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Reflectivity of Hybrid Microwave Absorbers Based on NiZn Ferrite and Carbon Black

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Abstract: *This study had as main objective to show that the adequate combination of magnetic and dielectric particles can improve the radar absorbing materials performance. For this, formulations of polyurethane resin loaded with carbon black and NiZn ferrite, with general composition MFe_2O_4, where M = Ni, Zn or both elements, homogenized by conventional mechanical mixture, were prepared. Reflectivity measurements of different coating formulations applied on aluminum flat plates (1.0 ± 0.1 mm-thickness) were performed using the Naval Research Laboratory arch technique, in the X-band frequency range. X-ray diffraction and magnetic susceptibility evolution analyses of the tested ferrite showed that this magnetic additive presents different phases. Attenuation values of ~4 dB (~60% of the wave absorption) for the polyurethane/carbon black/ferrite formulation, 49/1/50 in wt.%, respectively, were found. This low attenuation values (~4 dB) is attributed to the presence of different phases in the NiZn ferrite, as shown by both the X-ray pattern and the magnetic susceptibility analyses, and also to the thickness and the additives concentration used. As main result, this study shows that the adequate combination of carbon black and NiZn ferrite improves the processed radar absorbing materials performance due to the adequate adjustment of the impedance matching, which favors the microwave absorber-electromagnetic wave interaction.*

Keywords: *Coatings, Radar absorbing materials, RAM, NiZn ferrites, Carbon black.*

INTRODUCTION

As a consequence of the technological advances, the use of electromagnetic radiation in the microwave range has become intense in the last years. The telecommunication area has contributed intensively for this with a wide variety of commercially available artifacts, for example: cellular telephones, reception/transmission antennas and safety systems used in apparatus of aircraft, ships and vehicles in general. Then, the electromagnetic radiation noise level in different environment systems has increased continuously (Dias, 2000).

Aiming to eliminate or reduce the spurious electromagnetic radiation levels in different applications, the research and the development of radar absorbing materials (RAM) have increased. RAM makes use of energy-exchange properties of any specific dielectric and magnetic iron compounds which are able to transform the electromagnetic radiation in heat, in determined frequency bands. The attenuation of the electromagnetic wave can also be favored by the adequate combination of the phase canceling phenomenon by adjusting the electrical thickness of RAM (Faez *et al.*, 2005; Dias, *et al.*, 2005; Folgueras, *et al.*, 2007; Gama *et al.*, 2011; Pinto and Rezende, 2012). The following applications are among the most important for the RAM area: (a) to improve patterns of antennas, (b) to reduce undesirable reflections from objects and devices, (c) to cover inside test rooms (anechoic chambers) in order to achieve "free space" conditions for measurements of components and systems, (d) to reduce the radar cross section (RCS) of targets, (e) to achieve both "free space" termination and waveguide and coaxial termination (dummy loads), and (f) to improve the shielding of enclosures and containers when used as gasket materials.

In general, microwave absorbers are processed using different polymeric matrices. Among them, polyisoprene, neoprene or silicon rubber sheets or epoxy, phenolic or polyurethane (PU) coatings, loaded with carbon and/or iron particles and/or ferrites and/or conducting polymers can be

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cited. Usually, these materials need to attend the following requirements: low weight, good weatherability, good flexibility, minimum thickness, wide operational band with low reflection, extreme temperature capability, low outgassing and low cost (Dias *et al.*, 2005; Gama and Rezende, 2010).

RAM CHARACTERISTICS

Unique materials and electrical designs are used to attenuate or essentially trap radar signals. The radar transparency and the reflectivity are function not only of the target's shape, but also of the electrical and magnetic properties of the used material and the characteristics related to the incident radar signal. The low detection (LO) characteristics of a structure depend on the material properties, particularly their magnetic (permeability) and dielectric (permittivity) properties. Experimentally this study considers the cumulative effects of the losses, relating indirectly the absorption phenomena with the permittivity and permeability by reflectivity measurements, using the Naval Research Laboratory (NRL) arch technique. These physical parameters are given by Eq. 1 and 2 (Cullity, 1972; Lee, 1991; Dias, 2000):

$$\varepsilon_r = \varepsilon'_r + i\,\varepsilon''_r, \quad (1)$$

$$\mu_r = \mu'_r + i\,\mu''_r \quad (2)$$

where ε_r and μ_r are the relative permittivity and permeability, respectively, which are normalized by the values in the vacuum ε_0 e μ_0.

The real parts, ε'_r and μ'_r, are related to the stored energy, while the imaginary parts ε''_r and μ''_r to the losses. Considering that in dielectric absorbers the loss mechanisms are related to the material conductivity, σ, is convenient to express ε''_r, as (Cullity, 1972; Dias, 2000):

$$\varepsilon''_r = \sigma/\omega\varepsilon_0 \quad (3)$$

where ω is the radiation angular frequency.

The dielectric and magnetic loss tangents are given as Eq. 4 and 5, respectively:

$$\tan\delta = \varepsilon''_r/\varepsilon'_r \quad (4)$$

$$\tan\delta_m = \mu''_r/\mu'_r \quad (5)$$

The refraction index, *n,* is the relation between the wave number *k*, characteristic of the wave propagation within the material, and the wave number k_0 related to the wave propagation in vacuum, Eq. 6 (Cullity, 1972; Dias, 2000):

$$n = k/k_0 = \sqrt{\mu_r \varepsilon_r} \quad (6)$$

where $k_0 = \omega\sqrt{\mu_0\varepsilon_0}$

Likewise, the relative permittivity and permeability define the intrinsic impedance *Z* of the material, Eq. 7:

$$Z = Z_0\sqrt{\mu_r/\varepsilon_r} \quad (7)$$

where Z_0 is the impedance in vacuum, equal to 377 Ω.

The intrinsic impedance is the value 'observed' by the electromagnetic wave, that impinges the material surface in normal incidence. In practical applications a dielectric material is applied on a conductor surface and the normalized impedance η is given by Eq. 8 (Cullity, 1972; Dias, 2000):

$$\eta = \sqrt{\mu_r/\varepsilon_r}\, tg\left(-k_0 d\sqrt{\mu_r\varepsilon_r}\right) \quad (8)$$

where *d* is the dielectric layer thickness of material.

The normalized impedance may be used to calculate the reflection coefficient *R,* Eq. 9.

$$R = \frac{\eta - 1}{\eta + 1} \quad (9)$$

where *R* is a complex number between 0 and 1.

This reflection coefficient may also be expressed in decibels (dB), Eq. 10.

$$|I|(dB) = 20\log_{10}|R| \quad (10)$$

Thus, RAM technology includes the combination of materials in such way that |*R*| be as small as possible in a wide frequency range. This condition is usually attended satisfactorily by associating polymeric substrates loaded with microwave absorber centers, as microwave ferrites and/or conducting polymers and/or carbon/iron particles. When RAM atenuates simultaneously the magnetic and electric fields they are called hybrid absorbers (Dias, 2000; Rezende, *et al.*; 2004; Dias *et al.*, 2005; Martins *et al.*, 2006).

RAM efficiency can be available by measurements of free space radar reflection coefficient of flat samples using the NRL arch technique (Smith *et al.*, 1994; Dias, 2000). The reflectivity reduction of electromagnetic radiation, in dB, is correlated with the percentage of absorbed energy, as shown in Table 1 (Lee, 1991; Dias, 2000).

Table 1. Relationship between reflectivity reduction and the absorbed energy (Lee, 1991).

Reflectivity reduction, dB	Absorbed energy, %
0	0
-3	50
-10	90
-15	96.9
-20	99
-30	99.9
-40	99.99

Although permittivity and permeability measurements are useful to support the RAM processing, as shown previously in Eq. 6 to 8, the present study is based on reflectivity measurements, using the NRL arch technique. This type of measurements has a direct correlation with the permittivity, permeability and impedance parameters of the studied material, as depicted previously (Eq. 6 to 10). In this context, this work involves reflectivity measurements using the NRL arch technique, in the X-band frequency range, of different formulations of hybrid RAM based on NiZn ferrite and carbon black (CB) loaded in PU resin. Thus, the main objective of this study was to evaluate the mixture of dielectric (CB) and magnetic (NiZn ferrite) on the RAM performance.

EXPERIMENTAL

Coatings preparation

Formulations of a commercial polyester PU resin (two components: resin and catalyst, both colorless, at 1:1 rate) loaded with dielectric and magnetic fillers were prepared, as depicted in Table 2.

Table 2. The coating formulations prepared.

Formulation	Polyurethane matrix (wt.%)	Carbon black CB (wt.%)	Ferrite (wt.%)
1	100	0	0
2	99	1	0
3	84	1	15
4	69	1	30
5	54	1	45
6	49	1	50
7	50	0	50

Mechanical stirring at 500 rpm were used. The used dielectric filler was CB, type XC-72 with particle medium size of 12 nm and bulk density of 0.26 g/cm^3, supplied by Cabot Company, used as received (Cabot, 2004). The magnetic filler was NiZn ferrite, from IMAG Brazilian Industry of Ferrites, with nominal formula $Ni_{1-x}Zn_xO.Fe_2O_3$, with x = 0.50, density of 5.01 g/cm^3 and particle average size of 4.4 μm, determined by using a Sharples Micromerograph equipment. After mechanical stirring homogenization, the formulations were applied on aluminum (Al) flat surfaces (30 × 30 cm), positioned in the horizontal, using conventional painting techniques. The complete polymerization of coatings was obtained at 60ºC, for 40 minutes. The average thickness of coatings was 1.0 ± 0.1 mm.

Ferrites characterization

The crystallographic structure of the NiZn ferrite was determined by X-ray diffraction analyses, using a Philips diffractometer model PW 1830, operated at 40 kV tension and 20 mA current. The magnetic susceptibility evolution of the NiZn ferrite was carried out using thermal-magnetic equipment at apparent magnetic field of 40 A/m rms, at frequency of 333 Hz, in argon atmosphere.

Reflectivity measurements by using NRL arch technique

NRL arch technique measures the free space radar reflection coefficient of flat RAM. NRL arch was standardized by Naval Research Laboratory (United States), where the first measurement system was made (Dias, 2000; Rezende *et al.*, 2003). This system uses two calibrated horn type antennas in the microwave range. One antenna is connected to a microwave transmitter and the other one to a microwave receiver. The microwave energy launched from the transmitter horn travels and impinges the sample. The electromagnetic wave reflected from the sample surface travels and is collected by the receiver horn. The far field condition was taken into account in these measurements. Pyramidal absorber is placed around the NRL arch to eliminate undesirable spurious microwave energy that travels around the sample. Measurements were carried out at room temperature over the frequency range 8 to 12 GHz, using a polished Al flat plate as the reference material. The reference material reflectivity is considered as 100% of reflection (Knott *et al.*, 1993; Balanis, 1997; Dias, 2000). The reflectivity measurements were standardized using reference-absorbing materials purchased from Emerson & Cumming Inc. These absorbers consist of 2 to 20 mm-thickness PU foam plates, loaded with carbon particles (Jauman absorbers). These microwave absorbers are usually used to recover the interior of anechoic chambers. The errors of the reflectivity measurements were experimentally determined comparing the obtained reference reflectivity curves with that one furnished by Emerson & Cumming Inc. supplier. The determined errors stay below 1% in the frequency range of 8 to 12 GHz (Dias, 2000; Rezende *et al.*, 2003).

RESULTS AND DISCUSSIONS

Figure 1 shows the X-ray patterns of the NiZn ferrite used in the present study. Table 3 compares the pattern obtained for the NiZn ferrite with those of $ZnFe_2O_4$ and $NiFe_2O_4$ ferrites from the literature (JCPDS, 2008).

Comparing the X-ray patterns of $ZnFe_2O_4$ and $NiFe_2O_4$ ferrites, from literature, it is possible to observe that the d(Å) and hkl values are very close, showing that these ferrites can present different phases with similar crystallographic parameters. Correlating these values with those obtained from the tested NiZn ferrite, it is possible to observe that this sample has a mixture of phases, making difficult to assume that the three strongest lines in the pattern of the analyzed sample are due to the $NiZnFe_2O_4$. From these analyses, it can be concluded that the ferrite used in this study presents the general formula MFe_2O_4, where M can be substituted for Ni, Zn or both elements.

According to the literature (Verwey and Helmann, 1947; Cullity, 1972; Marcel Dekker, 1990; Valenzuela, 1994; Dias, 2000), the chemical composition of the studied NiZn ferrite indicates that this one belongs to the spinel class, with the possibility of application as microwave absorbing center in RAM processing (Cho *et al.*, 1996; Dias, 2000).

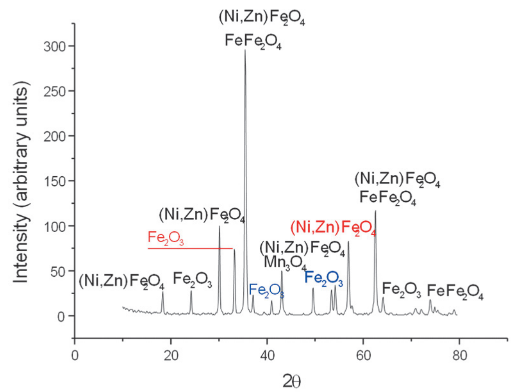

Figure 1. X-ray pattern of NiZn ferrite studied.

Figure 2 shows the magnetic susceptibility evolution curves of the studied NiZn ferrite. It is observed that the NiZn

Table 3. Comparison of the patterns of NiZn, Zn and Ni ferrites.

Ferrite	$ZnFe_2O_4$*	$NiFe_2O_4$*	NiZn ferrite (this study)
Name	Iron zinc oxide (Franklinite)	Iron (III) nickel oxide (Trevorite)	NiZn ferrite (commercial name)
System	Cubic	Cubic	Cubic
Index number	22 – 1012	10 – 325	–
Type	Spinel	Spinel	Spinel
(I/Io) (d(Å)) (hkl)	(100) (2.54) (311) (35) (1.49) (440) (35) (2.98) (220) (7) (4.87) (111)	(100) (2.51) (311) (40) (1.48) (440) (30) (2.95) (220) (20) (4.82) (111)	(100) (–) (311) (36) (–) (220) (32) (–) (440) (8) (–) (111)
Preparation conditions	Temperature: 700 - 800°C	Temperature: 1400°C, oxidant atmosphere	Temperature: 1020°C, oxidant atmosphere

*From (JCPDS, 2008).

ferrite does not show magnetic transitions. Then, the Curie temperature is not defined, confirming that the analyzed sample is constituted of a mixture of different phases.

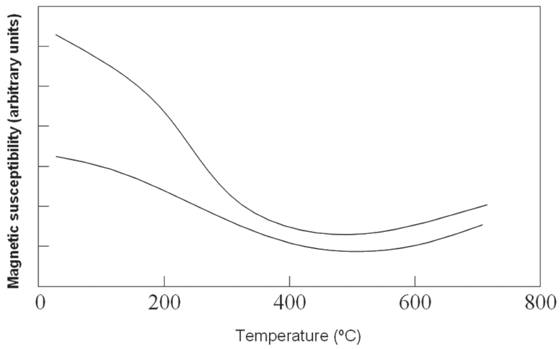

Figure 2. Magnetic susceptibility evolution curves of NiZn ferrite studied.

Figure 3 shows the reflectivity curve of the pure PU matrix (formulation 1, Table 2) applied on Al plate and also the Al plate curve used as reference. These curves are nearly covering one another, showing that the pure PU matrix applied on the Al plate does not contribute to reduce the incident signal, in the 8 to 12 GHz range. This behavior guarantees that the PU resin used in coating formulations does not interfere in the reflectivity measurements. Each reflectivity curve was obtained, in the interval of 8 to 12 GHz, with 400 points.

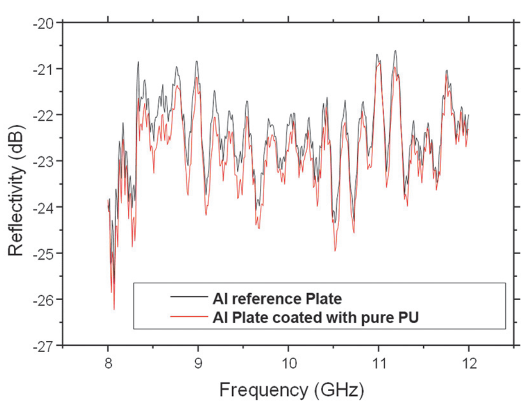

Figure 3. Reflectivity curves of the pure polyurethane polymer and the aluminum flat plate (reference).

Figure 4 presents the reflectivity curves of the formulations 2 to 7 (Table 2) applied on Al flat plates. Figure 4a shows that the PU/CB formulation, in proportion of 99/1 (wt.%), respectively, does not contribute to attenuate the incident electromagnetic wave. Figure 4b, representative of the PU/CB/NiZn ferrite (84/1/15, wt.%) formulation, shows a slight displacement between the reference curve and that one obtained for this formulation. Figure 4c to Fig. 4e show that the ferrite amount increase from 30 to 50% (wt.%) in the PU formulation promotes the curves debonding with the consequent increase of the attenuation values, from 1 to 4 dB, in the frequency range of 8 to12 GHz, respectively. Figure 4d shows higher attenuation values for frequencies above 9 GHz. Figure 4e is typical for RAM named broad-band type (Afsar *et al.*, 1986; Dias, 2000). Figure 4f (formulation 7 based on PU/ferrite, 50/50 wt.%) shows the attenuation values decreasing (≈ 2 dB), when compared to those determined for formulation 6, which contains simultaneously CB and ferrite.

Correlating the results, it is possible to conclude that the formulation containing only CB particles does not contribute to attenuate the incident radiation in the 8 to 12 GHz range. Similar behavior is observed for formulation 7, containing only the studied NiZn ferrite. Comparing the reflectivity values with that one from literature (Rezende *et al.*, 2001; Soto-Oviedo *et al.*, 2006), it is also verified that the processed RAM samples present low performance (up to 4 dB). This behavior is attributed probably to the presence of different phases in the NiZn ferrite, as determined by X-ray diffraction and magnetic susceptibility evolution analyses and, also, to the frequency range (8 to 12 GHz) adopted in the reflectivity measurements, the coating thickness and the additives concentration used.

Higher attenuation values are obtained when both additives (ferrite and CB) are loaded simultaneously within the PU matrix. This behavior is attributed to the great difference between the density values of both additives (0.14 and 5.01 g/cm^3 for CB and NiZn ferrite, respectively). This density difference promotes a heterogeneous distribution of the particles into the coating layer applied on the Al flat plate. Considering that the Al plate was kept horizontal during the application of the formulations, the heavier particles (NiZn ferrite) moved towards the Al plate. Consequently, the outer surface of the coating makes richer in lighter particles (CB). This feature observed in hybrid coating induced a better adjustment of the impedance of the material with the air. In this condition, the wave propagation into the material is favored, and the RAM efficiency is improved, as mentioned previously in Eq. 7 and 8 (Cullity, 1972; Dias, 2000).

From this initial condition, different mechanics of wave energy loss can occur. As cited previously, RAM makes use of energy-exchange properties of carbon and specific magnetic iron compounds which are able to transform

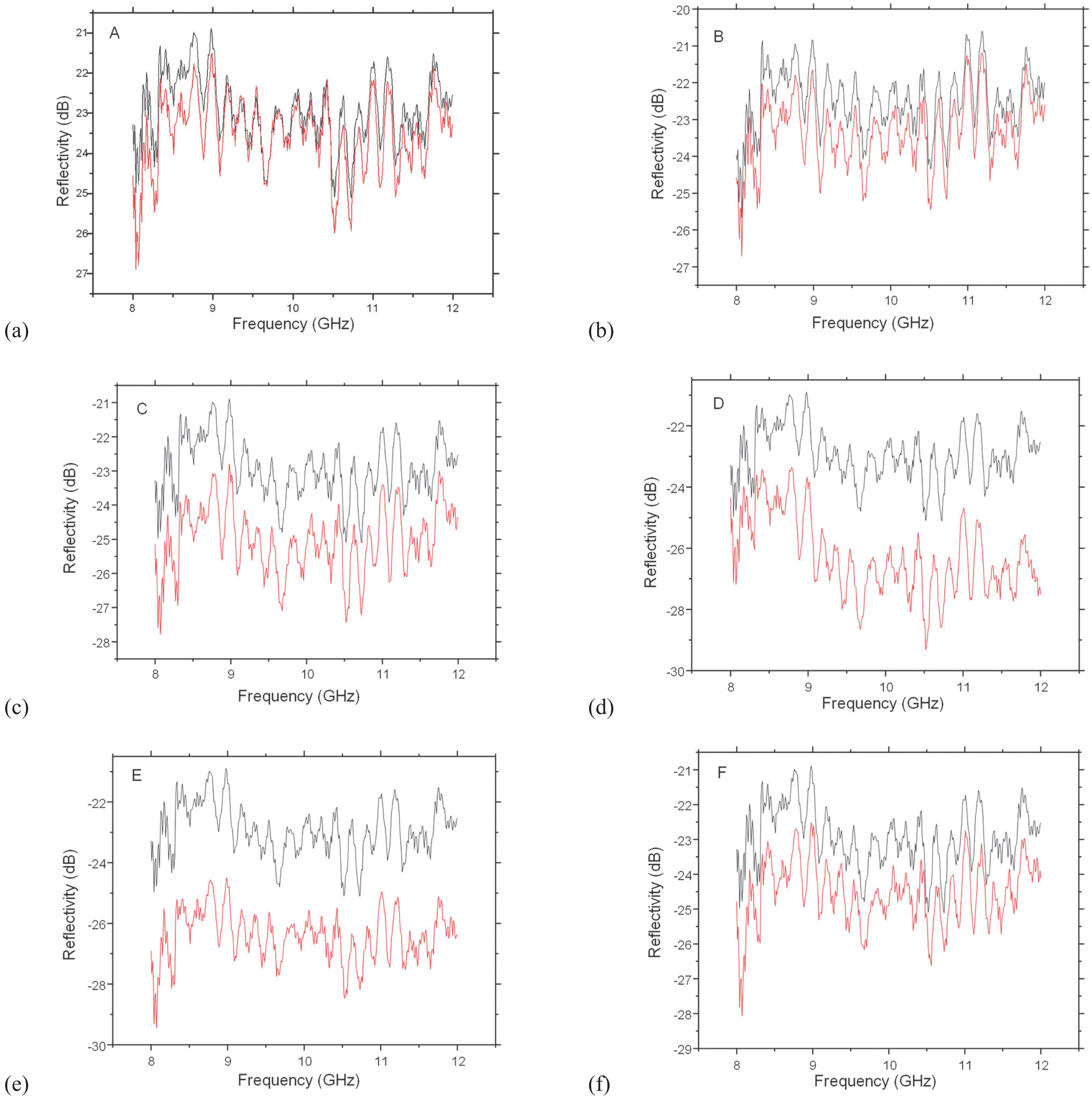

Figure 4. Reflectivity curves of the formulations. Curve in black is the reference (Al plate) and curves in red refer to the prepared formulations, as follow CB/NiZn ferrite in percentage in mass, respectively: (a) 1/0, (b) (1/15), (c) 1/30, (d) (1/45), (e) 1/50 and (f) 0/50.

the electromagnetic radiation in heat. Ohmic loss can be promoted by carbon particles and the ferrite particles can favor spin inversion, and it is known that both phenomena lead to the wave energy attenuation. The electromagnetic wave attenuation can also be improved by adjusting the electric thickness of the RAM which favors the wave attenuation by wave phase canceling (Lee, 1991; Knott *et al.*, 1993; Rezende *et al.*, 2001; Rezende *et al.*, 2002).

CONCLUSIONS

This study showed that the adequate combination of CB and NiZn ferrite in PU formulations allowed obtaining RAM with better performance compared to those prepared with CB or NiZn ferrite separately. The better performance of the hybrid RAM is attributed to an adequate adjustment of the impedance of the material with the air, which favors the RAM-electromagnetic wave interaction. This optimized condition is a consequence of the heterogeneous distribution of the particles (with different density values) in the coating layer. Attenuation values of ~4 dB for the PU resin/CB/NiZn ferrite formulations (49/1/50 wt.%, respectively) were obtained.

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