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Study of electromagnetic characteristics of polymer materials based on single-walled and multi-walled carbon nanotubes

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Abstract. The results of the study of the electromagnetic characteristics of polymer composite materials containing various carbon fillers are presented. Samples based on epoxy resin with single-walled and multi-walled carbon nanotubes, as well as conductive ABS plastic with carbon fibers were made. The frequency dependences of the complex dielectric constant on the frequency for these materials are shown. Based on the data obtained, the electromagnetic response from samples of composites located in free space and on the metal, taking into account the thickness, was calculated. The influence of the material thickness on the electromagnetic response from it was simulated. A composite material containing 4 wt.% SWCNTs is effective narrowband absorber at a frequency of 5 GHz, at a thickness of 3.0 mm. Or it can be used as a shielding high-frequency radiation material at frequencies from 7 GHz with a thickness of more than 2.5 mm.

1. Introduction

In recent years, the development of modern science and technology is ahead of theoretical research in obtaining the latest materials for the industrial complex. In structural and functional composites, reinforcing elements usually provide the necessary mechanical characteristics of the material (strength, stiffness, etc.), and the matrix ensures that the reinforcing elements work together and protect them from mechanical damage and aggressive chemical environment. These materials are used in all areas of industrial production. The use of protective materials and coatings to reduce the mutual influence of radio components, to improve the electromagnetic compatibility of various systems, as well as to improve the environmental situation is the most important direction of technological development [1]. As fillers of modern high range radio composite materials, ferrites with different crystal structures [2], the carbon material (amorphous carbon, graphite, fullerenes, carbon nanostructure compound) [3], carbonyl iron and other metal compounds [4] are commonly used. At present, we are getting closer to the limit values of the electromagnetic characteristics of materials that can be achieved using traditional fillers. Further development prospects in this area are associated with the development and use of new nanoscale high-tech materials. A promising class of materials for use in electronic devices are carbon nanotubes (CNTs) [5]. CNTs have a low bulk density, mechanical strength, ductility, and widely varying conductivity. They allow the development of high-strength and lightweight coatings based on them. By varying the concentration of CNTs, it is possible to produce materials both shielding and absorbing electromagnetic radiation [6, 7]. Therefore, it is of interest to investigate the

difference in the electromagnetic properties of composites based on single-walled carbon nanotubes (SWCNT) and multi-layered carbon nanotubes (MWCNT) in the microwave radiation range.
At present, the manufacture of composite materials and structures based on additive technology is actively developing. Recently, the manufacture of plastic-based composite materials for 3D printing with the addition of fillers that effectively interact with electromagnetic radiation has become very popular [8]. Most often it is conductive plastics. This plastic consists of polymer resin and an appropriate filler. As fillers, either powders of well-conducting metals or various carbon structures are used [9]. It is the presence of carbon fiber in the composite that allows this type of ABS plastic to effectively conduct electric current. However, most conductive plastics we have today still are of high resistance. They are promising as functional and constructive radio materials.

In this paper, we study the electromagnetic characteristics of polymer radio materials based on carbon nanotubes and compare them with the results obtained for industrially produced carbon-containing ABS plastic of the “Conductive” brand.

2. Materials and Methods
The structure of the materials was determined by X-ray analysis. Images were obtained on X-Ray Diffractometer Shimadzu XRD 6000 with copper radiation (CuKα) and Wavelength Dispersive X-Ray Fluorescence Spectrometer XRF-1800. Powder samples and composites samples were studied. Shooting modes are tube voltage of 40 kV, anode current of 30 mA, goniometer speed when shooting is 2 deg/min, X-ray diffraction is $2\theta=(20\div60)^{o}$.

The structure of material was studied by optical microscope and by scanning electron microscopy. Electron-microscopic measurements were carried out with a scanning electron microscope with a focused ion beam QUANTA 3D.

2.1. Materials
Composite materials consist of a binder (matrix) and a filler. The epoxy resin EDP-20 with hardener PEPA was used as the polymer base of the composite material. Single-walled powders (SWCNT) and multi-walled carbon nanotubes (MWCNT) were used as fillers. Their main characteristics are presented in Table 1. The SWCNT was a Tuball material produced by Plasma-Chemical Technologies. It contains more than 70% of the main phase. The average diameter of carbon nanotubes is d = 1.8 nm. Used MWCNTs were synthesized by catalytic gas-phase deposition of ethylene [10] at the Institute of Catalysis G.K. Boreskov SB RAS. They contain more than 97.5% of the main phase with an average tube diameter d = 9.4 nm. MWCNT and SWCNT in concentrations from 2 to 4 wt.% Were mixed with epoxy resin.

Table 1. Comparative characteristics of MWCNT and SWCNT

Characteristics	MWCNT	SWCNT
CNT content	More than 97.5 wt.%	More than 70 wt.%
The average diameter of the nanotubes	9.4 nm (4 – 21 nm)	1.7 nm (1.66 – 2.28 nm)
Impurities of metals	Less than 1.7 wt.% (FeCo, Al_2O_3)	Less than 15 wt.% (FeCo)
External specific surface	320 m^2/g	> 300 m^2/g
Number of layers	7-9	1-2

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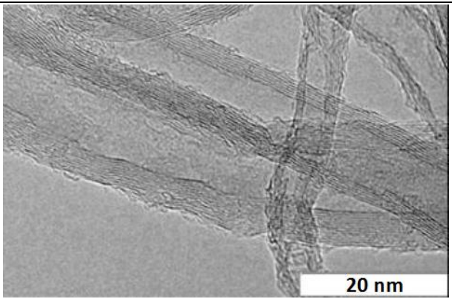
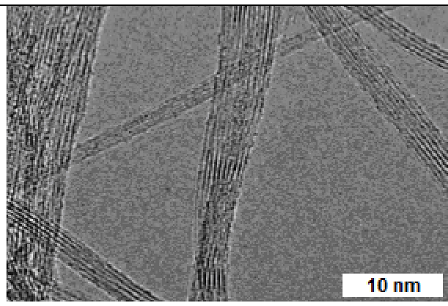
TEM images of nanotubes		

2.2. Obtaining experimental samples
For the manufacture of the samples the following scheme was used. At the first stage, the initial components were selected (epoxy resin with hardener, MWCNT and SWCNT). We carefully weighed the filler and the binder on an electronic scale (accuracy ~ 1 mg). After that, the components of the composite were combined in appropriate proportions (by weight) and thoroughly mixed until homogeneous state (using ultrasonic dispersers for 5 minutes at a power of 80 watts). Composite mixtures were obtained with appropriate concentrations of fillers by weight. The resulting mixture was poured into a coaxial form of fluoroplast (this material has a low adhesion to epoxy resin). Polymerization of samples occurred at room temperature for several hours. Next, the polymerized samples were processed to their full compliance with the dimensions of the selected measuring cell. This processing was performed by grinders devices. The samples are gradually ground off surplus from all sides, and also plane-parallel faces are formed. The fabricated samples are washers with the following dimensions: outer diameter d_{out} = 7 mm, internal diameter d_{in} = 3 mm, thickness h = 1.6 mm.

Thus, a series of experimental samples of composites for measurements were made. Their main characteristics are presented in table 2.

Table 2. Manufactured samples

Sample No	Content of epoxy resin, wt.%	Content of the filler, wt.%	
		MWCNTT	SWCNT
1	98	2	–
2	97	3	–
3	96	4	–
4	98	-	2
5	97	-	3
6	96	-	4

Also, using additive technology (printing on a 3D printer), a sample of the shape of a conductive plastic washer was made. Its size is fully consistent with the previously obtained samples. As a conductive plastic ABS plastic brand "Conductive" was used. It contains up to 20 wt.% carbon nanofibres and has a specific electrical resistance ρ = (40 ÷ 80) 10^3 Om / cm.

Thus, 7 experimental samples of composites for measurements were made.

2.3. Measuring equipment
Microwave measurements of electromagnetic characteristics were carried out in coaxial cells on a vector analyzer of P4M-18 circuits manufactured by “Mikran”. The “to pass” measurement scheme was used when the experimental sample was installed in the center of the cell, and the elements of the dispersion matrix were measured at frequencies from 2 to 18 GHz. This method characterizes the

interaction of electromagnetic radiation with a sample located in free space. A block diagram of the measurement setup is shown in Figure 1.

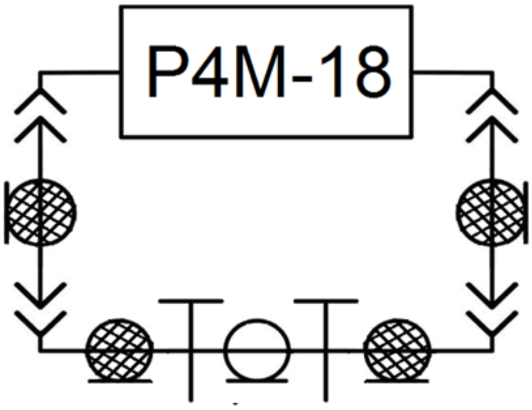


Figure 1. Block diagram of measurements "to pass"

The "to pass" scheme is used to measure *S*-parameters (*S*11, *S*12, *S*21 and *S*22). They correspond to the radiation power transmitted through the sample (*T*) and reflected (*R*) from the front face of the sample during the passage of an electromagnetic wave in the forward and backward directions. After that, according to the well-known formula, you can find the absorption coefficient: $A=1-T-R$. On the basis of the S-parameters obtained, taking into account the change in their phase, it is possible to calculate the spectra of the complex permeability and permittivity. For this purpose, the Becker-Jarvis technique [11] was used in this work. In the Mathcad programming environment, the corresponding software module was implemented.

The obtained values allow us to calculate the electromagnetic response from the materials at different thicknesses in further research. Two new modules have been created in the Mathcad programming environment. They allow to calculate the electromagnetic response from the material in free space (*T*, *R*, *A*) and on the metal (*RL*). To do this, they need a file with the data of values of electromagnetic parameters, calculated earlier. All calculation formulas are obtained in the approximation of plane waves.

In order to reduce the calculation error, an additional study of the effect of metallic impurities in CNT on the magnetic permeability of composites was conducted. This effect is most pronounced in the low-frequency region of microwave radiation. Therefore, a measurement setup based on the Keysight E4991B impedance analyzer was used. It has a test signal frequency range from 1 MHz to 3 GHz.

3. Results and discussion

The following are the results obtained for composites with MWCNTs (Figure 2) and for composites with SWCNTs (Figure 3). In addition, the results of the sample printed from carbon-containing ABS plastic "Conductive" were added to the graphs.

From the graph in Figure 2 it can be seen that with a change in the concentration of MCNTs, the dielectric constant increases nonlinearly. This is especially noticeable at lower frequencies. With increasing concentration of multi-walled carbon nanotubes, a significant increase in values of real (from 5 to 7.5 relative units) and imaginary parts of the permittivity (from 0.4 to 2 relative units) is observed. However, at frequencies above 5 GHz, a noticeable decrease in the real part of the complex permittivity can be noted. This type of behavior is associated with both the polarization characteristics of carbon nanotubes and the significant contribution of the conductive properties of the composite to the value of the complex permittivity. With increasing frequency, the contribution of conductivity to ε decreases, which we see in the graphs (decrease in permittivity with increasing frequency). The

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carbon-based ABS plastic “Conductive” has higher complex permittivity values than a composite with 4 wt.% MWCNT.

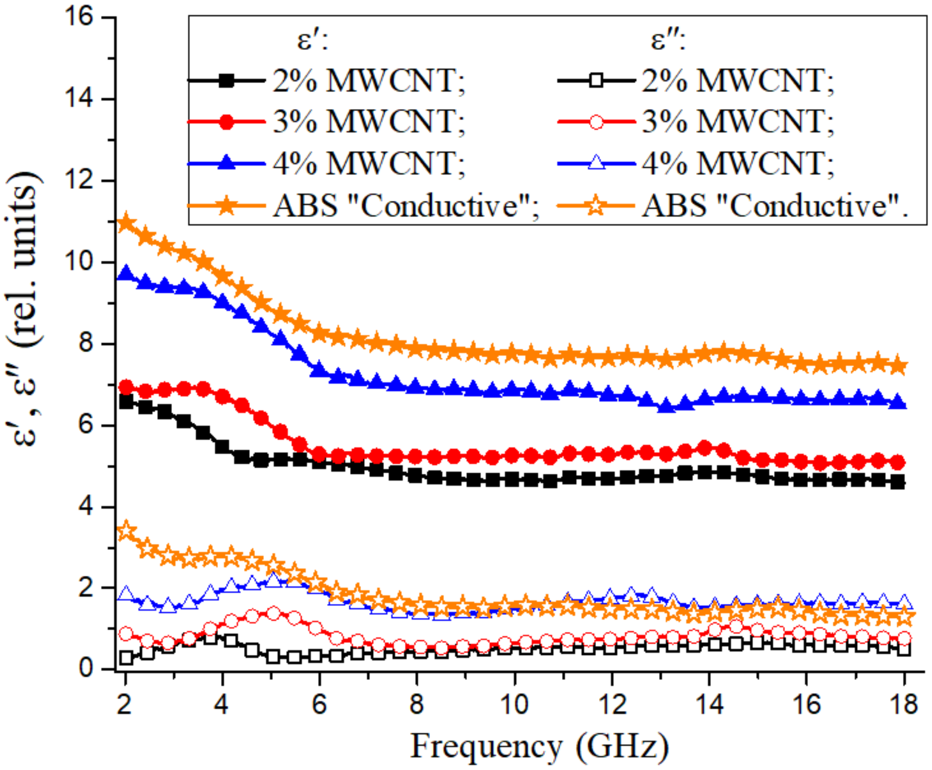

Figure 2. Frequency dependence of the complex permittivity of composites with MWCNT and ABS “Conductive” plastic

For composites with single-walled carbon nanotubes, the values of complex permittivity are several times greater than those for composites with MWCNT. When the concentration of the filler is 2 wt.% ε′ varies within 22 ÷ 7 rel.units for the SWCNT and 7 ÷ 4 rel.units for MWCNT. This is probably due to high conductivity values of the material with a single-walled carbon nanotube, since only a few first layers of carbon nanotubes make a contribution to the electrical properties (i.e., for the MWCNTs, most of the layers make no contribution to the electrical properties and permittivity). A composite containing 4 wt.% of a single-walled carbon nanotube has already proved to be partially conductive. Resonance phenomena are observed in the frequency dependence of the permittivity in the range from 4.5 GHz to 7.5 GHz, which is probably due to the conductive properties of the composite. The material containing 4% by weight of single-walled carbon nanotubes has two times higher values of complex dielectric constant than carbon-containing ABS plastic.

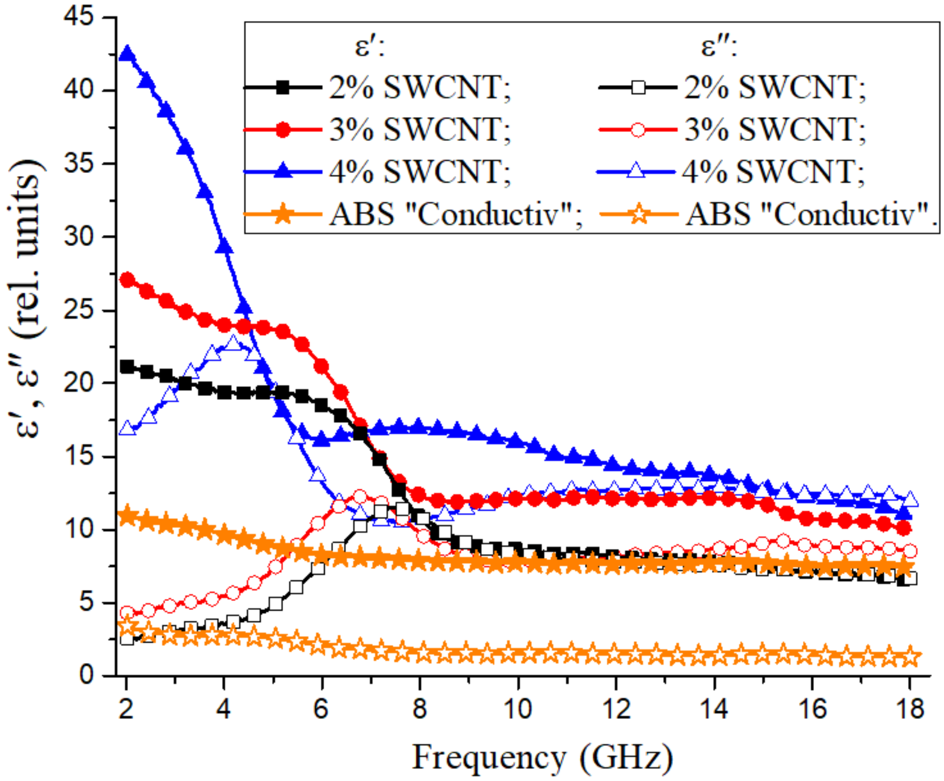

Figure 3. Frequency dependence of the complex permittivity of composites with single-walled carbon nanotubes and ABS “Conductive” plastic

To ensure that the features on the resulting frequency dependencies are not related to the presence of magnetic properties (due to the impurities of metals in carbon nanotubes), we conducted a study of complex magnetic permeability. It can be noted that composites based on carbon nanotubes are practically non-magnetic (μ '= 1, and μ ''= 0.01 ÷ 0.05).

On the basis of the obtained data about the complex dielectric constant, and in the absence of actual magnetic properties, the electromagnetic response was simulated from a layer of material located in the free space (*T*, *R*, *A*) and on the metal (*RL*). Distribution plots were obtained for the corresponding coefficients depending on the thickness and frequency of the layer.

The best shielding and absorbing properties are possessed by composite containing 4 wt.% SWCNT. Figure 4 shows the simulation results of the electromagnetic response from a layer of material in free space. This material has a good shielding ability. With increasing frequency and thickness of the material, the transmission coefficient *(T*) decreases. With a layer thickness of more than 2.5 mm at frequencies greater than 8 GHz, less than 10% of the radiation penetrates through the composite. In this case, more than 50% of the radiation is absorbed, and the rest is reflected. With increasing thickness and frequency, more and more radiation is shielded and at the maximum considered parameters less than 1% of radiation passes. Reflection is maximal (from 70 to 80%) at frequencies from 4 to 6 GHz with a material thickness of more than 3 mm. Composites based on 4 wt.% MWCNTs and ABS «Conductive» behave similarly. However, they interact with radiation two times weaker. At the same time, in a wide frequency band (from 4 to 18 GHz), they reflect more than 50% of the radiation. Only at very high frequencies with large thickness, they exhibit absorbing properties. Composites based on single-walled carbon nanotubes are several times better at shielding radiation (*T* ranges from 5% to 20% at frequencies higher than 5 GHz) than composites based on MWCNT (*T* ranges from 40% to 90% at frequencies above 5 GHz).

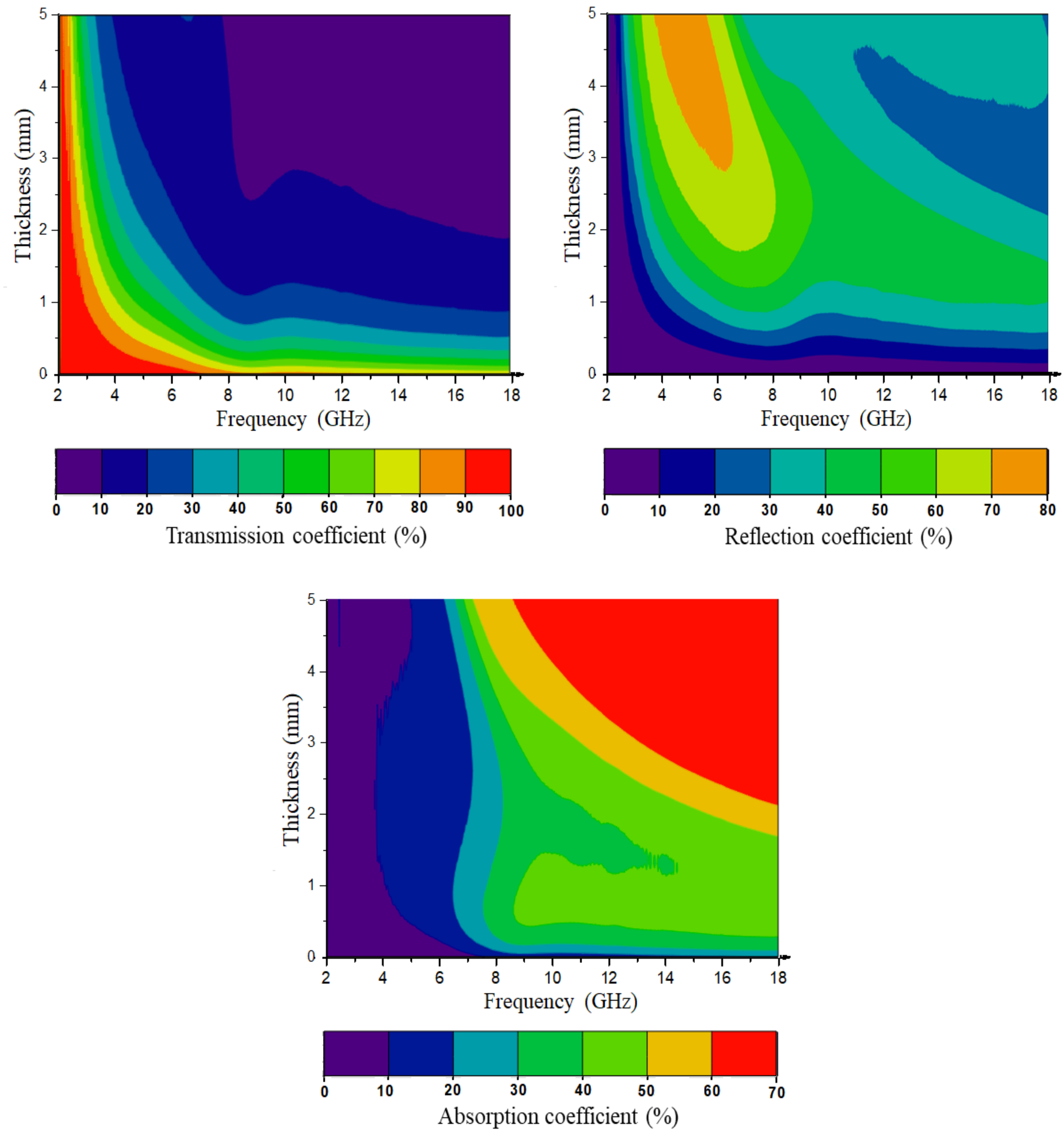

Figure 4. Dependence of electromagnetic response (*T*, *R*, *A*) from frequency and layer thickness for a composite material containing 4 wt.% SWCNTs in free space

Next, we simulated the electromagnetic response from the composite layer on the metal. Surface plots with level lines for reflection losses (*RL*) were obtained. Figure 8 shows the distribution of reflection loss from the frequency and layer thickness for a composite material containing 4 wt.% of a single-walled carbon nanotube in metal. It can be seen from the graph that the coating of this composite is a very narrowband absorber. The maximum attenuation of the radiation can reach -35 dB (more than 3160 times) at a frequency of 5 GHz with a thickness of 3.0 mm to 3.2 mm. In general, the level of attenuation of radiation is much less. In this case, the optimum thickness is 2-3 mm. With this thickness at frequencies above 6 GHz, the reflected power will be reduced by 3-10 times.

Other composites samples attenuate the level of the reflected radiation much weaker.

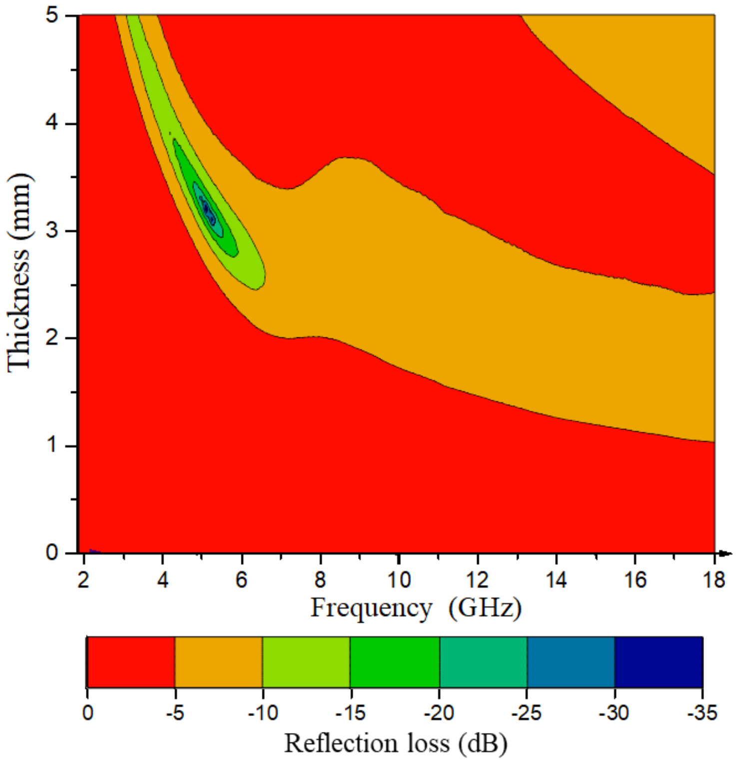

Figure 5. The dependence of the reflection loss on the frequency of radiation and layer thickness for a composite material containing 4 wt.% SWCNT

4. Conclusions

Electromagnetic response from materials with SWCNTs, MWCNTs and ABS «Conductive» has been investigated. It is shown that a composite material containing 4% by weight of single-walled carbon nanotubes is an effective narrowband absorber at a frequency of 5 GHz with a thickness of 3.0 mm. Or it can be used as a shielding high-frequency radiation material at frequencies from 7 GHz with a thickness of more than 2.5 mm. Investigated MWCNT and "Conductive" ABS plastic are more suitable for creating screening coatings, since they have high values of reflection coefficients.

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