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Electromagnetic response from composite radiomaterials based on multiwall carbon nanotubes at microwave frequencies

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***Abstract*— This paper presents results of a study of electrophysical characteristics of composite radio materials in the frequency range from 10 MHz to 18 GHz. The composite materials are based on epoxy resin with multiwall carbon nanotubes (MWCNT) of various diameters. Coatings containing MWCNT have higher reflection and absorption coefficients. Varying filler concentration in the composite materials changes characteristics of the protective coating from reflective to absorbing electromagnetic radiation.**

***Keywords*— composites, electromagnetic response, carbon nanostructures, MWCNT, absorption, reflection coefficient.**

I. Introduction

Each year the rate of electronics development is becoming faster. The number of new radioelectronic devices which work in microwave range is growing. They are used for mobile communication, in modern computers and in different digital devices of various applications. Promotion to higher frequencies can significantly reduce the geometrical dimensions and weight of radio elements, achieve compaction of their location, reduce power consumption which leads to miniaturization of the equipment. However, a lot of materials working well at low frequency lose their properties and stop working at microwave range. For further miniaturization of devices it is necessary to use new materials that can lessen size and weight of radioelements [1], provide electromagnetic compatibility of working units of radioelectronic equipment [2] and reduce the influence of radiation from these devices on the human body [3, 4]. Therefore, interest in new radio materials which have prospects of application in microwave devices is growing.

Currently the prospects this area are connected with design and application of new composite materials with nanosized fillers [5, 6]. Solid materials have great values of the electromagnetic parameters but they are heavy. Composite materials is easily to process, they can have higher strength, elasticity, flexibility and improved electromagnetic characteristics and some other features that pure materials can not possess [7, 8]. As for active phase fillers, specialists pay special attention to materials, actively interacting with electromagnetic radiation: reflectors and absorbers. It is known that as fillers of composites microwave radiomaterials various metal powders [9], nanostructured magnetic materials [10], carbon nanostructures (graphene, fullerenes, single and multi-walled carbon nanotubes, onion structures) [11] and powders of multiferroic [12] have proven themselves to be efficient.

A new promising material for application in electronic devices is Carbon nanostructures (CNS) [13]. CNS have special characteristics, namely - high conductivity, low bulk density, mechanical strength, ductility, low thermal conductivity. CNS are used for developing of high-strength and lightweight coverage. Moreover, we can get reflective and absorptive coating by changing the concentration of the CNS [14, 15].

Thus, it is useful to research behavior of reflective and absorptive properties of composite materials based on multiwall carbon nanotubes of different diameter in microwave range.

II. Experimental Section

A. *Means of measurement*

The structure of the materials was determined by X-ray analysis. Images were obtained with the help of 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 were – 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 JEOL-JSM6700F.

The study of electromagnetic characteristics was conducted by using a waveguide coaxial measuring cell with outer diameter of 7.0 mm and inner diameter of 3.0 mm. Ultra high frequency path is based on the vector network analyzer (Agilent E8363B) in the 1–18 GHz region. Block diagram of

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experimental device used to measure electromagnetic characteristics is shown in Figure 1. Measurement scheme “in passing” was used. Transmission (S_{21}) and reflection (S_{11}) coefficients were measured and absorption coefficient was calculated.

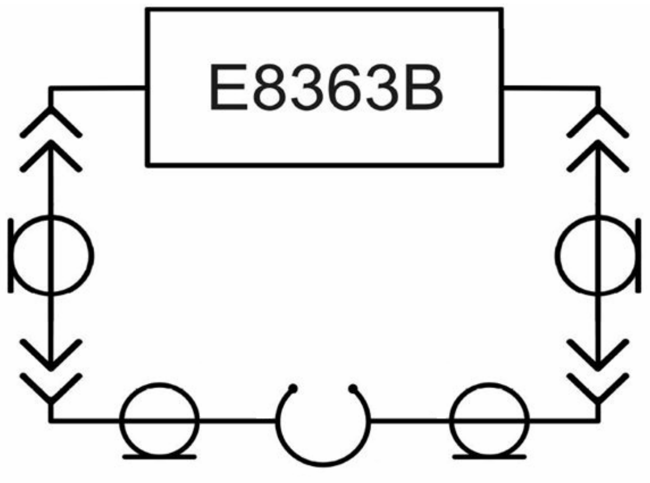

Fig. 1. Block diagram of the experimental setup

The samples were produced by using developed forms of a washer with outer diameter of 7.0 mm, inner diameter of 3.0 mm, which exactly fits the dimensions of the coaxial measuring cell. Particular attention was paid to installation of the sample in the cell without gaps and distortions. Measurement of the electromagnetic response was conducted at ambient temperature 22.0 ± 1.0°C. Samples of composite materials with different diameters of MWCNT and different weight content of fillers were examined.

B. Investigated materials

MWCNT were produced by catalytic vapor deposition of ethylene with catalysts FeCo at temperature 680°C. Prepared nanotubes were cleaned through dephlegmation in HCl, filtered, washed up to neutral pH and dried during 24 hours at 40°C. The leftover accelerant in MWCNT is metal particles inside of the tube.

Two sets of multiwall carbon nanotubes were chosen for the research:

- MWCNT-A, with average diameter of nanotubes *d*=9.4 nm.
- MWCNT-B, with average diameter of nanotubes *d*=18.6 nm.

The analyzed nanostructured carbon-materials have high degree of purity. They contain more than 90% of multiwall carbon nanotubes.

Their main characteristics, morphology and microstructure data are given in the tables 1 and 2. Analysis of the morphological features of the sample shows that multiwall carbon nanotubes – light powder of black colour which contains separate nanotubes, components of nanotubes and associated metal particles that are encapsulated in inner tubules of nanotubes.

TABLE I. PRODUCT SPECIFICATIONS OF MWCNT-A

Characteristic	Value
Average diameter of nanotubes (diameter range)	9.4 nm (4 – 21 nm)
MWCNT content, wt.%	More than 97.5
Impurities (according to TEM)	$FeCo/Al_2O_3$, particles, encapsulated in nanotubes
Ash content	<2.4 wt.%
Metal impurities (Fe, Co according to X-Ray Fluorescence analysis)	< 1.7 wt.%
Outer specific surface (including mesopore surface)	320 m2/g
True bulk density (according to helium pycnometry)	2.052 g/sm3
Size of coherent-scattering region, wall thickness of MWCNT	4.0 nm; 7-9 layers

TABLE II. PRODUCT SPECIFICATIONS MWCNT-B

Characteristic	Value characteristics
Average diameter of nanotubes (diameter range)	18.6 nm (7 – 38 nm)
MWCNT content, wt.%	More than 90%
Impurities (according to TEM)	Fe-Co particles, encapsulated in nanotubes
Ash content	<10 wt.%
Metal impurities (Fe, Co, Ca according to X-Ray Fluorescence analysis)	< 7 wt.%
Outer specific surface (including mesopore surface)	115±10 m2/g
True bulk density (according to helium pycnometry)	2.099 g/sm3
Size of coherent-scattering region, wall thickness of MWCNT	4,6 nm; 12-14 layers

In the Fig. 2 and 3 the microstructure of investigated multiwall carbon nanotubes is shown.

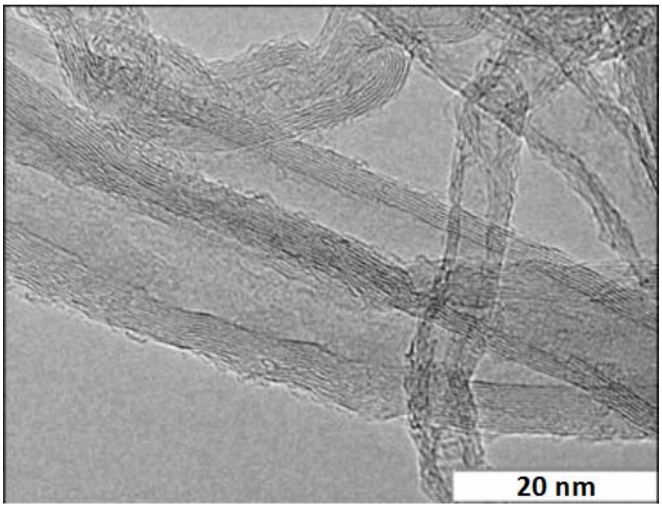

Fig. 2. TEM images of the powders •MWCNT-A

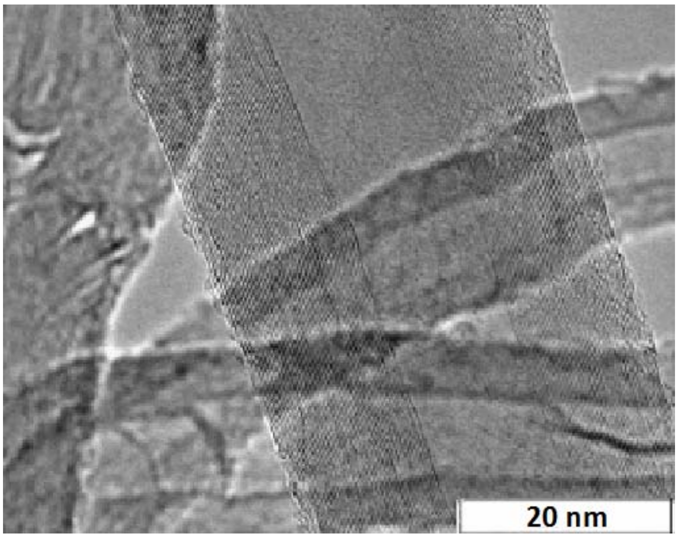

Fig. 3. TEM images of the powders •MWCNT-B

C. Obtaining experimental samples

To create samples, we used the following scheme. There were a filler and a binder. The filler and the binder were weighed on Shimadzu AUX-320 Analytical Balance (error ~ 0.5 mg). Thereafter, the composite components were mixed in the appropriate parts (by weight). Then the mixture was blended until homogeneous state (using an ultrasonic disperser and a magnetic stirrer). Manufactured mixture was placed in a special form. Finished composite sample is a toroidal shape with thickness of 2.8 mm. Polymerization of the finished product was carried out for several hours at room temperature.

We used epoxy as binder. MWCNT were used in different concentrations as binders too. Characteristics of samples that were obtained are given in the Table 3.

TABLE III. COMPOSITION OF THE SAMPLES

Samples №	Consist (wt.%)		
	Epoxy	*MWCNT-A*	*MWCNT-B*
1	98	2	–
2	96	4	–
3	94	6	–
4	92	8	–
5	98	–	2
6	96	–	4
7	94	–	6
8	92	–	8

III. MEASUREMENT RESULTS

The results of measurement of the transmission coefficients (*T*) of the composite samples based on multiwall carbon nanotubes are shown in the figure 4, 5.

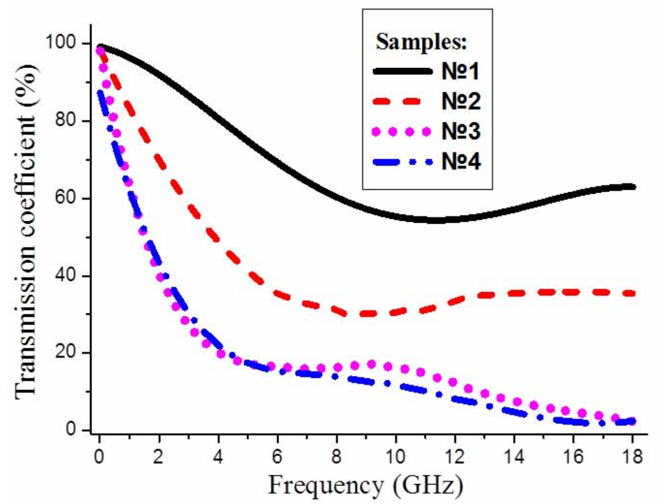

Fig. 4. Frequency dependence of the transmission coefficients of the composite samples based on MWCNT-A

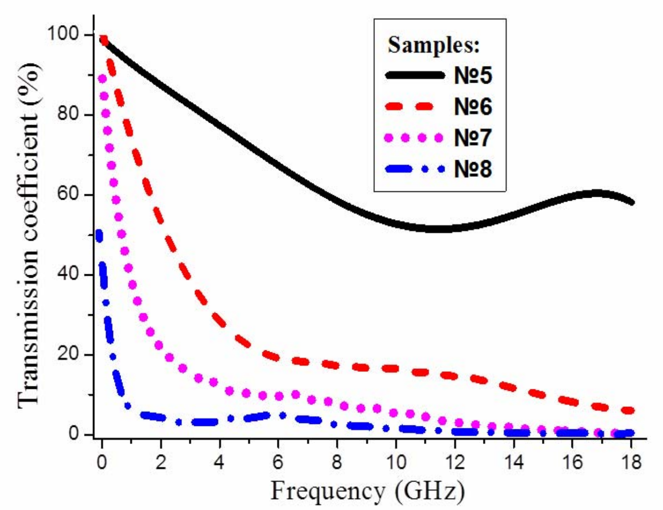

Fig. 5. Frequency dependence of the transmission coefficients of the composite samples based on MWCNT-B

In the charts of frequency dependence of the transmission coefficient there are two linear plots. At first one there is a sharp decrease in *T* with the frequency growth, and the second *T* varies weakly. The frequency at which the transition from one plot to another, with increasing concentration of MWCNTs significantly reduced: from 10 to 5 GHz for MWCNT-A and from 10 to 1.5 GHz for MWCNT-B. Transmission coefficient decreases significantly with increasing concentration of carbon nanotube in the composite. The dependence of T is nonlinear with respect to changes in the concentration of MWCNTs. It is seen that composites with larger diameter nanotube better shield radiation. They are particularly effective in the low frequency region of the electromagnetic radiation where the transmittance becomes less than 5% at frequency of 2 GHz with a concentration of MWCNT 8 wt.%.

The results of measurements of the reflection coefficients (*R*) of the composite samples based on multiwall carbon nanotubes are shown in the figures 6, 7.

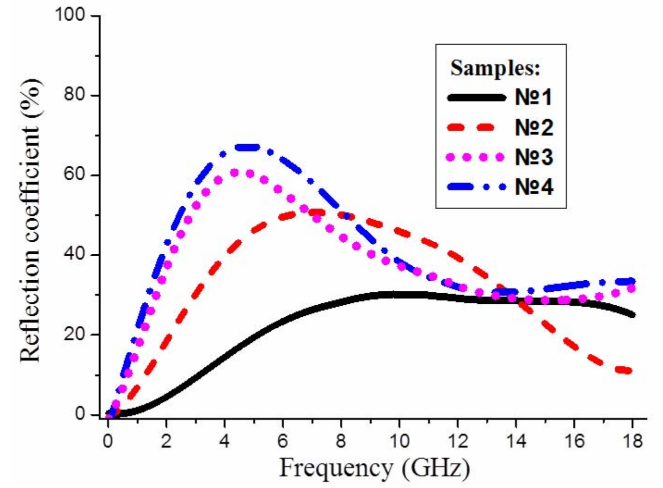

Fig. 6. Frequency dependence of the reflection coefficients of the composite samples based on •MWCNT-A

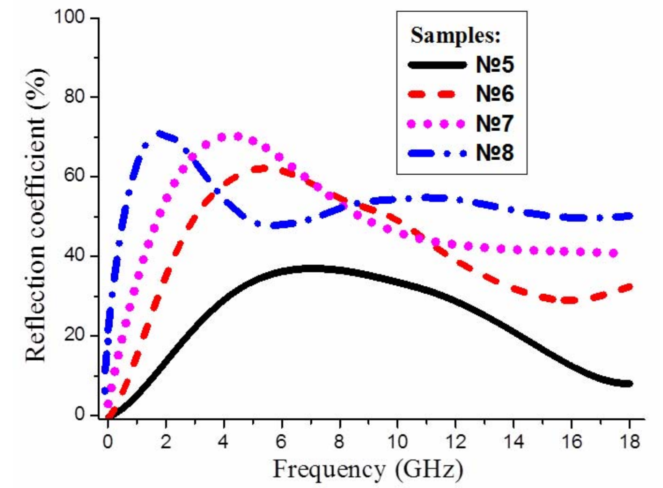

Fig. 7. Frequency dependence of the reflection coefficients of the composite samples based on MWCNT-B

In the frequency dependence chart for the reflection coefficients there is a maximum. It shifts to the lower-frequency region with increasing concentration of filler. From 12 to 4 GHz for MWCNT-A and from 7 to 1 GHz for MWCNT-B. The concentration dependence of the reflection coefficient in the general case is nonlinear.

Generally, the reflection coefficient value is higher for MWCNT-B composite. This is probably due to the greater length of the nanotubes and the presence of significant amounts of impurities, and hence higher values of conductivity of the material.

On the basis of the data the absorption coefficient (*A*) was calculated. To do this we used the following equation:

$$T + R + A = 100\%$$

The results of calculations of the absorption coefficient of the composite samples based on MWCNT-A and MWCNT-B are shown in the figure 8 and 9.

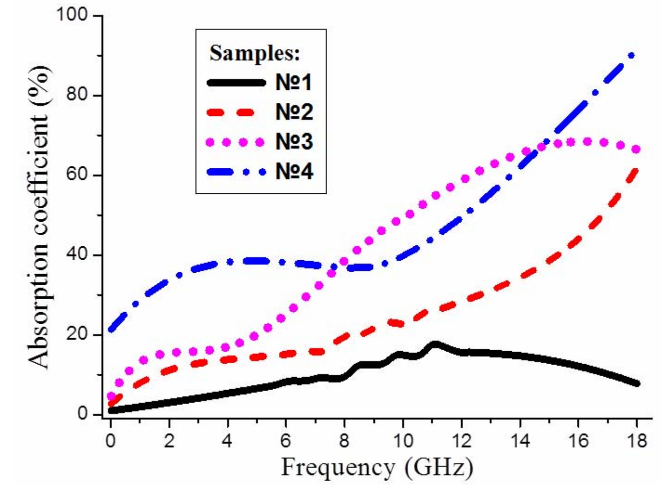

Fig. 8. Frequency dependence of the absorption coefficients of the composite samples based on MWCNT-A

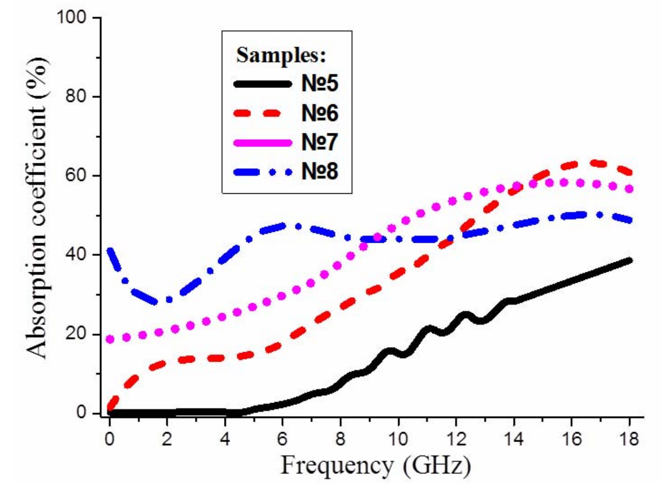

Fig. 9. Frequency dependence of the absorption coefficients of the composite samples based on MWCNT-B

The dependence of the absorption coefficient is nonlinear with respect to the concentration of MWCNTs and frequency. At low frequencies at microwave range composites with nanotube diameter d=18.6 nm have the best absorbing properties, and after 12 GHz composites with nanotubes of diameter d=9.4 nm possess higher absorption coefficient. The graphs show that for radiation absorbing material it is better to have concentration of MWCNTs composite in the region of 6-8 wt.%.

IV. Conclusion

This study shows the possibility of using multiwall carbon nanotubes as an active phase of composite radiomaterials interacting with high-frequency electromagnetic radiation. Selected range of radiation is being extensively used to create electronic equipment for various purposes, therefore investigated composites have prospects to be used in electronic devices of microwave range. Composite coatings based on them may be applied for electromagnetic compatibility of radio electronic facilities, for protection of biological objects from the influence of microwave radio emission produced by scientific and household appliances, etc. With increasing thickness of the composite materials electromagnetic radiation shielding effectiveness will grow.

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