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MICROWAVE RADIATION SHIELDING EFFECTIVENESS OF COMPOSITE LIQUID-CONTAINING MATERIALS IN DEPENDENCE ON HYGROSCOPIC PROPERTIES OF THE COMPOUNDS

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Summary: Composite shielding materials based on capillary-porous matrixes impregnated with liquid solutions possessing resistive and dielectric losses for microwave electromagnetic radiation (EMR) are developed.
Meeting the objectives the EMR attenuation obtained by the proposed materials can be higher than 12…19 dB, with the reflection level lower than -2…-8 dB in the frequency range 8…11.5 GHz.
Study of liquid content dynamics upon the surface of non-sealed sample revealed that synthesis of 40…60 mass. % solution results in stabilization of liquid content of capillary-porous matrix at the level not lower than 100…108 % mass. of the initial value.

Keywords: composite shielding material, electromagnetic radiation, sorption.

1. Introduction

There is a wide range of structures, materials and coatings capable to shield incident electromagnetic waves in a certain frequency range due to reflection, absorption, scattering and some other physical mechanisms [1]. Composite liquid-containing materials based on porous matrixes are promising to be used to shield electromagnetic radiation in a SHF frequency range [2]. Inorganic oxides, carbon and various natural sorbents, polymers, porous metals, composites and their mixtures possess high sorption properties. The internal porous structure of the material can be formed by powder, fiber or solid elements of the matrix.
The absorptive properties of the matrix strongly depend on its internal structure, pores dimensions, and the material it is made of. From this point of view the physicochemical properties of the material, such as hygroscopicity, wettability, swelling factor are of great importance.
Certain non-organic salts, their mixtures. solutions and crystalline hydrates introduced into the pores of the matrix significantly increase the hygroscopic capability of composite materials and thus affect their EMR shielding capability.

2. Experimental

The EMR shielding effectiveness (SE) produced by the composite liquid-containing materials depends on their structural features as well as the filling solution content, forming a dispersed liquid structure with various types of physical and chemical bonds thus forming layers of liquid having various properties [3, 4].
Polar dielectric liquids are usually used as a base for filling solution of the described composite materials. Synthesis of solutions allows to vary their physical and chemical properties in a certain range thus affecting the shielding effectiveness and the reflection and absorption levels of such materials [5]. The capability to absorb the energy of the electromagnetic wave by polar liquids is caused by the process of orientational polarization relaxation of the dipoles and complex structures formed by the liquid molecules. In the SHF range the permittivity dispersion of the polar dielectric liquids is described by the Debye equation [6]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau}, \quad (1)$$

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2}, \quad \varepsilon''(\omega) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2}\omega\tau, \quad (2)$$

where ε_s and ε_∞ – are the static and high-frequency values of the permittivity; ω – is the frequency of the external alternating electric field; τ – is the relaxation time of liquid molecules.

As numerous experiments show the SE of liquid-containing composites can vary from 0 up to 35 dB in the frequency range of 1…118 GHz by varying the liquid content and its composition for 3 mm thickness.

Composite shielding materials based on porous matrixes filled with powders, fibers or liquid are widely used in the SHF range. Materials of these kinds always contain some amount of moisture within their capillary-porous space, this amount being determined by the material operating conditions and the environment. When contacting with the humid air the dry porous matter containing small-sized capillaries within its structure become moist as a result of capillary condensation [7]. For example, if the air humidity is $\varphi = 0.35$ all the capillaries smaller than 10^{-9} m in diameter are filled due to moisture condensation, if $\varphi = 0.9$ — all the capillaries smaller than 10^{-8} m in diameter are filled. The equilibrium moisture content of the capillary-porous materials at the environment temperature of 20°C and the humidity of 80 % is 0.01 grams per gram.

In order to keep the liquid molecules within the composite structure the salts of alkaline-earth metals were chosen to be used as solution components, as they are characterized by high absorptive properties [8]. The ions leave the salt crystal surface contacting the liquid as a result of natural oscillations of the microparticles as well as because they are attracted by liquid molecules.

This process leads to the substance solving and the diffusion of ions of the solved substance in the liquid thus forming the solution. The chemical bonds between the dissociated salt ions and the liquid molecules prevent the liquid molecules evaporation from the matrix pores, thus keeping stable the level of liquid content in the composite porous material.

The solution of the anhydrous alkaline-earth metal salt continues to absorb the liquid reaching the equilibrium concentration until the vapor tension above the solution is counterbalanced by the air vapor tension at a certain environment temperature. The salt ions interact with the liquid molecules through the hydrogen bonds. As the ions of the anhydrous alkaline-earth metal salt are more electronegative than the hydrogen ions the liquid structure is broken thus forming a new structure of the alkaline-earth metal salt solution. The solution with an equilibrium concentration of the non-organic salt allows stabilizing the liquid content of the shielding materials regardless the operating conditions of the EMR shields based on such kind of composite materials.

This investigation is aimed to study the hygroscopicity of various porous matrixes impregnated with a non-organic salt solution, as well as at gravimetric investigation of the liquid-containing porous materials and obtaining their shielding effectiveness characteristics in the super high frequency (SHF) band. Using the obtained results we can analyze the relation between the shielding characteristics and the hygroscopic properties of the capillary-porous fiber and powder matrixes filled with a solution.

Three kinds of samples were studied differing by the matrix material, structure and capillary condensation conditions. The samples description is given in Table 1.

Table 1. Samples description

№	Matrix type	Filling solution
1	Knitted fabric of polyacrylonitrile fibers (matrix thickness d=1 mm)	45% mass. solution of the anhydrous alkaline-earth metal salt
2	Cellulose non-woven matrix (matrix thickness d=2 mm)	45% mass. solution of the anhydrous alkaline-earth metal salt
3	Solid hydrophilic sorbent d=4 mm in thickness, placed on the cellulose base	45% mass. solution of the anhydrous alkaline-earth metal salt

The knitted fabric has a highly dense and porous structure made by solid synthetic fibers with the maximum pore size of 2 μm.

The cellulose non-woven matrix is anisotropic and has a pressed structure with the average diameter of macropores from 10^{-6} to 10^{-7} m

Solid hydrophilic sorbent shaped in spherical granules for the third kind of samples was patterned into a field-interleaved structure placed on the cellulose base 2 mm in thickness. The average pore size of the solid hydrophilic sorbent is 6 nm.

All the samples were impregnated with the 45% mass. solution of the anhydrous alkaline-earth metal salt for 1 day to a complete saturation. No additional sealing was applied for the samples. The liquid content of the impregnated matrixes was gravimetrically studied during 100 days. At the same time the SE of the matrixes was measured in the frequency range of 8...11.5 GHz by the scalar network analysis method using the panoramic meter of the VSWR and attenuation of the P2 type and rectangular waveguide measurement path with horn antennas.

The shielding effectiveness of the samples was estimated through the EMR attenuation and EMR reflection frequency behavior produced by the liquid-containing matrixes.

Attenuation of electromagnetic radiation is determined by the ratio between the power of incident electromagnetic wave and the power of the wave transmitted through the sample under study. The reflection level indicates the portion of electromagnetic energy retransmitted by the sample

back to the direction of the radiation. The measurements were carried after a standard calibration procedure under the normal incidence of electromagnetic waves on the sample.
The EMR reflection coefficient was measured in a matched waveguide section and a section loaded with metallic reflector. In the first case the obtained electromagnetic energy reflection level is determined mainly by waves reflected from the front interface free space / composite and waves scattering within the non-regular dispersed liquid structure. Shielding materials are normally applied to the devices containing metal parts, this can result in change of electromagnetic energy level reflected back to the radiation source. So it is important to estimate the EMR reflection coefficient of samples in the waveguide section loaded with metallic reflector, placed behind the sample.

Measurements were conducted at the first, seventh and the 100th day of the experiment.

3. Results and discussion

The results of the gravimetric investigations show the liquid content of the samples was kept stable during 100 days with a deviation not more than 8 % from the initial level. The results of the gravimetric investigations performed during the first seven days are given in Fig. 1.

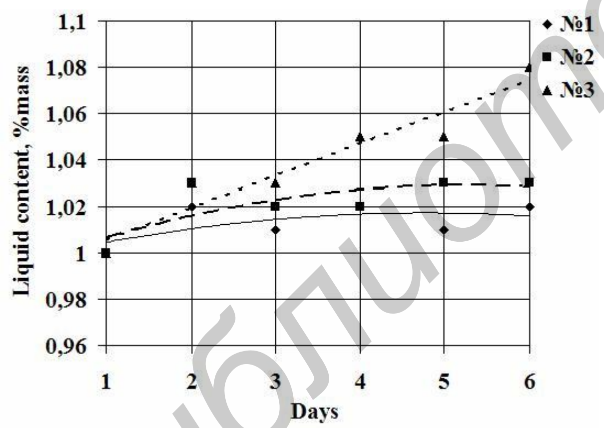


Fig. 1. Dynamics of liquid content of the composite porous matrixes: 1 – synthetic knitted fabric; 2 - cellulose non-woven matrix; 3 - solid hydrophilic sorbent

The difference of the liquid content dynamics for different samples can be explained through the difference of the hygroscopic properties of the matrixes.
It is obvious from the Fig. 1 that the samples of groups 1 and 2 absorb the liquid molecules from the ambient air to reach the equilibrium concentration. This process is ensured by the porous structure and the properties of the matrix fibers. During the matrix impregnation with the filling solution the liquid travels on the surface and moves inside the matrix pore space.
The liquid content of the samples increases as a result of liquid molecules attraction in a direction which is parallel to the porous matrix surface thus forming a thin layer of the saturated solution. According to that the maximum level of the liquid content depends on the hydrophilic properties of the surface fibers of the matrix material.
In the case of synthetic knitted fabric used as a matrix a physical absorption occurs caused by the intermolecular interaction between the solid surface and the absorbed molecule as well as by capillary soaking of liquid under surface tension force. The liquid molecule keeps its individuality though it can be curved or stretched because of the surface proximity and the chemical bonds are not broken or formed.
When the cellulose molecules interact with the liquid molecules their hydration with swelling occur. The cellulose materials have a complex fibril structure. The cellulose macromolecule structure determines the elongated morphology of the material. The liquid molecules combine with the cellulose hydroxyl groups forming chemical bonds that results in increasing the liquid content of samples and cellulose molecules characteristics changing.
As for the third group of samples, its liquid content dynamics is produced by a great surface area of the hydrophilic sorbent, thus increasing the absorption ability in comparison to the other kinds of samples. An intensive increase of the liquid content of the third group of the samples is determined by the presence of the hydroxyl groups (-OH) on the surface of the sorbent granules forming the reactive centers which combine with the liquid molecules as a result of chemical absorption. Thus the higher level of liquid content of this kind of samples comparing to the others is provided by two different mechanisms of liquid sorption from the ambient air.
During the whole investigation period the liquid content level within the capillaries and micropores of the matrixes changed by not more than 8 % with reference to the initial liquid content level. But the best hygroscopic properties possess the third group of samples due to their composite structure made by cellulose base and the granular hydrophilic sorbent. The spherical micropore surface of the granules is filled with the anhydrous alkaline-earth metal salt solution which increases the absorption of liquid molecules from the ambient air.
When the solid hydrophilic granular materials are impregnated with the solution both physical and chemical absorption mechanisms occur. Under the physical absorption the adsorbate molecules cover the surface and fill the pores of the material. Under the chemical absorption the solution molecules combine with the organic-silicon sorbent as OH-groups.

The liquid content dynamics of the non-sealed granular sorbent impregnated with water was studied [5]. The results show that their parameters decrease significantly at room temperature during a relatively short time (48 hrs.) as a result of water evaporation. The developed samples are characterized by a stable and higher liquid content at the level of 35-40 % during 100 days comparing to 20-30 % water content level in the pores of the granules under normal conditions.

The results of shielding effectiveness investigation show (Fig. 2) the dynamics of liquid content influenced the shielding characteristics of the samples.

Attenuation of the electromagnetic radiation in the frequency range 8...11.5 GHz produced by the samples and measured at the first day of the experiment is from 12.0 to 14.5 dB (Fig. 2, a). Comparing to the similar porous materials impregnated with water which ensure 9.0…11.0 dB [5] attenuation, solution application increases the effectiveness of the composite materials of this kind.

The reflection factor in the studied frequency band varies from -9.7 to -1.8 dB (Fig. 2, b). When the short-circuit is placed behind the sample (Fig. 2, c) the reflected signal is decreased by 1…3.5 dB for the first kind of samples.

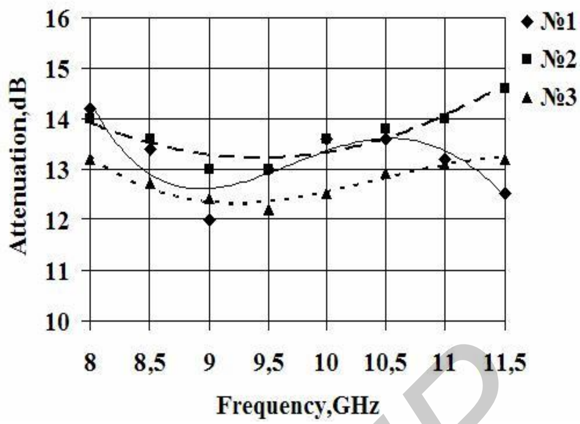
The samples based on cellulose matrixes followed by the metallic reflector have the same characteristics. The reflectivity of the third group of samples with a short-circuit increases by 1…2 dB. The difference between the values is ensured by the matrixes of different types.

The reflectivity of composite samples followed by the metallic reflector change as the electromagnetic radiation is reflected from the material-air and air-metal interfaces thus producing the total reflection factor affected by multiple reflected signals.

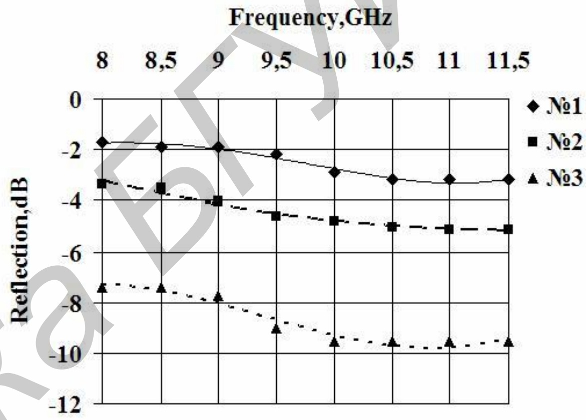
The attenuation of electromagnetic radiation produced by capillary-porous materials filled with the solution of the anhydrous alkaline-earth metal salt is ensured due to several mechanisms. First, the electrodynamic processes depend on the dielectric losses ensured by the polar dielectric liquid as a result of dipoles orientational polarization in the SHF range caused by the electrical component of the incident radiation.

Second, the synthesized metal salt solution has light electrolyte properties with ion conductivity. The conduction currents are induced within the solution as a result of electromagnetic field irradiation, thus providing the additional losses of electromagnetic energy.

Third, the electromagnetic wave is reflected from the samples as the wave impedance of the material differs from the impedance of the free space. The air impedance is constant and equal to 120π. The impedance of a material depends on its conductivity, permittivity and permeability and varies depending on the frequency.



a)



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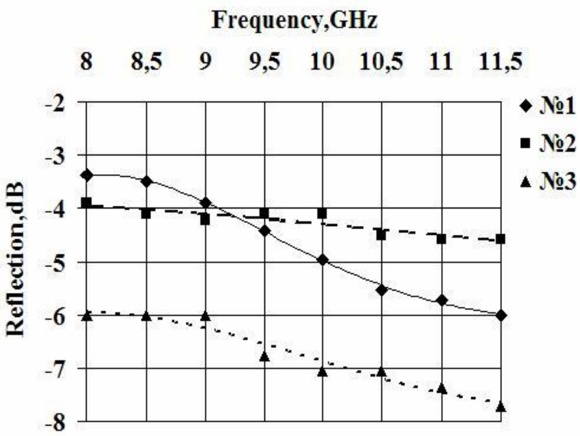


c)

Fig. 2. Shielding effectiveness in the frequency range of 8.0...11.5 GHz ensured by liquid-containing porous matrixes: 1 – synthetic knitted fabric; 2 - cellulose non-woven matrix; 3 - solid hydrophilic sorbent: a) EMR attenuation; b) EMR reflection; c) EMR reflection for the short-circuit mode of measurements. First day of the experiment

As the composite material contains lots of interfaces between air, solution and matrix material, the reflection is a complex process thus ensuring the total reflection level of the sample. The shape of the composite material surface also affects greatly the reflectivity of the sample.

Analyzing the frequency behavior of EMR reflectivity of different kinds of samples it is shown that the samples based on the knitted fabric have the highest reflection level due to their high liquid content and regular shape of sample surface formed by the fabric.

The lower EMR reflection factor of cellulose matrixes (-3.5…-5.0 dB) comparing to the knitted fabric (-1.5…-3.1 dB) can be explained by the fact, that the dielectric properties of the liquid change as its molecules are combined with cellulose molecules through chemical bonds and have a lower electric field susceptibility [9].

The shape of the samples based on the solid hydrophilic sorbent is formed by the spherical granules thus making the additionally scattering the electromagnetic radiation due to the irregularity of the sample surface and higher impedance matching between the free space and the sample in the lower frequency range. In the higher frequency range, when the radiation wavelength can be compared with the dimensions of the sphere, the uniform scattering in all the directions occurs and the level of radiation reflected backwards to the source decreases greatly. As a result of that the EMR reflection factor is lower comparing to the other samples down to -6.0...-7.8 dB.

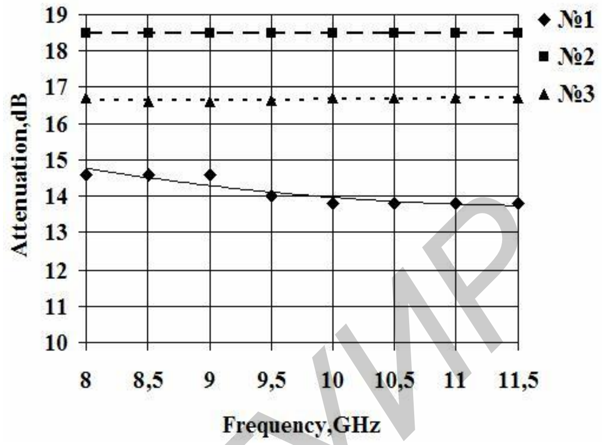
The metallic reflector placed behind the samples according to the standard measurement technique causes the increase of the total reflection level as in this case the reflection of the electromagnetic wave from the metal surface is included. This component influences the reflection level the less the greater is the thickness of the sample matrix as while the reflected wave is traveling through the sample it is attenuated and absorbed by the solution.

The electromagnetic characteristics of the samples were measured again in 100 days. The results are shown in Fig. 3.

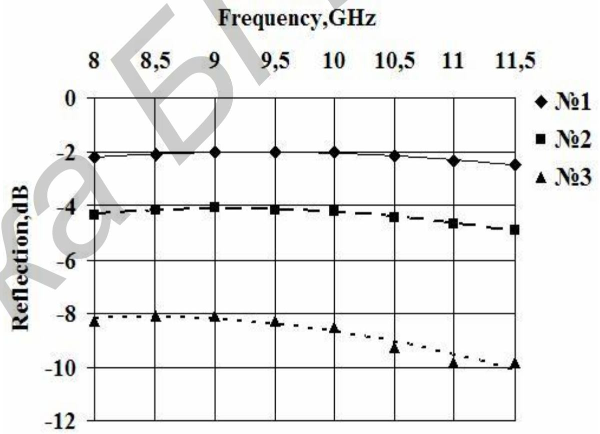
As it is evident from Figs. 2, 3 the shielding efficiency of samples in the super high frequency range is relatively stable as a result of keeping the liquid content about the initial level during the total time of the experiment.

As it is shown in Fig. 3, a, the EMR attenuation level ensured by the samples increased significantly for some groups of samples. The EMR attenuation for the second group of samples is increased by 5 dB and for the third group – by 2.5 dB and has a regular and linear frequency behavior in the overall experimental frequency range.

A small increase of the attenuation level for the samples with the fabric matrix (by 1.0…1.5 dB) can be explained by the lower hygroscopicity properties of the matrix and, as it is evident from Fig. 1, thus the lower liquid content dynamics comparing to the other groups of samples.



a)



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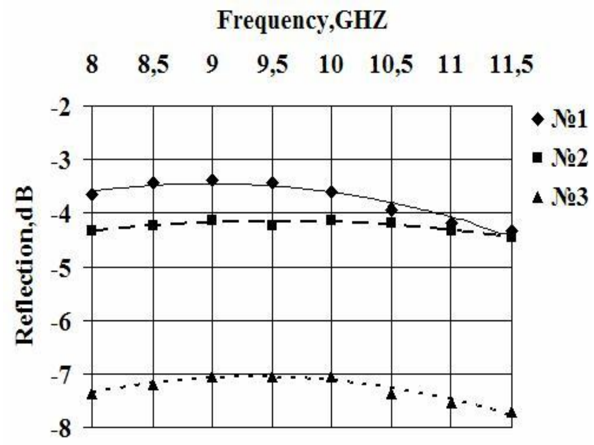

c)

Fig. 3. Shielding effectiveness in the frequency range of 8.0...11.5 GHz ensured by liquid-containing porous matrixes: 1 – synthetic knitted fabric; 2 - cellulose non-woven matrix; 3 - solid hydrophilic sorbent: a) EMR attenuation; b) EMR reflection; c) EMR reflection for the short-circuit mode of measurements. 100th day of the experiment

The reflection factors for all kinds of samples keep stable during the overall time of experiments (Fig. 3, b). The reflection level lightly changes in the sort-circuit mode (Fig. 3, c), as a result of additional reflection of the electromagnetic wave from the metallic reflector surface and its additional scattering during the reverse propagating within the composite material.

4. Conclusion

As a result of the investigations the hygroscopic properties of the samples were studied gravimetrically. The liquid-containing composite samples differ from each other in the kind of porous matrix, impregnated with the 45% mass. solution of the anhydrous alkaline-earth metal salt.

The results of the gravimetrical measurements show that the liquid content of all kinds of samples is relatively stable and the maximum deviation is not more than 8 % from the initial level during the overall time of the experiment. It testifies the higher hygroscopic and absorptive properties of the developed materials.

The composite liquid-containing materials for electromagnetic shielding developed under the experiment are capable to keep the certain level of liquid content during the operation life thus ensuring the stability of their shielding effectiveness and allowing to decrease the sealing requirements or even to avoid the sealing layers application.

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