Microwave absorbing materials based on hybrid filler

Kamelia Ruskova*

Department of Chemistry, Faculty of Electronic Engineering and Technologies,
Technical University of Sofia 8 Kl. Ohridski, 1000, Sofia, Bulgaria

Abstract. Composite elastomer microwave absorbers were developed based on two-phase hybrid filler. Nanosized magnetite was synthesized for the first time in the porous texture of activated carbon. Combination of fillers with high dielectric losses such as active carbon, and magnetite with high magnetic losses into hybrid filler is considered as a new Hightech for generation of microwave absorbers with specific technical characteristics. The influence of the obtained filler on the microwave shielding effectiveness of composite rubber absorbers was examined. The fillers were characterized by X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM), Brunauer-Emmet-Teller (BET) method for the surface area analysis and texture parameters. The influence of the concentration of the synthesized filler on the microwave characteristics and shielding effectiveness was investigated.

1 Introduction

Nowadays electromagnetic pollution runs up as a great ecological problem and is considered to be very toxic. Many electronic communication devices (cell phones, computers, microwave ovens, bluetooth devices, laptops, power lines generate electromagnetic energy in the form of electromagnetic waves. They are sources of nonionizing radiation (NIR). Exposure to such kinds of radiation can cause biological effects when interacting with biological tissues. Electromagnetic waves in the frequency range 1÷3 GHz are considered as very active for biological systems and for human health. The basic method for protection from harmful electromagnetic radiation is shielding the whole device and for that aim various absorbing materials are developed. Microwave absorbers are used for electromagnetic shielding in a biological range, for anti-radar camouflage for mobile and immobile military facilities, in medicine, for antenna applications in aim to reduce undesirable noises and signals [1,2].

Most present-day microwave absorbers are composite materials based on a dielectric matrix and different functional fillers such as metal fibers, active carbon, magnetite, ferrites, micro- and nano- sized metal powder etc. [3,4]. Incorporating in a polymer matrix of fillers with high dielectric losses, such as active carbons (ACs) and magnetite with high values of magnetic losses, will provide a good microwave interaction of absorbing materials. This will expand the absorption for oscillations with different frequencies of the waveband.

The aim of study is to synthesize nanoscale magnetite in a porous texture of AC. ACs are characterized as a micro- mesoporous material. Our assumption is that if a magnetite id synthesized directly in a porous structure of AC, it will be nanoscaled also. As a contrast of micro sized fillers, nanostructured particles are monodomain and have superparamagnetic properties in some conditions and their specific magnetic properties have not been well investigated and present a great interest.

2 Experimental

2.1 Synthesis of the two-phase hybrid filler

For the aim of our study, natural wood based active carbon type “Norit” is used. Magnetite was prepared by the Karyakin method [5]

In order to develop high surface area and to obtain high meso- and micro-porosity, activated carbon was prepared via chemical activation with potassium hydroxide. At the same time synthesis of nanosised magnetite in the porous texture of AC was done.

The hybrid filler was obtained as follows: Iron sulfate $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.9H_2O$ in a molar ratio 1:2 were dissolved in 200 ml distilled H_2O. 100g of active carbon was soaked with the prepared solution and so they stayed for 1 hour. Synthesis of the magnetite was generated upon the next reaction:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$

2.2 Rubber composite materials preparing and vulcanization

The rubber composition was prepared by the following steps and ingredients before vulcanization process (Table1). Natural rubber (NR), sulfur as a vulcanizing agent, and zinc oxide as an activator of the curing process, stearic acid and TBBS (N-tert-Butyl-2-benzothiazolesulfenamide as an accelerator.

* Corresponding author: kruskova@tu-sofia.bg

This composition was homogenized for 10 minutes and then the rubber compounds were prepared in an open two-roll laboratory mill (L/D 320x160 with friction 1.27. The temperature of the rolls was 70ºC.

Table 1. Composition of natural rubber-based composites, phr.

Composites	MC-0	MC-1	MC-2	MC-3
Natural rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
AC powder	70	70	70	70
TBBS	0.8	0.8	0.8	0.8
Sulfur	2.25	2.25	2.25	2.25

The curing process was done on a hydraulic electric at 10 MPa pressure. The optimal vulcanization time was done using vulcanization isotherms with a vulcameter MDR 2000 (Alpha Technologies) at 150ºC according to ISO 3417:2002 standard.

3 Results and Discussion

3.1 Characterization of the hybrid filler

Quantachrome Instruments NOVA 1200e apparatus and low-temperature nitrogen adsorption was used to determine the specific surface area and the texture characteristics of the obtained samples. The nitrogen adsorption-desorption isotherms were analyzed to evaluate the following textural parameters: specific surface area (S_{BET}) based on BET equation, the total pore volume (V_t), volume of the micropores (V_{micro}) and mesopores (V_{meso}) was also determined [6]. The results obtained (Table 2) show that increasing the amount of the magnetite phase leads to the surface area decreasing for all samples with, compared the control sample MC-0, without magnetite.

Table 2. Textural characteristics of the control sample and obtained hybrid fillers.

Sample	Fe_3O_4 conten, mass %	S_{BET} m^2/g	A_{EXT} m^2/g	V_t cm^3/g	V_{micro} cm^3/g	V_{meso} cm^3/g
MC-0	-	541	154	0.37	0.21	0.16
MC-1	2.7	468	144	0.33	0.17	0.16
MC-2	3.5	451	128	0.30	0.16	0.14
MC-3	5.1	456	136	0.33	0.17	0.16

From the table results it is evident that for all samples mesopore volume (V_{meso}) is similar, but for the V_{micro} the volume of the samples decreases from 0.21 cm^3/g for MC-0 to 0.16 cm^3/g for MC-2 and MC-3. V_t also decreases with the rising of the magnetite amount, evidence that nanoscale synthesized magnetite fills the fine carbon micropores.

3.2 Chemical and surface analysis of the samples

The iron content was measured using Thermo SOLAR M5 atomic spectrometer. All measurements were performed in air-acetylene flame under standard conditions.

The electronic structure and the film composition were observed by X-ray photoelectron spectroscopy (XPS). The measurements were done on AXIS Supra electron-spectrometer (Kratos Analytical Ltd.) using monochromatic AlK_α radiation with photon energy of 1486.6 eV. The binding energies were measured with ±0.1 eV accuracy. Chemical and surface analysis of the samples were done monitoring the areas and binding energies of *C1s*, *O1s* and *Fe2p*- photoelectron peaks. The concentrations of the different elements (in atomic %) were calculated by normalizing the areas of the photoelectron peaks to their relative sensitivity factors, using the commercial data-processing software.

Table 3. Binding energy of the Fe($2p_{3/2}$) and O(1s) peaks.

Samples		MC-1	MC-2	MC-3
Fe($2p_{3/2}$)	*Fe_3O_4*	710.7	710.6	710.4
	γ-FeOOH	711.2	711.2	711.4
	Fe_2O_3	711	711	711
O(1s)	*Fe_3O_4*	530.2	530.3	530.3
	γ-FeOOH	-	-	530.2
	Fe_2O_3	-	-	530.7

It the presence of Fe content (Table 3) in the samples can be seen, as well as its dominant location (on their external surface or in their volume), examined by XPS. The obtained photoelectron spectra for Fe in *2p*-excitation range for all samples show the characteristic binding energies for Fe in Fe_3O_4 [7], as well as the possibility of the existence of γ-FeOOH and Fe_2O_3.

The comparison of Fe/C ratio evaluated by XPS (Table 4) with data from chemical analysis (cha) of the samples according to [8] allows to determine distribution of the impregnation Fe-phase the samples on the external surface of or inside in the volume of active carbon.

Table 4. Fe/C ratio determined by XPS and chemical analysis.

Samples	MC-1	MC-2	MC-3
Fe/C(XPS)	0.056	0.093	0.175
Fe/C(cha)	0.034	0.044	0.068
Fe/C(XPS)/ Fe/C(cha)	1.647	2.114	2.574

The data results show that for all samples iron phase is predominantly distributed over the external surface than in the volume (internal surface). With increasing the magnetite content, the amount of the Fe-phase over the external surface also increases.

3.3 Scanning electron microscopy characterization of the samples

Fig. 1 gives the SEM micrographs of the initial MC-0 and two-phase hybrid filler MC-3, containing maximum amount of magnetite in the porous texture of activated carbon. Fig.3a shows empty pores of the initial sample without magnetite and on Fig.3 b can be seen the presence of a magnetite phase in the porous structure of AC.

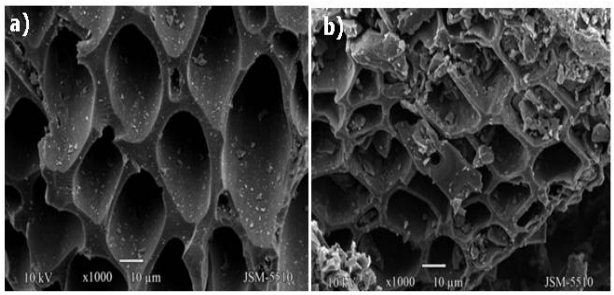

Fig. 1. Scanning electron microscopy of a) the initial activated carbon MC-0 and b) MC-3.

3.4 Microwave properties of the obtained absorbers

Mechanism of interaction of the absorbing material with the electromagnetic wave, an incident power P_I. is presented on Fig. 2. When encountering the shielding materials, the electromagnetic wave will undergo a combination of reflection, absorption, and transmission. One part of the wave is reflected power (P_R) from the surface of the absorbing material. The other part of the incident power transforms into the material as a heat, this is the absorbed power (P_A), and the rest is the transmitted power of the material (P_T).

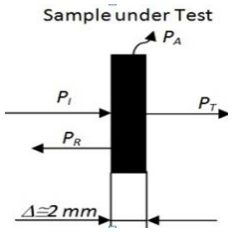

Fig. 2. Mechanism of interaction of the absorbing material with the electromagnetic wave.

The shielding effectiveness (*SE*) of the microwave absorber can be determined as the ratio between the incident power P_I and transmitted power P_T, the power passing through the absorbing material and can be calculated based on the following equation (1) [9-11].

$$SE = 10 \log (P_I/P_T) \quad (1)$$

The total shielding effectiveness (*SE*, in dB) and the reflective shielding effectiveness of the absorbing material surface (SE_R, in dB) can be determined according to the equations (2-3) [10].

$$SE = -10 \lg T \quad (2)$$

where $T = |P_T/P_I| = |S_{21}|^2$,

$$SE_R = -10 \lg (1- R), \quad (3)$$

$$R = |P_R/P_I| = |S_{11}|^2.$$

where S_{11} and S_{21} are the complex scattering parameters (S_{11} corresponds to the reflection coefficient, S_{21} – to the transmission coefficient), T is the transmission factor (in dB).

The absorptive shielding effectiveness (SE_A in dB) is the difference between (2) and (3) and can be determined according to the next equation (4) [10].

$$SE_A = SE - SE_R \quad (4)$$

To define the shielding components for the absorbing material, the P_I, P_T and $|\Gamma| = |S_{11}|$ were measured, and P_R was calculated based on the magnitude of the coefficient of reflection ($P_R = |\Gamma|^2 P_I$). The shielding effectiveness was measured according to ASTM D4935 standard [12].

The total *SE* of the composite absorbing materials, containing the hybrid filler, is given on Fig. 3 as a frequency function from 1 ÷ 12 GHz.

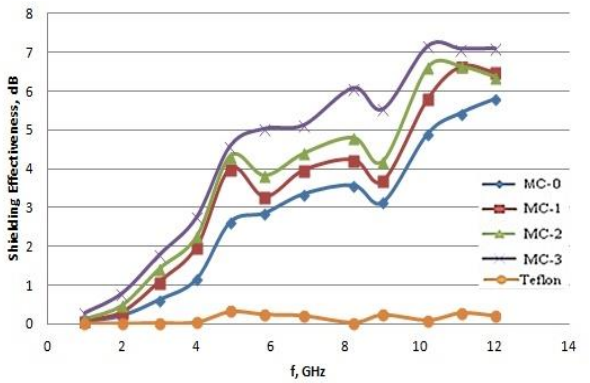

Fig. 3. Total shielding effectiveness of the obtained absorbing materials and Teflon.

From the results obtained it is evident that in the whole frequency range all absorbing materials show similar behavior. Increasing the amount of the magnetic phase, the shielding efficiency increases. The trend of change of total *SE* in frequency range 5 ÷ 12 GHz is similar for all examined samples, in a range of approximately 2.5 dB, reaching a maximum value for MC-3 of 7.16 dB at a frequency of 10 GHz. Sample MC-0 has the lowest sensitivity compared to all composite materials. The better shielding effectiveness exhibits MC-3 with the highest magnetite phase. Throughout the whole band, Teflon does not show protective shielding properties, as expected.

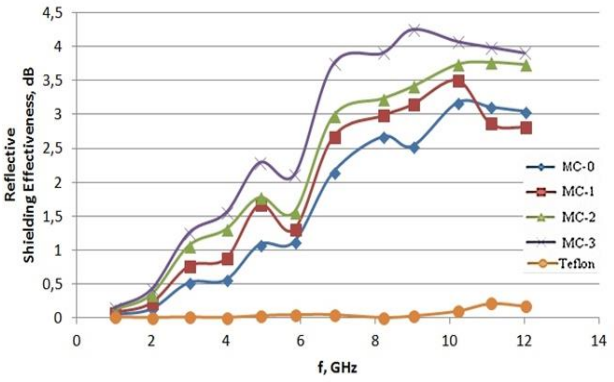

Fig. 4. Reflective shielding effectiveness of the absorbing materials and Teflon.

The results for SE_R are shown in Fig. 4. It is seen that the composite materials MC-1, MC-2 and MC-3 have the greatest protective properties due to the mechanism of reflection. Reflective *SE* improves with increasing the amount of the magnetic phase. It is evident that SE_R increases monotonously for all absorbing materials in the frequency range from 1 to 12 GHz. Sample MC-0 has the lowest values of SE_R for this frequency range.

Fig. 5 gives the results for the absorptive shielding effectiveness (SE_A). It can be seen that the absorption of the examined composite materials is in strong dependence from the frequency. It achieved a dynamic range around 2 dB at frequencies of 5.7 GHz, 11 GHz and 12 GHz and high values of 3 dB, 3.9 dB and 3.7 dB. Sample MC-3 has the best absorptive (SE_A) shielding effectiveness (Fig.5).

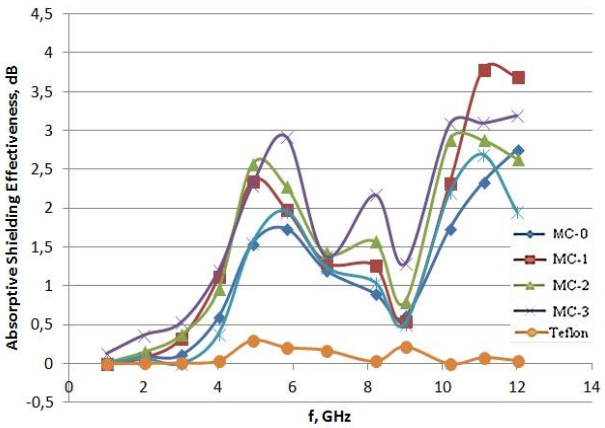

Fig. 5. Absorptive shielding effectiveness of the absorbing materials and Teflon.

Frequency dependence of the attenuation coefficient of the absorbing materials is presented in Fig. 6. From the data it is evident that all samples have strong frequency dependence of the attenuation coefficient with well-pronounced minimums and maximums.

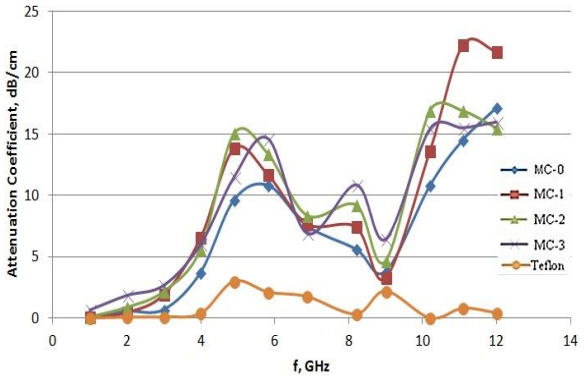

Fig. 6. Frequency dependence of the attenuation coefficient of the absorbing materials and Teflon.

An increase of attenuation coefficient is observed for the frequency range between 10 ÷ 12 GHz. Maximum value of the attenuation coefficient, greater than 20 dB/cm was observed for all samples at 11-12 GHz frequency.

4 Concussion

The influence of the two-phase hybrid filler on the microwave characteristics was examined. It was found that the total *SE* of composite microwave absorbers is mainly due to the mechanism of reflection of electromagnetic power SE_R. However, for all samples, the SE_A has a decisive role in the 5-6 GHz band. The results obtained show that the highest total shielding effectiveness among the studied absorbing materials has the sample MC-3 with maximum content of magnetic phase.

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