Effect of activated carbon/in situ synthesized magnetite hybrid fillers on the microwave properties of natural rubber composites

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Abstract

The purpose of the study is to synthesize nanosized magnetite in situ the nanosized porous texture of activated carbons and to examine the impact of the resulting hybrid filler upon the microwave properties and electromagnetic interference shielding effectiveness of composites based on natural rubber. The fillers have been characterized by X-ray diffraction and photoelectron spectroscopy establishing the influence of the magnetite layer on the texture characteristics. Studies have been carried out on the effect that the fillers synthesized have on the microwave properties, the real and imaginary part of the permittivity and permeability as well as on the dielectric and magnetic loss angle tangent of the composites. It has been found that filler comprising externally about 5% of magnetite phase is the most effective. The introduction of the magnetic phase contributes to the improvement in the microwave characteristics and expanding the frequency range in which the composites are of good microwave properties due to the combination of high dielectric and the high magnetic losses. Copyright © 2017 VBRI Press.

Keywords: Natural rubber, hybrid fillers, activated carbon, magnetite, microwave properties.

Introduction

Recently the production of materials possessing microwave absorbing and electromagnetic interference (EMI) shielding properties has gained significant importance. The most important applications of microwave absorbing composites are as follows: in antenna techniques and production – for improving the antenna parameters; for protection of humans and other biological objects from the harmful effect of the electromagnetic waves; military application - for anti-radar camouflage, to reduce the radar cross section of objects; for improving the electromagnetic compatibility between different electronic devices, reducing undesirable reflections from objects and devices; for improving the shielding of enclosures and containers acting as gasket sealing materials [1, 2].

Most of the present-day microwaves absorbing composites are produced of a dielectric rubber matrix and specific functional fillers. Those fillers - carbon black, graphite, activated carbon, carbon or metal fibers, micro- and nanosized metal powders - possess high values of the imaginary part of the complex permittivity and/or magnetic permeability, and absorb high frequency energy [3-9]. As the electromagnetic radiation has both a dielectric and magnetic component, it is obvious that both dielectric and magnetic materials are effective for the absorption of microwave radiation. Therefore, it has been of interest to combine components of high dielectric and magnetic losses into a hybrid filler what opens new opportunities of preparing modern microwave absorbers of specific properties.

In our publication [10] we have shown that under certain conditions, activated carbons possess properties of
reinforcing and functional fillers for elastomeric materials with microwave application. For the activated carbon/rubber composites a reasonable assumption for \( \mu = 1 - j 0 \) (\( \mu'' = 1 \) and \( \mu''' = 0 \)) has been made. However, only the real and imaginary part of the permittivity have been measured. That limits the absorptive properties of the composite with respect to the electromagnetic waves. On the other hand, there is a wide use of magnetite (natural or synthetic) as a functional filler for elastomers for different microwave application. Being very effective and often used in a broad frequency range for various applications, this filler has been intensively investigated. We have also studied it in hybrid fillers obtained by impregnation technologies [11].

Our main hypothesis is that the porous texture of activated carbon contains a significant amount of nanosized pores. By steric reasons, if magnetite synthesized in situ these pores it will be nanosized too. Expectedly, after the modification of activated carbon with magnetite the microwave properties of composites containing hybrid fillers carbon/nanosized magnetite will improve as besides the dielectric losses, magnetic losses will also contribute to the formation of the composites absorption properties.

There are no publications devoted to the study of the microwave properties of elastomer composites containing hybrid fillers such as activated carbon/nanoscale magnetite synthesized in situ the porous texture of activated carbon. The working hypothesis allows us to formulate the aim of the study - to synthesize nanosized magnetite in situ the porous texture of activated carbon (as a template) and to examine the impact of the resulting hybrid filler upon the microwave properties and electromagnetic shielding effectiveness of composites based on natural rubber. The main task in the implementation of the formulated objective is measuring the real and imaginary part of permittivity and magnetic permeability, as well as the tangent of dielectric and magnetic angle losses because the knowledge of the permittivity and permeability of rubber composites is essential to modelling microwave absorber performance. If those values are known, then material performance is completely determined. Another aspect of the study is related to the influence that the ratio between the two phases has on composites microwave properties.

**Experimental**

**Activated carbon**

Activated carbon Norit from wood was used in the research.

**Preparation of the hybrid fillers via magnetite synthesis in situ the porous texture of the activated carbon**

The hybrid fillers were synthesized using two routes: by Karyakin and Angelov method [12] and by modified version of the same.

The substrate virgin activated carbon was marked as MAC-0. The samples obtained according to the Karyakin and Angelov method comprising various amounts of magnetite phase are marked as MAC-1, MAC-2 and MAC-3, respectively.

According to the modified version of the method, the initial solution of ferrous sulphate was obtained by dissolving in advance the mixture of iron (III) sulphate and iron (II) sulphate in a little distilled water and then CH3OH was added till the solution reached 300 ml. The sample obtained by the modified version of the method was marked as MAC-4.

**Characterization of the substrate activated carbon and hybrid fillers**

The samples under investigation were characterized by means of low-temperature nitrogen adsorption (at 77.4 K) using a Quantachrome Instruments NOVA 1200e (USA) apparatus.

The following textural parameters were calculated on the basis of the adsorption-desorption equilibrium nitrogen isotherms, applying the specialized software belonging to the apparatus: specific surface area (\( A_{BET} \)); volume of the micropores (\( V_{M} \)); total pore volume (\( V_{T} \)); volume of the mesopores (\( V_{MES} \)); size distribution of the micropores and mesopores; average pore diameter (\( D_{AV} \)); the external surface area (\( A_{EXT} \)).

A Thermo SOLAR M5 flame atomic spectrometer was used to determine the iron content.

All measurements were performed in air-acetylene flame under standard conditions.

The isoelectric points (IEP) of the carbons were determined by the method of Noh and Schwarz [13]. X-ray diffraction (XRD) data were obtained using a Bruker D8 Advance diffractometer with Cu-Kα radiation and SolX detector. The composition and electronic structure of the hybrid fillers were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were carried out on an AXIS Supra electron-spectrometer (Kratos Analytical Ltd.) using monochromatic AlKα radiation with a photon energy of 1486.6 eV and a charge neutralization system.

**Samples preparation and vulcanization**

The formulations of the prepared composites are shown in **Table 1**.

The vulcanization was carried out on a hydraulic press at a pressure of 10 MPa.

**Table 1.** Composition of the NR based rubber composites, phr.

<table>
<thead>
<tr>
<th></th>
<th>MAC-0</th>
<th>MAC-1</th>
<th>MAC-2</th>
<th>MAC-3</th>
<th>MAC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>SMR 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Activated carbon powder</td>
<td>MAC-0</td>
<td>MAC-1</td>
<td>MAC-2</td>
<td>MAC-3</td>
<td>MAC-4</td>
</tr>
<tr>
<td>TBBS</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.25</td>
<td>2.25</td>
<td>2.25</td>
<td>2.25</td>
<td>2.25</td>
</tr>
</tbody>
</table>

**Note:** The amounts of activated carbons in the studied samples are 70 phr.
Microwave properties measurement

The shielding effectiveness is defined as the ratio between the incident power on the sample \( P_I \) and the transmitted power \( P_T \) in accordance with Eq. 1 [14-16]:

\[
SE_T = 10 \log \frac{P_I}{P_T} \tag{1}
\]

The total shielding effectiveness \((SE_T, \text{ in dB})\) and the reflective shielding effectiveness of the sample surface \((SE_R, \text{ in dB})\) are determined by Eqs. 2 and 3 [15]:

\[
SE_T = -10 \lg T, \tag{2}
\]

\[
SE_R = -10 \lg (1 - R), \tag{3}
\]

where \( T = |P_T / P_I| = |S_{21}|^2 \)

\[
R = |P_R / P_I| = |S_{11}|^2
\]

The absorptive shielding effectiveness \((SE_A)\) is calculated as the difference between Eqs. 2 and 3, as it is shown in Eq. 4 [15]:

\[
SE_A = SE_T - SE_R \tag{4}
\]

To determine the shielding components for the composites, the \( P_I, P_T \) and \( \Gamma = |S_{11}| \) were measured, and \( P_R \) was computed from the magnitude of reflection coefficient \( (P_R = |\Gamma|^2 . P_I)\).

Permittivity and permeability measurement

The electromagnetic properties of the composite materials were measured by the resonant perturbation method. [17]. The formulas for the real and imaginary parts of the relative permittivity are as follows [18, 19]:

\[
\varepsilon' = \left( \frac{f_c - f_a}{2f_s} \right) \cdot \left( \frac{V_c}{V_s} \right) + 1 \tag{5}
\]

\[
\varepsilon'' = \left( \frac{V_c}{4V_s} \right) \cdot \left( \frac{1}{Q_s} - \frac{1}{Q_c} \right) \tag{6}
\]

where \( f_c \) and \( Q_c \) are resonance frequency and \( Q \)-factor of the cavity without an inserted sample, \( f_s \) and \( Q_s \) are with the sample inserted, respectively. \( V_c \) is the volume of the cavity; \( V_s \) is the volume of the sample.

The formulas for the real and imaginary parts of the relative permeability are as follows [20, 21]

\[
\mu' = \left( \frac{f_c - f_a}{f_s} \right) \cdot \left( \frac{V_c}{V_s} \right) \cdot \left( \frac{2g + 4a^2}{8a^2} \right) + 1 \tag{7}
\]

\[
\mu'' = \left( \frac{V_c}{V_s} \right) \cdot \left( \frac{1}{Q_s} - \frac{1}{Q_c} \right) \cdot \left( \frac{2g + 4a^2}{16a^2} \right) \tag{8}
\]

where \( \lambda_g = 2d/L \), is the guided wavelength and \( L = 1, 2, 3,...; \) \( d \) is cavity length and \( a \) is cavity width.

The measurements were carried out at room temperature varying from 19°C up to 24°C within the frequency range of 1 GHz to 12 GHz.

Results and discussion

Characterization of the fillers

Table 2 summarizes the adsorption-texture parameters of the fillers calculated on the basis of the isotherms.

<table>
<thead>
<tr>
<th>Content (mass. %)</th>
<th>MAC-0</th>
<th>MAC-1</th>
<th>MAC-2</th>
<th>MAC-3</th>
<th>MAC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_{\text{ABET}} ) m(^2)/g</td>
<td>541</td>
<td>468</td>
<td>451</td>
<td>456</td>
<td>431</td>
</tr>
<tr>
<td>( \rho_{\text{AV}} ) cm(^3)/g</td>
<td>154</td>
<td>144</td>
<td>128</td>
<td>136</td>
<td>138</td>
</tr>
<tr>
<td>( \rho_{\text{Vf}} ) cm(^3)/g</td>
<td>0.37</td>
<td>0.33</td>
<td>0.30</td>
<td>0.33</td>
<td>0.39</td>
</tr>
<tr>
<td>( \rho_{\text{VML}} ) cm(^3)/g</td>
<td>0.21</td>
<td>0.17</td>
<td>0.16</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>( \rho_{\text{VMM}} ) cm(^3)/g</td>
<td>0.16</td>
<td>0.16</td>
<td>0.14</td>
<td>0.16</td>
<td>0.24</td>
</tr>
<tr>
<td>( D_{\text{AV}} ) nm</td>
<td>2.7</td>
<td>2.8</td>
<td>2.7</td>
<td>2.9</td>
<td>3.6</td>
</tr>
<tr>
<td>IEP</td>
<td>7.2</td>
<td>6.9</td>
<td>7.0</td>
<td>6.7</td>
<td>7.1</td>
</tr>
<tr>
<td>( V_{\text{Maves/Aext}} \times 10^{-6} )</td>
<td>10.4</td>
<td>11.1</td>
<td>10.9</td>
<td>11.8</td>
<td>17.4</td>
</tr>
</tbody>
</table>

As the Table shows, with increasing the magnetite phase the specific surface area of the samples decreases, if compared to that of the substrate activated carbon. The decrease is most pronounced in the case of sample MAC-4 obtained by deposition of the precursors form organic medium.

The Table also shows that mesopore volume values for all the samples, but MAC-4, are equal to the ones of the substrate activated carbon (MAC-0). That suggests that, the magnetite phase either does not penetrate the activated carbon or if it does, the amount of magnetite is negligible. On the other hand, the mesopore volume value for sample MAC-4 is about 50% higher than that of MAC-0, what evidences that magnetite fills the fine carbon pores. That is also confirmed by the increase in the average diameter \( (D_{\text{AV}}) \) of MAC-4 (3.6 nm) in comparison to those of MAC-0 (2.7 nm) and of the rest samples.

According to the data of XRD patterns, the phase distributed into the nanosized porous texture of the samples comprises predominantly magnetite. Probably maghemite and arcancite are also present. Magnetite and maghemite have similar XRD patterns [22] and it is difficult to distinguish them by XRD method.
According to [23], the comparison of Fe/C ratios determined by XPS (Table 3) with those from the chemical analysis (cha) of the samples allows to locate the distribution of the impregnation phase (Fe-phase) over the external surface or inside the samples volume.

Table 3. Fe/C ratios as determined by XPS and chemical analysis (cha).

<table>
<thead>
<tr>
<th></th>
<th>Fe/C (XPS)</th>
<th>Fe/C (cha)</th>
<th>(Fe/C)<em>{XPS} / (Fe/C)</em>{cha}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAC-1</td>
<td>0.056</td>
<td>0.034</td>
<td>1.647</td>
</tr>
<tr>
<td>MAC-2</td>
<td>0.093</td>
<td>0.044</td>
<td>2.114</td>
</tr>
<tr>
<td>MAC-3</td>
<td>0.175</td>
<td>0.068</td>
<td>2.574</td>
</tr>
<tr>
<td>MAC-4</td>
<td>0.178</td>
<td>0.073</td>
<td>2.438</td>
</tr>
</tbody>
</table>

As the Table shows, the magnetite phase is distributed predominantly over the external surface and not in the volume (internal surface) of all samples. With the increasing magnetite amount the phase over the external surface also enlarges.

Noteworthy is the fact that although the ratios of the values determined by XPS and by chemical analysis (cha) of the samples are similar (Table 3), the sample obtained by the modified method (MAC-4) has a lower ratio (2.438 against 2.574 in MAC-3). Accordingly, the precursor phase from the organic medium is distributed in the internal surface (volume) to a extent greater than that in the case of using an aqueous medium.

Microwave properties

Fig. 1 presents the results for the total shielding effectiveness of the control sample polytetrafluoroethylene (PTFE - Teflon) and the studied fillers as a function of frequency in the 1 GHz to 12 GHz range. As seen, in the entire frequency range all samples exhibit the same behavior dependent on frequency changes. In the range of 5 GHz to 12 GHz the tendency of changing the total shielding effectiveness of the sample studied remains the same in a diapason of 2.5 dB and reaching a maximum value of 7.16 dB for sample MAC-3 at 10 GHz. Total shielding effectiveness values start at about 0.5 dB at 1 GHz and increase monotonously with the increasing frequency. In the frequency range studied sample MAC-0 is the least sensitive. Sample MAC-4 exhibits behavior closest to the one of the substrate carbon, i.e. the modified preparative method does not produce the expected result. That is probably due to the internal (in the carbon volume) and not external distribution of the magnetite phase. There is an obvious drop of the values for all samples at 9 GHz. PTFE does not exhibit shielding properties in the entire frequency range and its total shielding effectiveness tends to zero.

Fig. 2 presents the results for the reflective shielding effectiveness (SE_R) of the studied composites. It allows the conclusion that the absorption by the samples is affected strongly by the frequency changes. The achieved dynamic diapason of the values is less than 2 dB at frequencies 5.8 GHz, 11 GHz and 12 GHz, and the maximum values are 2.9 dB, 3.8 dB and 3.7 dB, respectively. Sample MAC-3 has the highest SE_R values, while sample MAC-1 has the highest values at the highest frequencies.

Fig. 3 presents the results for the absorptive shielding effectiveness (SE_A) of the studied composites. It allows the conclusion that the absorption by the samples is affected strongly by the frequency changes. The achieved dynamic diapason of the values is less than 2 dB at frequencies 5.8 GHz, 11 GHz and 12 GHz, and the maximum values are 2.9 dB, 3.8 dB and 3.7 dB, respectively. Sample MAC-3 has the highest SE_A values, while sample MAC-1 has the highest values at the highest frequencies.
In the frequency range 1 GHz to 4 GHz and at 7 GHz the dynamic diapason of the values remains slightly sensitive to frequency changes (less than 1 dB for all the samples).

As seen from Figs. 1-3, the total shielding effectiveness of the composites studied is due mainly to the mechanism of electromagnetic power reflection. The absorption mechanism predominates only at frequencies in the 5 GHz - 6 GHz range. As far as the location of the oxide phase is concerned, it is obvious that it is chiefly in the volume of the finest pores and has not any well pronounced positive effect.

**Complex permittivity and permeability**

Absorbers are characterized by their permittivity and magnetic permeability. The permittivity is a measure of the materials effect on the electric field in the electromagnetic wave and the permeability is a measure of the materials effect on the magnetic component of the wave. The real part of the permittivity, \( \varepsilon' \), named dielectric constant, measures how much energy from an external electric field is stored in the material. The imaginary part, \( \varepsilon'' \), named loss factor, accounts for the loss energy dissipative mechanisms in the materials, quantifying it as a measure of the attenuation of the electric field caused by the material. Both components contribute to wavelength compression inside the material. Additionally, due to coupled electromagnetic wave, loss in either the magnetic or electric field will attenuate the energy in the wave.

Figs. 4 and 5 present the frequency dependence of the real and imaginary part of permittivity for the composites comprising hybrid fillers with an *in situ* synthesized magnetite phase at various concentrations. Fig. 6 plots the frequency dependence of the tangent of dielectric loss angle.

The real part of relative permittivity for samples MAC-0, MAC-2 and MAC-3 decreases with the increasing frequency in the studied range, while for samples MAC-1 and MAC-4 practically there is no such dependence. Sample MAC-3 possesses the highest values of the parameter in the 1 GHz to 7.5 GHz range, while in the range over 7.5 GHz the values become practically equal for all materials except for sample MAC-0. Regarding the imaginary part of dielectric permittivity as a frequency function, there are two ranges: 1 to 7.5 GHz where MAC-3 and MAC-2 possess the highest values decreasing rapidly with the increasing frequency; and 7.5 to 12 GHz wherein the values for all samples are very close and the frequency dependence of the parameter is slightly pronounced. As far as the dependence of the tangent of dielectric loss angle is concerned, sample MAC-3 has distinguishable values in the 1-5 GHz range, while the values for MAC-0 are the highest in the 5-12 GHz range, while the values for MAC-0 are the highest in the 5-12 GHz range.

The results in Figs. 4-6 allow the conclusion that, the dielectric properties of most materials vary considerably with the frequency of the applied electromagnetic field.

An important phenomenon contributing to the frequency dependence of the dielectric properties is polarization, arising from the orientation of molecules which have permanent dipole moments with the imposed electric field.

![Figure 4](image1.png)

*Fig. 4. Frequency dependence of the real part of the permittivity for the composites investigated and Teflon.*

![Figure 5](image2.png)

*Fig. 5. Frequency dependence of the imaginary part of the permittivity for the composites investigated and Teflon.*

![Figure 6](image3.png)

*Fig. 6. Frequency dependence of the tangent of dielectric loss angle for the composites studied and Teflon.*
The mathematical formula developed by Debye to describe the permittivity for polar materials \[24\] can be expressed as:
\[
\varepsilon = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau}
\]
(9)

where \(\omega = 2\pi f\) is the angular frequency, \(\varepsilon_\infty\) represents the dielectric constant at frequencies so high that molecular orientation does not have time to contribute to the polarization, \(\varepsilon_s\) represents the static dielectric constant, i.e., the value at zero frequency (dc value), and \(\tau\) is the relaxation time in seconds, the period associated with the time for the dipoles to revert to random orientation when the electric field is removed. Separation of Eq. 9 into its real and imaginary parts yields:
\[
\varepsilon' = \varepsilon_x + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\tau)^2}
\]
(10)
\[
\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2}
\]
(11)

Obviously, \(\varepsilon_\infty, \varepsilon_s\) and in particular, \(\tau\), are specific parameters for each of the fillers used, which depend on the chemical nature and crystallographic structure of the two different filler phases (the activated carbon one and that of Fe_3O_4). The dependence of \(\varepsilon_\infty, \varepsilon_s\) and \(\tau\) on activated carbon/magnetite ratio in the synthesized fillers explains why in some frequency ranges (usually at lower frequencies) the dielectric properties change monotonously, while in some higher frequency ranges, when relaxation is hindered, the increase is drastic. According to the Debye theory of dielectric properties \[24\], \(\varepsilon''\) is generally determined by relaxation and electrical conductivity losses. It is clear that, both polarization, relaxation and electrical conductance can affect \(\varepsilon''\). As all other conditions are identical, obviously, that peculiarity is due to the specific chemical nature and crystallographic structure of the activated carbon and magnetite phases.

On the other hand, since the elastomer matrix is non-polar, apparently, the relaxation and polarization processes are greatly dependent on the fillers used and on their specific features. With regard to those specifics, the polarization may proceed according to three different mechanisms: electronic, ionic and orientational. All non-conducting materials are capable of electronic polarization. Therefore, we consider the polarization of the elastomer matrix used for the studied composites to proceed according to that mechanism. The more polarization mechanisms of a composite are, the higher its dielectric constant will be. The more easily the various polarization mechanisms can proceed, the higher the dielectric constant will be. For example, among elastomers, the more mobile the chains are (i.e. the lower the degree of crystallinity), the higher the dielectric constant will be. It is important for the composites investigated, because the natural rubber crystallizes and the chemical nature of the fillers used and their amounts can change the degree of crystallinity and the dielectric constant.

**Figs. 7 and 8** present the frequency dependencies of the real and imaginary part of magnetic permeability. **Fig. 9** plots the frequency dependency of tangent of magnetic loss angle.

**Fig. 7.** Frequency dependence of the real part of magnetic permeability for the composites investigated.

**Fig. 8.** Frequency dependence of the imaginary part of magnetic permeability for the composites investigated.

In the 1 GHz to 4 GHz range \(\mu'\) is close to 1, and \(\mu''\) is almost zero, what means that there are no magnetic losses. In the 4 GHz to 12 GHz range an increase in \(\mu'\) and \(\mu''\) with the increasing frequency up to about 8 GHz has been observed. After that \(\mu'\) and \(\mu''\) values decrease with the increasing frequency. The frequency fluctuation of the permeability curves reveals natural resonances in the composite which can be ascribed to small size of Fe_3O_4 nanoparticles \[25\].

**Fig. 9.** Frequency dependence of the tangent of magnetic loss angle of the studied composites.
At a higher amount of the magnetite phase the real part of magnetic permeability increases negligibly, while the imaginary part and tangent of magnetic loss angle increase considerably.

As seen from the results presented in Figs. 1-3, in the frequency range 4 GHz to 12 GHz $\varepsilon''_a$ values exhibit resonance properties, while in the ranges 4 to 6 GHz the absorption is the predominant shielding mechanism, could be related to the increase in the values of tangent of magnetic loss angle plotted in Fig. 9. $\text{Fe}_3\text{O}_4$ nanoparticles act as tiny dipoles which get polarized by the activation of electromagnetic field and result in better microwave absorption. The magnetic loss $\mu''$ is a combined result of eddy current effect, natural resonances and anisotropy energy of the sheet. In the microwave ranges, the eddy currents are attributed to ferrite nanoparticles preset in the sheet [26].

Conclusions

Dual-phase hybrid fillers based on activated carbon, containing up to 5.4 mass% of nanosized magnetite synthesized in situ the porous carbon texture have been obtained for the first time implementing an especially developed methodology. The fillers have been characterized in detail by X-ray diffraction and photoelectron spectroscopy establishing the influence of the magnetite layer on the texture characteristics.

Studies have been carried out on the effect that the fillers synthesized have on the microwave properties, the real and imaginary part of the permittivity and magnetic permeability as well as on the tangent of dielectric and magnetic loss angle of the composites based on natural rubber.

It has been found that the total shielding effectiveness of the composite materials based on activated carbon modified with magnetite is due mainly to the mechanism of reflection of electromagnetic power (reflective shielding effectiveness). However, in the 5 to 6 GHz range it is the mechanism of absorption (absorptive shielding effectiveness) that has a crucial role for all studied composites.

It has been found that filler comprising externally about 5% of magnetite phase has the highest total shielding effectiveness amongst the dual phase fillers studied. The amount of magnetite phase above that concentration as well as the internal distribution (inside the volume of the finest pores) does not contribute to the improvement of the microwave characteristics probably on account of steric hindrance. The absorption of electromagnetic waves is much more frequency dependent than the reflection.

The microwave properties of the tested composites are to a great extent due to their dielectric and magnetic characteristics, and mostly to the dielectric and magnetic loss. The dielectric properties (the values of real and imaginary part of permittivity) are associated with the polarization and relaxation phenomena. The magnetic properties are determined by magnetic moments on the tetrahedral site occupied by ferric species, which are ferromagnetically aligned, while magnetic moments on octahedral sites occupied by ferrous and ferric species are antiferromagnetic, yielding as a result a ferromagnetic behavior. Hence, the crystallochemical nature, the crystallographic structure and the ratio between the carbon and magnetite phases have an apparent role in the properties of the studied fillers. That opens the opportunity to tailor the microwave properties of composites containing those fillers.

Definitely the introduction of the magnetic phase contributes to the improvement in the microwave characteristics of the composites because the co-existence of the dielectric and magnetic losses expands the frequency range in which the composites are of good microwave properties, determined in some cases by the high dielectric, and in other by the high magnetic losses.

The determined microwave characteristics of composites comprising the hybrid fillers obtained reveal the perceptiveness of the fillers and the possibility use them for manufacturing elastomer based microwave absorbers in antenna techniques, for protection of humans from the harmful effect of the electromagnetic waves, for anti-radar camouflage, to reduce the radar cross section of objects, for improving the electromagnetic compatibility between different electronic devices etc.

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