

Comparison of properties of natural rubber composites with hybrid fillers containing different modifying phase and their applicability in flexible antennas

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The paper presents a comparison of the effect that the chemical nature and structural specifics of the modifying oxide phase has upon dielectric and magnetic properties of natural rubber based composites. The fillers used have been prepared by impregnation of conductive carbon black with modifying oxides, SiO₂ and Fe₃O₄. The applicability of the composites as substrates in small flexible wearable antennas was investigated. It has been found that the chemical and crystallographic nature of the oxide modifying phase are the crucial factors determining the real parts of permittivity and permeability and loss angle tangents of the composites comprising the hybrid fillers. All composites developed meet the requirements of the rubber substrate antenna material. When better antenna characteristics are required, it is preferable the antenna substrate to be of a composite comprising hybrid filler with a silica phase. When focusing on the miniaturization of the antenna, it is preferable to use a hybrid filler with a magnetite modifying phase.

Keywords – dielectric properties; magnetic properties; natural rubber based composites; hybrid fillers; oxide modifying phase; flexible wearable antenna

INTRODUCTION

Recently, the markets for equipment for high-frequency wireless LAN, RFID (radio frequency identification), UWB, GPS, terrestrial digital broadcasting, home network, etc. have been dramatically expanding. In this context, a diversity of dielectric antennas are currently used. Conventional antennas often consist of a ceramic material whose relative dielectric constant cannot be arbitrarily selected. Consequently, the degree of freedom in designing antenna is low. Furthermore, these conventional antenna materials are hard and brittle, lack flexibility and are vulnerable to impact [1]. Therefore, the elastomer based composites are an alternative to conventional antenna materials used as substrates.

The requirements and typical features of **the rubber substrate antenna material** may be summarized as follows [1,2]:

- Relative dielectric constant can be selected arbitrarily (4-20). According to other authors, the dielectric constant of the various flexible substrates is in the range of 2.2-12.0 [3]. The lower dielectric

constant declines the surface wave losses which are related to the guided wave broadcast within the substrate [4].

- Low dielectric loss tangent (0.01 or lower)

Loss Tangent ($\tan\delta$) is also identified as a dissipation factor. It describes the amount of power turned into heat in the substrate material. The loss tangent in the following relation is defined as the ratio of the imaginary part to real part of the relative permittivity. The higher values of loss tangent results in additional losses in the dielectric substrate and higher losses outcomes in reduced radiation efficiency [5].

- Magnetic permeability, especially the tangent of the magnetic losses angle directly, is related to miniaturization of the antenna and its other important parameters like the geometric ones [6]. In literature [6,7] the values for these parameters, which depending on the frequency domain of the antenna, may vary between 1 and 6.5 for the real part of magnetic permeability between 0.003 and 0.5 for the tangent of magnetic losses angle.

As known, each environment is characterized by wave impedance [8] which is affected by the real and imaginary part of the

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dielectric and magnetic permeability. Our working hypothesis is that by appropriate choice of the dielectric permittivity and magnetic permeability of the elastomer based composites used as substrates in small flexible wearable antennas one can achieve the best their performance. The last includes a minimal absorption of electromagnetic power in the human body and most of power in the free space around it. In accordance with the further development of our hypothesis, the dielectric permittivity and magnetic permeability of the tested composites can easily and accurately be adjusted using optimal quantities of hybrid fillers, whose characteristics can be controlled by introducing an inorganic modifying oxide phase into a highly conductive carbon phase. The conductive aggregates and agglomerates could be insulated by introduction of a second less conductive phase to fill the space between the aggregate and agglomerates. The second phase would have its own contribution to the formation of the dielectric and magnetic losses of the composite. For the purpose we have chosen two oxide phases differing completely in their chemical, crystallochemical and crystallographic properties, namely SiO_2 (silica) and Fe_3O_4 (magnetite) as a modifying phase.

Taking into consideration the specific features of the impregnation technologies [9] we have found them to be the most appropriate for synthesizing hybrid dual-phase fillers, containing different modifying phase.

In accordance with the working hypothesis, the paper presents a comparative study on the effect that the chemical nature and structural specifics of the modifying oxide phase has upon dielectric and magnetic properties of natural rubber based composites filled with hybrid fillers based on conductive carbon black. The applicability of these composites as substrates in small flexible wearable antennas is also investigated. The fillers have been prepared by an impregnation technology at equivalent amounts of the oxide phases.

EXPERIMENTAL

Materials

Natural rubber SVR 10 supplied by Hong Thanh Rubber Pty. Ltd. was used as a polymer matrix. The other ingredients such as zinc oxide (ZnO), stearic acid, N-tert-butyl-2-benzothiazole sulfenamide (TBBS) and sulfur (S) were commercial grades and used without further purification.

Electroconductive carbon black (CCB) Printex XE-2B (produced by Orion Engineered Carbons GmbH) was used as a substrate of the hybrid fillers.

Hybrid fillers preparation

Preparation of the conductive carbon black-magnetite (CCB/M) hybrid fillers. Conductive carbon black (90 g) and 10 g of magnetite (containing 95-100% of Fe_3O_4 and 0-5% of silica, purchased from Inoxia, UK) were loaded into a ball mill, 1500 ml of ethyl alcohol were poured and the carbon black was impregnated for 2 h. Ethyl alcohol was used to avoid eventual oxidation of magnetite. The suspension thus obtained was dried at 50°C for 2 h. Then the temperature was raised to 150°C and the drying continued for 2 more hours till the product was completely dry. The yield was ground again in a ball mill for 2 h. After that the grind was loaded into the reactor and heated under 10^{-2} mm Hg vacuum at 440°C for 2 h. If necessary, the product was ground once more in a ball mill.

Preparation of conductive carbon black-silica (CCB/S) hybrid fillers. Conductive carbon black (90 g) and 32.5 ml of silicasol (containing 40% of SiO_2 , pH – 9 and density 1.3 g/cm^3) comprising 10 g of silica, were loaded into a ball mill and 1600 ml of distilled water were poured. The carbon black was impregnated for 2 h and the product was dried at 150°C till the complete evaporation of water. The dried product was ground again in a ball mill for 2 h. After that the grind was loaded into the reactor and heated under 10^{-2} mm Hg vacuum at 440°C for 2 h. Being removed from the reactor, the sample was ground once more in a ball mill and was ready for further experiments.

Preparation of rubber composites. The rubber compounds studied were prepared on a two-roll laboratory mill (rolls Length/Diameter 320x160 mm). Table 1 presents the compositions of the rubber compounds studied.

Table 1: Compositions of the investigated natural rubber based composites (phr)

	CCB	CCB/ /silica	CCB/ magnetite
Natural Rubber – SVR 10	100.0	100.0	100.0
Zinc Oxide	3.0	3.0	3.0
Stearic Acid	2.0	2.0	2.0
CCB	70.0	-	-
CCB/S(90:10)	-	70.0	-
CCB/M (90:10)	-	-	70.0
TBBS	1.5	1.5	1.5
Sulfur	2.0	2.0	2.0

The vulcanization of the natural rubber based compounds was carried out on an electrically heated hydraulic press using a special homemade steel mold at 150°C and 10 MPa. The optimum vulcanization time was determined by the vulcanization isotherms in accordance with ISO 3417:2002. The specimens needed for the

measurements cut from the obtained vulcanizates were 200x200x2 mm in size.

Measurements

Characterization of the studied fillers. The texture characteristics of the studied fillers were determined by low-temperature (77.4 K) nitrogen adsorption on a Quantachrome Instruments NOVA 1200e (USA) apparatus. The nitrogen adsorption-desorption isotherms were analyzed to evaluate the following parameters: specific surface area (S_{BET}) determined on the basis of the BET equation and total pore volume (V_t) estimated in accordance with the Gurvich rule [10]. The average diameter of the mesopores and their size distribution were determined by the method of Barrett-Joyner-Halenda (BJH) [11]. The volume of the micropores (V_{MI}) and the their specific surface area (S_{MI}), as well as the external specific surface area (S_{EXT}) were evaluated according to V-t-method [12]. Additionally, the pore-size distributions were calculated by the density functional theory (DFT) method using NLDFT equilibrium model [13]. All samples were outgassed for 16 hours in vacuum at 120°C before the measurements. The iodine adsorption number (IA) was determined in accordance with ISO 1304:2006; oil absorption number (OAN) – in accordance with ISO 4656:2012.

The hybrid fillers were also investigated by TEM to ascertain the distribution of carbon, silica and magnetite. The TEM investigations were performed on a TEM JEOL 2100 instrument at accelerating voltage of 200 kV. The specimens were prepared by grinding and ultrasonic dispersion in ethanol for 6 minutes. The suspension was dripped on standard holey carbon/Cu grids. The measurements of lattice-fringe spacing recorded in HRTEM micrographs were made using digital image analysis of reciprocal space parameters. The analysis was carried out by the Digital Micrograph software. TEM JEOL 2100; XEDS: Oxford Instruments, X-MAX^N 80T; CCD camera Orius 1000, 11 Mp, GATAN.

Characterization of the studied composites

Permittivity and permeability measurement. The electromagnetic parameters of the composite materials were measured by the resonant perturbation method [14]. For the rectangular cavity, the TE_{10n} modes were used for the complex permittivity and permeability measurements. The sample was placed at the position of maximum intensity of electric field, where $n=odd$ was always adopted, because the sample position could be located easily as the geometric center of the cavity is one of the maximum positions [15]. The formulas for

the real and imaginary parts of the relative permittivity areas are the following [16]:

$$\epsilon' = \left(\frac{f_c - f_s}{2f_s} \right) \left(\frac{V_c}{V_s} \right) + 1 \quad (1)$$

$$\epsilon'' = \left(\frac{V_c}{4V_s} \right) \left(\frac{1}{Q_s} - \frac{1}{Q_c} \right) \quad (2)$$

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

For permeability measurements the sample was placed at the position of maximum magnetic field, where $n=even$ was always adopted.

The formulas for the real and imaginary parts of the relative permeability areas are the following [17]:

$$\mu' = \left(\frac{f_c - f_s}{f_s} \right) \left(\frac{V_c}{V_s} \right) \left(\frac{\lambda_g^2 + 4a^2}{8a^2} \right) + 1 \quad (3)$$

$$\mu'' = \left(\frac{V_c}{V_s} \right) \left(\frac{1}{Q_s} - \frac{1}{Q_c} \right) \left(\frac{\lambda_g^2 + 4a^2}{16a^2} \right) \quad (4)$$

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

The measurements were performed at room temperature varying from 19°C to 24°C within the frequency range of 3.0 GHz to 9.5 GHz, at incident power ≤ 5 mW.

The loss tangents were calculated by the equations:

$$\tan \delta_\epsilon = \epsilon''/\epsilon' \quad (5)$$

$$\tan \delta_\mu = \mu''/\mu' \quad (6)$$

RESULTS AND DISCUSSION

Characterization of the studied fillers

Table 2 summarizes the main characteristics of the substrate carbon black and of the hybrid fillers with different modifying phase obtained.

The oil absorption number (OAN) or dibutylphthalate absorption (DBPA) of the fillers gives an idea of their ability to form different secondary structures – aggregates and agglomerates. Therefore OAN is a crucial parameter for most of the fillers used in rubber industry [18, 19]. As Table 2 shows, OAN of virgin Printex XE-2B carbon black is 420 ml/100g. The conductive carbon black/silica (CCB/S) filler obtained by impregnation has an OAN value of 505 ml/100g. That indicates the prepared hybrid filler to be more capable of forming different secondary structures than the non-modified carbon black. That is because the former filler comprises silica. As known, silica is hydrophilic – there are hydroxyl (silanol) groups interacting with each other via hydrogen bonds over its surface.

Table 2. Main properties of the studied fillers

Sample	OAN, ml/100g	IA, mg/g	S _{BET} , m ² /g	S _{MI} , m ² /g	S _{EXT} , m ² /g	V _t , cm ³ /g	V _{MI} , cm ³ /g	D _{AV} , nm
Printex XE-2B	420	1125	1000	-	-	-	-	-
Printex XE-2B/SiO ₂	505	770	870	74	817	1.67	0.025	7.6
Printex XE-2B/Fe ₃ O ₄	410	695	861	66	794	0.03	1.450	6.7

Hence, silica is more apt to agglomerate than carbon black. The hybrid filler comprising magnetite has an OAN value lower than that of the substrate carbon black because of the functional groups over its surface what favors the filler-filler interactions.

The iodine adsorption (IA) of fillers reveals their adsorption activity, towards the elastomer macromolecules, inclusive. Obviously, the adsorption ability of silica is greater than that of magnetite owing first of all to the adsorption centers and to polar functional groups available on the surface of its particles what determines its higher iodine number.

As seen from Table 2, the specific surface area (BET) of virgin carbon black (Printex XE-2B) is about 1000 m²/g. The introduction of a second phase lowers the specific surface area, as the specific surface area of the oxide phase, and particularly of magnetite, is lower.

Obviously, the difference in the properties of SiO₂ and Fe₃O₄ used for the modification is quite

significant and leads to differences in the adsorption-texture parameters of the hybrid fillers obtained. Some of those parameters (specific surface area of the micropores, external specific surface area, the average pore diameter) have close values but two of their texture characteristics differ significantly: the total pore volume of silica (1.67 cm³/g) is much higher than that of magnetite (0.03 cm³/g), while in the case of micropores volume it is on the contrary – that of magnetite (1.450 cm³/g) is higher than the one of silica. The differences are a consequence of the crystallographic and crystallochemical differences between amorphous SiO₂ and crystalline Fe₃O₄. As seen, the micropores dominate in Fe₃O₄ volume while mesopores are predominant in SiO₂.

The distribution of carbon, magnetite and silica phases within the hybrid filler obtained was investigated by scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS).

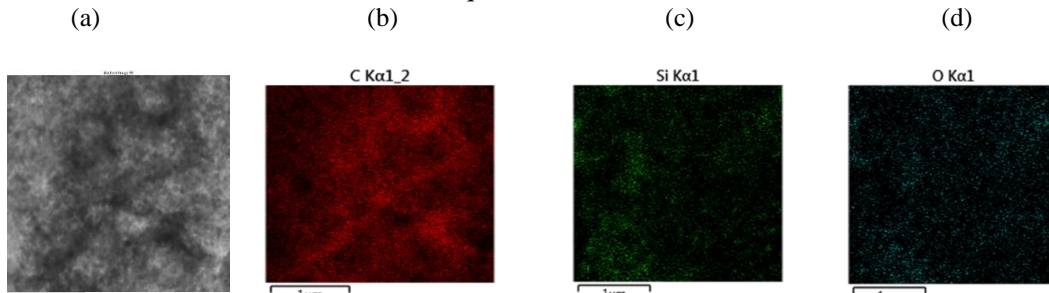


Fig. 1. a) Bright field STEM image of CCB/S hybrid filler; b) carbon map; c) silicon map; d) oxygen map

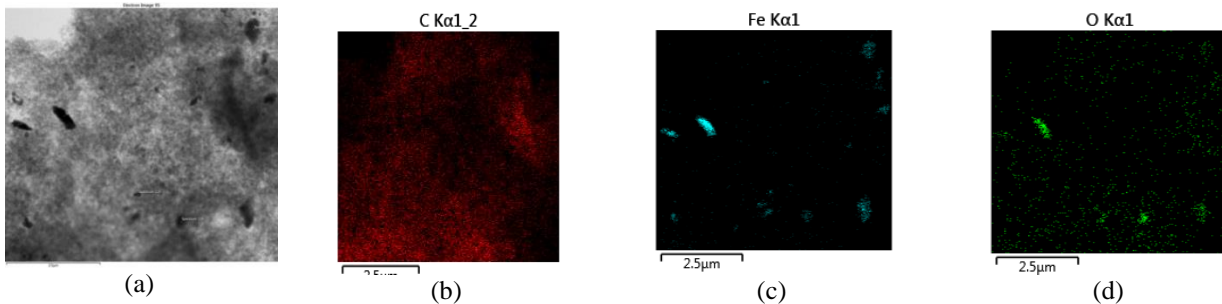


Fig. 2. a) Bright field STEM image of CCB/M hybrid filler; b) carbon map; c) iron map; d) oxygen map

Fig. 1 and Fig. 2 present the bright field STEM images and the compositional maps of the hybrid fillers investigated.

First of all figures 1 - 2 confirm the successful modification of conductive carbon black with the different oxide phases which yielded hybrid fillers of

a different type. The compositional maps of the fillers obtained demonstrate the silica phase to be distributed in the carbon one more homogeneously than the magnetite phase. Oxide phases are distributed mainly over the surface of carbon aggregates, though there are cases of greater aggregation when the oxide phase, especially magnetite, interpenetrates the aggregates. STEM is in agreement with the texture characteristics of the studied hybrid fillers and supports the data from the composition maps, confirming the fact that the oxide phases in both fillers hinder to a certain extent the contacts between carbon black aggregates and

agglomerates. That phenomenon could be a tool for tailoring the permittivity and permeability of elastomer composites by regulating the oxide phase amount and its chemical nature in the hybrid fillers used to reinforce the composites. TEM high resolution micrographs (x 400 000) are a good illustration of that effect (Fig. 3). The oxide phase distributed amongst (and probably inside) carbon black aggregates and insulating them, occurs on the image as darker and ordered structures. The effect is better pronounced for silica (Fig. 3c).

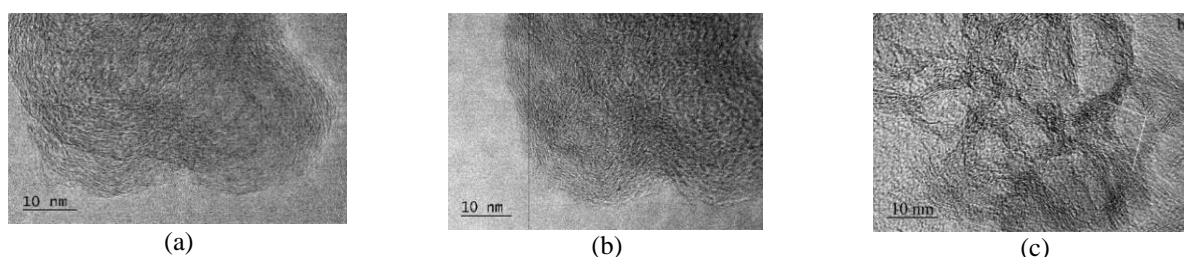


Fig. 3. High resolution TEM images of a filler comprising: a) 0 wt % magnetite; b) 10 wt % magnetite; c) 10 wt % silica

Obviously, the oxide phase having a resistance higher than that of conductive carbon black hinders the formation of electro conductive pathways. The process is more pronounced when silica is used as modifying phase.

Complex permittivity and permeability

Composites and their applicability as substrates for small flexible wearable antennas are characterized by their relative permittivity (ϵ_r^*) and permeability (μ_r^*). These properties are reported in terms of relative complex numbers: $\epsilon^* = \epsilon_r' - j\epsilon_r''$ and $\mu_r^* = \mu_r' - j\mu_r''$. They both express the interactions between composite materials and electromagnetic fields [20, 21]. The permittivity is a measure of the effect that a material has on the electric field in the electromagnetic wave and the permeability is a measure of the effect that a material has on the magnetic component of the wave. Figures 4-5 present the frequency dependences of the real part of the permittivity and the tangent of dielectric loss angle of the composites containing hybrid fillers with different oxide phase.

As seen from Fig. 4, the values of the real part of the relative permittivity for the composite comprising a hybrid filler with a silica phase are

expectedly higher than those of the composite comprising a hybrid filler with a magnetite phase. The values recorded in the 4-8 GHz range are in the 4-20 scale, i.e. those composites meet the requirements for materials with potential application as substrates for small wearable flexible antennas. The difference might be related to the difference in chemical and crystallographic nature of the two oxides.

Therefore the latter have a very different effect upon the factors determining the real part of the relative permittivity. It can be seen from Figure 5 that the tangent of the dielectric loss angle of the composite with the magnetite modifying phase is in the range of 0.7-3.5 while those for the composite comprising silica are in the 0.01-0.4 range (Fig. 5). It is obvious that composites with hybrid fillers containing silica as second modifying phase meet in higher extent the requirements to the rubber substrate antenna material [1, 2]. Figures 6-7 present the frequency dependences of the real part of the relative permeability as well as the frequency dependence of the of magnetic loss angle of the composites containing hybrid fillers with different oxide phase.

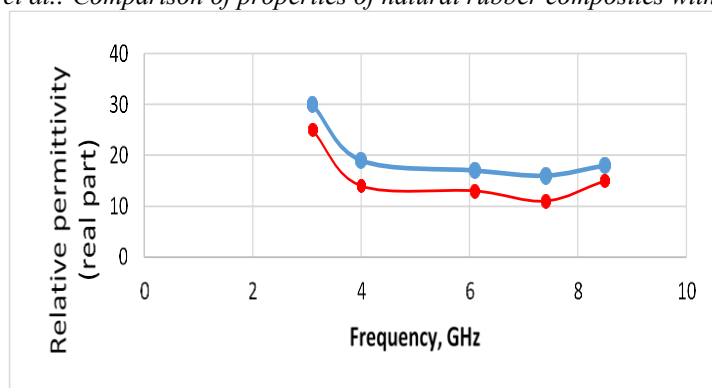


Fig. 4. Frequency dependence of the real part of the relative permittivity of composites containing hybrid fillers with different oxide phase

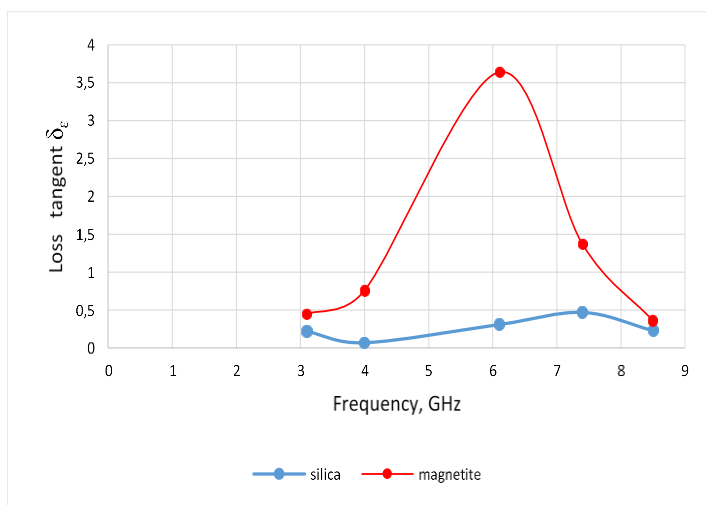


Fig. 5. Frequency dependence of the tangent of dielectric loss angle of composites containing hybrid fillers with different oxide phase

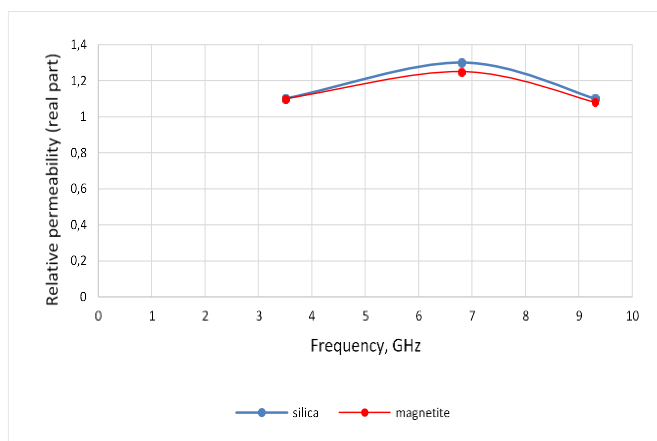


Fig. 6. Frequency dependence of the real part of the relative permeability of the composites containing hybrid fillers with a different oxide phase

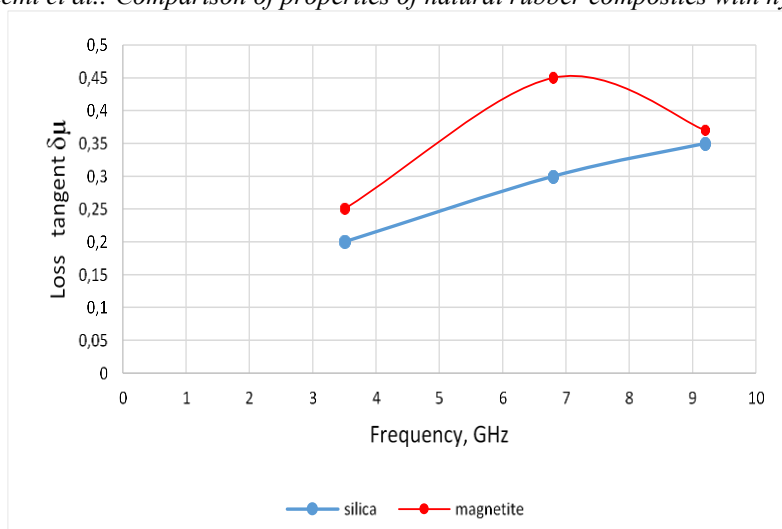


Fig. 7. Frequency dependence of the tangent of magnetic loss angle of composites containing hybrid fillers with a different oxide phase.

As seen from Figure 6, the real parts of the relative permeability for the two composites are quite close (around 1.1-1.3), while the values of the tangent of magnetic loss angle (Figure 7) for the composite with a hybrid filler comprising magnetite are higher (0.25-0.45) than the composites comprising silica (0.20-0.35) but in both cases they meet the requirements for substrates of wearable flexible antennas.

The properties of both dielectric matrix and conductive filler, as well as the morphology and structure of the composite affect the changes in the real and imaginary part of dielectric permittivity [14]. It is obvious that, the applicability of thus reinforced composites for wearable flexible antennas is affected by the modifying oxide phase in the hybrid fillers studied. It impacts mainly the imaginary part of the relative permittivity and permeability and the merit that each of the latter has to the dielectric and magnetic loss tangent. We suppose the introduction of magnetite into Printex XE2-B carbon black, which initially contains vanadium, nickel and iron, leads to the formation of different dipoles. These different dipoles have different relaxation time, giving rise to different relaxation frequencies. The different relaxation frequencies of the various dipoles formed in the composites, hopping of electrons (between Fe^{+3} and Fe^{+2}) and the relaxation due to interfacial polarization are altogether responsible for the resonant behavior of ϵ_r' and ϵ_r'' . The effects of the oxide phases are definitely related to the difference in their crystallochemical and crystallographic structure. The differences could be summarized as follows:

Magnetite, a high magnetic losses material, belongs to the spinel class and may be characterized by its low toxicity and great stability at high temperature [22]. On the other hand, magnetite crystal structure follows an inverse spinel pattern with alternating octahedral and tetrahedral-octahedral layers. The oxygen ions form a close-packed cubic lattice with the iron ions located at interstices between the oxygen ions. There are two different interstices that the metal ions can take: tetrahedral (A) sites and octahedral (B) sites – Fig. 8 [23]. It is known, that the octahedral sites in the magnetite structure contain ferrous and ferric species. The electrons coordinated with these iron species are thermally delocalized and migrate within the magnetite structure causing high conductivity exchange constants: ranging from $-28 \text{ J}\cdot\text{K}$ to $3 \text{ J}\cdot\text{K}$ between tetrahedral/octahedral sites and octahedral/octahedral sites, respectively [23]. Resultant conductivities range from 10^4 – $10^5 \text{ }\Omega^{-1}\text{m}^{-1}$. Magnetite's Curie temperature is observed at 850 K. Below the Curie temperature, the magnetic moments on tetrahedral sites, occupied by ferric species, are ferromagnetically aligned while the magnetic moments on octahedral sites, occupied by ferrous and ferric species, are antiferromagnetic and cancel each other; such a combined behavior is termed ferrimagnetic [23]. Amorphous silica (SiO_2) is an inorganic material commonly used in semiconductor circuits to isolate different conducting regions. Due to its mechanical resistance, high dielectric strength, and selectivity for chemical modification, amorphous silica has also become a key material in microelectronics. The spatial structure of amorphous silicon dioxide is presented in Fig. 9 [24].

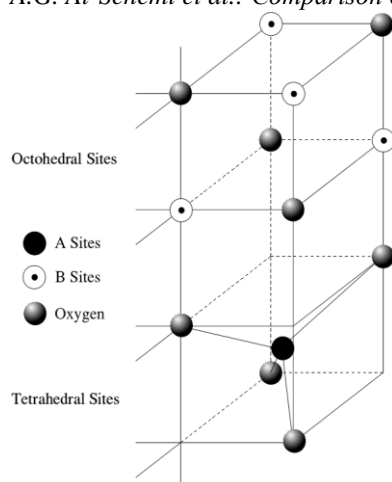


Fig. 8. Crystal structure of magnetite [23]

Comparing Fig. 8 and Fig. 9 one sees the great difference in the chemical, crystallochemical (the dependence of the crystals properties on their atom structure and type of bonds between the atoms) and crystallographic nature of the two oxide phases. That explains the different impact upon the hybrid fillers comprising them, as well as on the permittivity and permeability of the composites reinforced with the hybrid fillers. The crystallochemical factor is of particular importance in the case of magnetite. The comparison of FeO , Fe_2O_3 and Fe_3O_4 reveals that, the three compounds could be described as the densest packing of oxygen ions. However, in the case of the first oxide ferric ions occupy all the octahedral sites, in the case of the second one – $2/3$ of the octahedral sites and in the case of magnetite – half of all existing octahedral and $1/8$ of the tetrahedral sites. Meanwhile magnetite properties are much different from those of the other two ferric oxides and naturally are most favorable for applications in the manufacture of small flexible wearable antennas due to the existing magnetic losses. The magnetic losses for magnetic materials originate mainly from domain wall resonance, hysteresis loss, eddy current loss, and natural resonance [25]. The domain wall resonance normally happens at a frequency lower than 100 MHz, hence it can be neglected in the microwave range. The hysteresis loss is produced in a very strong external magnetic field, and there is no hysteresis loss in the weak magnetic field derived from microwaves. In this study the relative permeabilities were measured at a low microwave power (≤ 5 mW) and over a frequency range of 3.6 GHz to 9.3 GHz, so neither hysteresis loss nor domain wall resonance is the main contributor to magnetic loss. Therefore, the magnetic loss in the composites results from complex phenomena like eddy current loss and natural resonance. In our case,

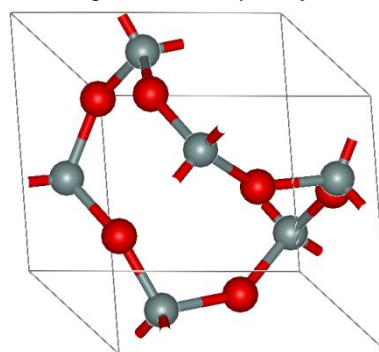


Fig. 9. Spatial structure of amorphous silicon dioxide [24]

the effect that magnetite has is doubtless. In fact, that is the major difference between magnetite and silica phases - the latter cannot produce such an effect. It is also important to note that the hybrid fillers and the changes in them due to the different oxide phase included influence on the interphase region between the rubber matrix and the filler.

Possible applications of the composites comprising hybrid fillers with different oxide phases for enhancing antenna performance

It is seen from the results obtained that both types of composites developed containing hybrid fillers with different modifying oxide phase meet the requirements to the materials which may be used as substrates in flexible antennas. Substrates containing a hybrid filler with one of the two oxide phases can be implemented when particular objectives and requirements should be met. When good characteristics are required, it is preferable the antenna substrate to be of a composite comprising hybrid filler with a silica phase. When focusing on the miniaturization of the antenna, it is preferable to use a hybrid filler with a magnetite phase. In certain cases, two-layered or three-layer substrates made of composite materials containing fillers with both phases - magnetite and silica - can also be used. Choosing one or another modifying oxide phase one can control the properties of the hybrid fillers, respectively the dielectric and magnetic properties of the composites containing them. However, the results from our further experiments have shown that composites with hybrid fillers containing silica as modifying phase are more suitable as flexible antenna substrates than composites containing hybrid fillers with magnetite. A conductive composite loaded with carbon black-silica hybrid filler described above was proposed to reduce human (head or body) effects on antenna performance and SAR values. The investigation was based on a half dipole antenna. The results show a sensible

dependence of the antenna performance and SAR reduction on the size of the composite sample and on the distance between composite sample and reference dipole. We have shown that an appropriate placement of the conductive composite loaded with carbon-silica hybrid filler next to the reference dipole can effectively reduce SAR (up to 70 %), increasing the radiation efficiency (up to 67 %) and the bandwidth (up to 110 %) of the antenna. Consequently, using this technique and such type of composite, SAR, efficiency and bandwidth of the antenna can be improved simultaneously. Other advantages of the techniques that use a conductive composite loaded with a carbon-silica hybrid filler to reduce SAR and human effects on antenna performance are the low cost of the material itself and easy implementation. The results from this work can provide useful information in designing of antennas for wireless devices and are described in details elsewhere [26].

The composites comprising hybrid fillers with different oxide phases with parameters close to those required have been used also as a substrate for manufacturing a small flexible wearable antenna in the 2.22–2.50 GHz band, with dimensions of only 58x40x4.1 mm. The fabricated prototype has good impedance matching ($VSWR < 1.4$) over the targeted frequency band, an operating bandwidth of 11.68% at 2.44 GHz and efficiency of around 19%.

CONCLUSIONS

The impregnation method allows preparing hybrid fillers with modifying oxide phases as well as tailoring the properties of the fillers via control over the oxide phase concentration and chemical nature. The effect that the modifying oxide phase in hybrid fillers based on conductive carbon black has upon the properties of natural rubber composites has been studied. It has been established that the chemical, crystallochemical and crystallographic nature of the oxide phase are the crucial factors determining the permittivity and permeability of the composites comprising the hybrid fillers. Natural rubber based composites containing hybrid fillers with silica as a modifying phase as a whole are more suitable as substrates in small flexible wearable antennas in comparison to composites containing hybrid fillers with magnetite. An appropriate placement of the conductive composite loaded with carbon-silica hybrid filler next to the reference dipole can effectively reduce SAR (up to 70 %), increasing the radiation efficiency (up to 67 %) and the bandwidth (up to 110 %) of the antenna. Consequently, using this technique and such type of composite, SAR, efficiency and bandwidth of the antenna can be improved simultaneously.

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REFERENCES

1. K. Oohira, *NTN Technical Review* **76**, 58, (2008).
2. M. Raees, S. H. Dar, J. Ahmed, *Int J Adv Comput Sci App*, **7**, 190, (2016).
3. C.A. Blannis, *Antenna Theory: Analysis and Design*, Third edition, Willey, 2005.
4. J. Bauer, M.D. Janezic, D.C. De Groot, *High Frequency Dielectric Measurements*, *IEEE Instru Meas Mag*, vol. 13, (2010).
5. B. Gupta, S. Sankarlingam, S. Dhar, In: *Proceeding of Mediterranean Microwave Symposium*, Turkey, 2010, p. 251.
6. L. Martin, D. Staiculescu, H. Li, S. Ooi, C. Wong and M. Tentzeris, *Investigation of the impact of magnetic permeability and loss of magnetic composite materials on RFID and RF Passives Miniaturization*, *IEEE 2007 Workshop on Computational Electromagnetics in Time-Domain*, 15-17 Oct. 2007, 1-4.
7. K. Borah, N. Bhattacharyya, *Compos Part B-Eng*, **43**, 1309, (2012).
8. Y. Wang, E. Edwards, I. Hopper, N. Clow, P. Grant *J Appl Phys A*, **120**, 609, (2015).
9. H. Marsh, E. Heintz, F. Rodrigues-Reinoso, (eds.) *Introduction to Carbon Technologies*, University of Alicante, Alicante, 1997.
10. L.J. Gurvich, *Zh Russ Fiz-Khim Obschestva Chem*, **47**, 805, (1915).
11. E.P. Barrett, L.G. Joyner, P.P. Halenda, *J Am Chem Soc*, **73**, 373, (1951).
12. S. Lowell, J. E. Shields, M. A. Thomas, M. Thommes, *Particle Technology Series*, **16**, 129, (2004).
13. R.G Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
14. L. F. Chen, C. K. Ong, C. P. Neo, V. V. Varadan, Vijay K. Varadan, *Microwave electronics: Measurement and materials characterization*. First ed., Chichester: John Wiley & Sons, Ltd., 2004.
15. J. Sheen, *Elsevier Measurement*, **42**, 57, (2009).
16. A. Verna, D. C. Dube, *IEEE Trans on Industrial Measurement*, **54**, 2120, (2005).
17. M. Lin, Y. Wang, M. N. Afsar, 30th Intl. Conf. on Infrared and Millimeter Waves & 13th Intl. Conf. on Terahertz Electronics, 2005, p. 62.
18. Donnet, J.-B. and E. Custodero, in: *The Science and Technology of Rubber*, J.E. Mark, B. Erman, C.M. Roland, (eds.), Academic Press: Boston. 2013, p. 383.

19. B. Rodgers, W. Waddell, in: The Science and Technology of Rubber, J.E. Mark, B. Erman, C.M. Roland, (eds.), Academic Press: Boston., 2013, p. 417.
20. D. Sirdeshmukh, L. Sirdeshmukh, K.G. Subhadra, C.S. Sunandana, Electrical, Electronic and Magnetic Properties of Solids, Springer, 2014.
21. A. Kaynak, A. Polat, U. Yilmazer, *Mater Res Bull*, **31**, 1195, (1996).
22. R.M. Cornell, U. Schwertmann, *The iron oxides*. VCH Press, Weinheim, Germany, 1996.
23. L. Blaney, *The Lihigh Review* **15-2007**, Paper 5, (2007).
24. R.W. Collins, A. S. Ferlauto, G. M. Ferreira, Chi Chen, J. Koh, R. J. Koval, *Solar Energy Materials and Solar Cells*, **78**, 143, (2003).
25. N.N. Song, H.T. Yang, H. L. Liu, X. Ren, H. F. Ding, X. Q. Zhang, A. H. Cheng, *Sci Rep-UK*, **3**, 3161, (2013).
26. A. A. Al-Ghamdi, O. A. Al-Hartomy, F. R. Al-Solamy, N.T. Dishovsky, N. T. Atanasov, G. L. Atanasova, *Int J Electron Communications*, **72**, 184, (2017).

СРАВНЕНИЕ НА СВОЙСТВАТА НА КОМПОЗИТИ НА БАЗАТА НА ЕСТЕСТВЕН КАУЧУК С ХИБРИДНИ ПЪЛНИТЕЛИ СЪДЪРЖАЩИ РАЗЛИЧНА МОДИФИЦИРАЩА ФАЗА И ТЯХНАТА ПРИЛОЖИМОСТ В ГЪВКАВИ АНТЕНИ

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(Резюме)

Статията представя сравнение на ефекта, който химичната природа и структурните особености на модифициращата оксидна фаза имат върху диелектричните и магнитни свойства на композити на базата на естествен каучук. Използваните пълнители са получени чрез импрегниране на проводящи въглеродни сажди с модифициращите оксиди, SiO₂ и Fe₃O₄. Изследвана е приложимостта на композитите като подложки за малки гъвкави носими антени. Установено е, че химичната и кристалографска природа на модифициращата оксидна фаза са решаващите фактори, определящи реалните части на диелектричната и магнитна проникваемост и тангенса от ъгъла на загубите на композитите, съдържащи хибридни пълнители. Всички разработени композити отговарят на изискванията към материалите за каучукови подложки на антени. Когато се изискват по-добри характеристики на антената, за предпочитане е подложката на антената да бъде от композит, съдържащ хибриден пълнител с модифицираща фаза от силициев диоксид. Когато фокусът е върху минитюаризацията на антената, за предпочитане е да се използва хибриден пълнител с магнетитна модифицираща фаза.