signal is applied between the active electrode and the guard electrode) and the volume of the material (when the signal is applied between the active electrode and the guard electrode). Determination of electrical conductivity of composite materials consisted of calculating the electrical conductivity [10]. As any polymer is an electric insulator the electric conductivity

was evaluated via electric resistance measurement using an insulation analyzer TerraOhmMeter, model MI2077 5 kV [11].

Results and discussions

To facilitate the results presentation the code designation for the formed materials is as follows: C1, E1, H1- epoxy resin with 5% (weight ratio) strontium ferrite; C2, E2, H2- epoxy resin with 5% barium ferrite; C3, E3, H3- epoxy resin with 5% strontium and 5% barium ferrite (10% weight ratio). Further will be exhibited relative variations of the studied parameters. All the results are average values of the values obtained from at least five measurements.

Figure 2 shows relative electric conductivity of all samples containing C, E and H epoxy resin and the three mentioned amounts of ferrites. As it can be seen for C resin, the best relative electric conductivity is at 10 kHz for all reported ferrite based composites. For epoxy resin E and H, the relative electric conductivity is very low. Since all the presented values are relative to the value of electric conductivity of epoxy resin results that adding nano-sized ferrites into the polymer matrix leads to a decrease of the electrical conductivity (measured on variable measurement signal). Although for relative electric permittivity (fig. 3) the same remark is not available. Here were obtained good values for all three resins at 1kHz with differences induced by the resin (C and H having the same behaviour). At the other two frequencies of measurement signal the materials dielectric behaviour is different being influenced both by the matrix and the modifying agent.

Figure 4 shows the variation of relative magnetic permeability for all composites. High variations from the

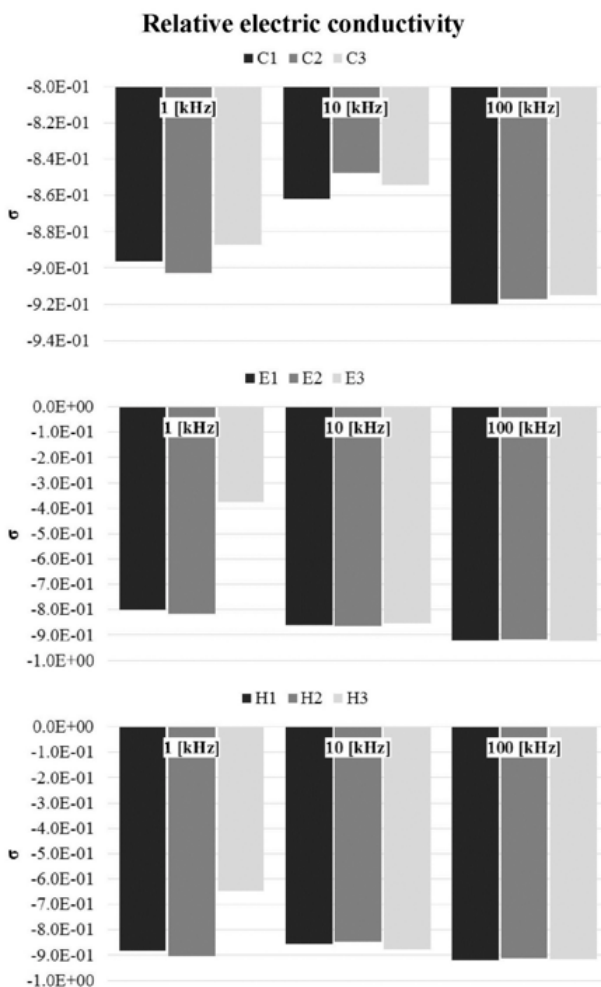


Fig.2. Relative electric conductivity - electro-technique method measurement

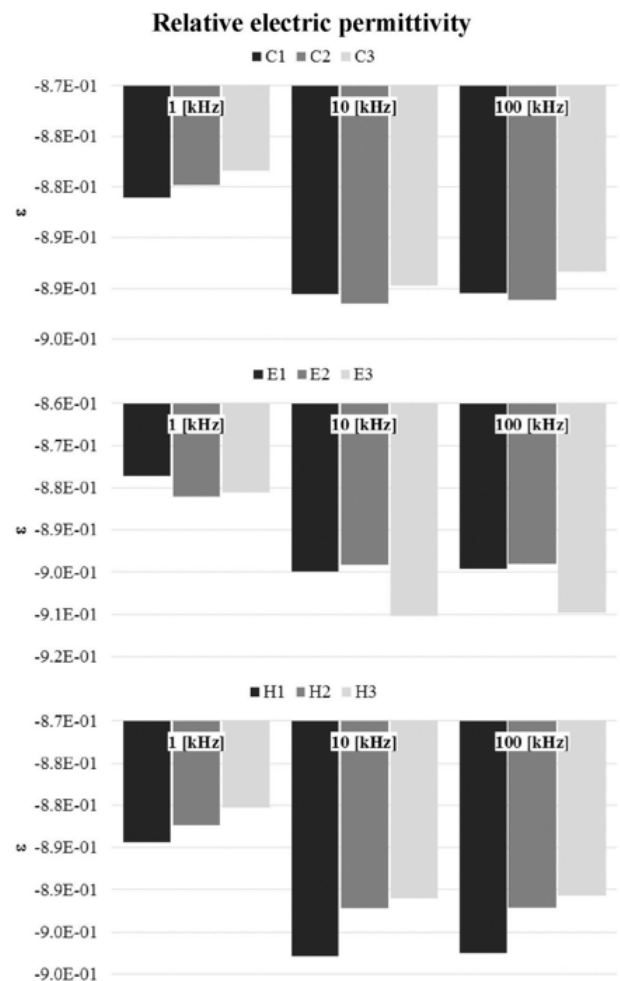


Fig.3. Relative dielectric permittivity - electro-technique method measurement

Table 2
ELECTRIC CONDUCTIVITY OF MATERIALS σ [S/m]

	Plate	Cylindrical		Plate	Cylindrical		Plate	Cylindrical
C	4.79E-06	4.78E-06	E	4.89E-06	4.58E-06	H	4.56E-06	4.26E-06
C1	4.96E-06	4.81E-06	E1	4.70E-06	4.47E-06	H1	4.45E-06	4.40E-06
C2	4.77E-06	5.01E-06	E2	4.92E-06	4.66E-06	H2	4.51E-06	4.90E-06
C3	4.73E-06	4.82E-06	E3	4.68E-06	4.20E-06	H3	4.57E-06	4.63E-06

Table 3
ELECTRIC CONDUCTIVITY OF EXTERNAL MAGNETIC MATERIALS σ [S/m]

E	4,58E-06		C	4,78E-06		H	4,26E-06	
	PF	AF		PF	AF		PF	AF
E1	4.50E-06	3.75E-06	C1	4.21E-06	3.61E-06	H1	4.44E-06	3.64E-06
E2	4.65E-06	3.69E-06	C2	4.63E-06	3.84E-06	H2	4.58E-06	3.89E-06
E3	4.53E-06	3.90E-06	C3	4.38E-06	3.94E-06	H3	4.15E-06	3.57E-06

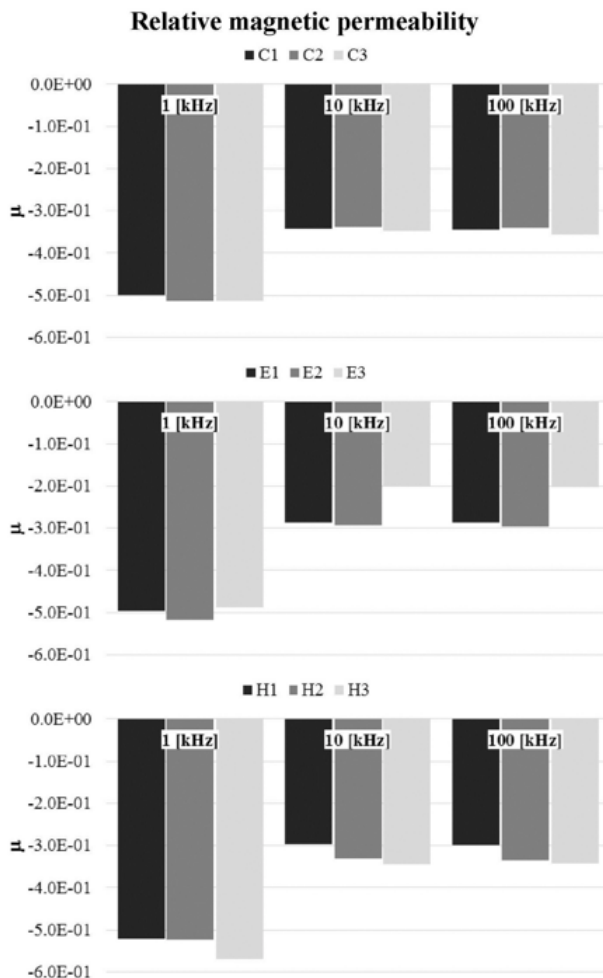


Fig.4. Relative magnetic permeability - electro-technique method measurement

value of magnetic permeability of epoxy resin are noticeable at 1kHz frequency while at the other two values of the frequency the behaviour of materials is the same.

Regarding the electrical conductivity measured by means of insulation resistance method the results are presented in table 2 and table 3. The measurement method had been applied both for cylindrical and plate samples and the results are close (table 2). Regarding the electrical conductivity for external magnetic field formed materials (table 3) there are some differences that can be considered as effects of ferrites presence, especially on antiparallel measurement relative to the magnetic field direction.

Conclusions

The composites had lower relative electric conductivity than pure epoxy resin excepting for 10kHz. All samples containing the same amount of ferrite particles showed distinct behaviour for the three different used epoxy resins.

Meanwhile, the relative electric permittivity of all epoxy resin composites showed a significant improvement for 1kHz and this property is to be taken into account when materials have to be designed. There are not spectacular modifications regarding the electromagnetic properties when 5% weight ratios of ferrites are dispersed into the polymers. However, it is expected that the presence of ferrite particles to determine a better tribological behaviour of materials and, perhaps a better mechanical behaviour. Thermal properties of materials have to be studied and they could offer an opportunity to verify the rule of mixtures for nano-sized particles (taking into account the relatively high concentration of ferrites).

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References

- MATTHEWS, F.L., RAWLINGS, R.D., Compo site Materials: Engineering and Science, Woodhead Publishing Limited, ISBN 978-1-85573-473-9, 2008.
- *** Composite materials -Index 4.3.1, Advancing the Chemical Sciences, pp.1-3.
- BARBERO, E.J., Introduction to Composite Materials Design, Second Edition, CRC Press, Taylor and Francis Group, ISBN 978-1-4200-7915-9, 2011.
- J. KULIKOWSKI J. MAGN., Mater. 41, 1986, 56.
- M.A. EL HITI, Dielectric behavior and ac electrical conductivity of Zn-substituted Ni-Mg ferrites, Journal of Magnetism and Magnetic Materials 164, 1996, pp.187- 196.
- LIU, J.R., HONGA, R.Y., FENG, W.G., BADAMI, D., WANG, Y.Q., Large-scale production of strontium ferrite by molten-salt-assisted coprecipitation, Powder Technology 262, 2014, pp.142-149.
- T.P. XIE, L.J. XU, C.L. LIU, S.H. DING, J. Y.W.L.WU, Synthesis and adsorption properties of high specific surface area strontium ferrite from industrial strontium residue, Vacuum 93, 2013, pp. 71-78.
- R.C. PULLAR, A.K. BHATTACHARYA, Crystallisation of hexagonalMferrites from a stoichiometric sol-gel precursor, without formation of the α -BaFe₂O₄ intermediate phase, Mater. Lett. 57, pp. 537-542.
- GHODAKE, U.R., CHAUDHARI, N.D., KAMBALE, R.C., PATIL, J.Y., SURYAVANSHI, S.S. Effect of Mn²⁺ substitution on structural, magnetic, electric and dielectric properties of Mg-Zn ferrites, Journal of Magnetism and Magnetic Materials, 2016, pp.60-68.
- CIRCIUMARU, A., BRIA, V., BIRSAN, I.G., ANDREI, G., DIMA, D., Electrical Properties of Filled Epoxy; High Fillers Concentration, Proceedings of The 12th International Conference on Mechanical Engineering, Bratislava, Slovakia, VI-12, 1-5, ISBN 978-80-277-2982-6, 13-14 november 2008.
- IULIA GRAUR, BRIA, V., CIRCIUMARU, A., BIRSAN, I. G., Electrical Properties of Ultra sonicated Epoxy Resin, The Annals of Dunarea de Jos, University of Galati, Fascicle IX, Metallurgy and Materials Science, nr.1, ISSN 1453-083X, 2015

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