Dielectric permeability of multiwall carbon nanotubes based composites, which are measured by a resonator method

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Abstract. The paper presents the results of measurements of the dielectric constant of composite materials, both solid and porous, containing multi-walled carbon nanotubes (MWCNT) as an inclusion, and water-dispersion color as a binder. The rectangular cavity was used to measurements. It is shown that the location of the sample in the cavity affects the accuracy of measurements. The permittivity spectra of the solid samples shows that the addition of nanotubes to the binder leads to shifting the dispersion range to the low-frequency region. The results show that materials can be used as radar absorbers.

1. Introduction

It is known that the structure of the polymer composite material (CM) is a continuous polymer phase (matrix) and a dispersed phase (filler), which is distributed in a certain way in the matrix [1]. Currently, there are many composite materials that employ various structures as a matrix, such as copper oxide, ceramics, rubber, polyurethane [2], etc. As the active phase of radio materials, various types of dielectric and magnetic fillers are used. The carbon nanostructures are used to nanoelectronics and nanosystems engineering. Also, the new materials and devices are appearing. Due to the unique physical, mechanical and electrical properties of carbon nanotubes, they can be used as a probe for scanning probe microscopy [3], sensitive elements of sensors [3], conducting channels of transistors [4], and also as composite materials fillers [5–7]. The making of CMs based on MWCNTs is explained by several advantages of MWCNTs, such as strength, high electrical conductivity, and a high degree of shape anisotropy (aspect ratio can reach 100 – 1000), which can significantly change the electrical conductivity of the matrix composite material with small volume fractions of the fillers [8]. The making of CMs with the necessary parameters at a set position on the substrate is an one of current task. Also, the lightweight radar absorbing materials are required to solve the problem of electromagnetic compatibility. This can be helped by porous carbon materials, which are widely used in sorption processes and as EMP absorbers. Such materials, due to the carbon-containing components, provide a wide range of losses in the dielectric and are used to eliminate volume resonances, surface currents, and spurious RF emissions.

The aim of this work is to study the complex dielectric constant of composites containing multi-walled carbon nanotubes.

2. Materials and methods

2.1. Materials
Two types of composite materials were investigated in this work: solid and porous. LACRA water dispersion color (LACRA SYNTHESIS LLC, Moscow, Russia) was used as a binder, and 9.4 nm diameter multi-walled carbon nanotubes (MWNTs) were used as filler (Institute of Catalysis SB RAS, Novosibirsk, Russia). MWNTs were synthesized by gas-phase deposition of ethylene in the presence of a FeCo / Al2O3 catalyst according to the technology described in [9].

Composites for measurements were prepared as follows. MWNTs of the appropriate concentration were added to a sample of water dispersion color. The resulting mixture was thoroughly mixed manually for 15 minutes. Then the mixture was placed in a glass container and processed using an ultrasonic apparatus for the required number of minutes by immersing the working tool inside the mixture. Ultrasonic treatment makes it possible to obtain an isotropic distribution of the filler throughout the sample volume. Due to the increase in viscosity and difficulties with ultrasonic treatment of the mixture, mixtures with a concentration of 0.25, 0.5; 0.75; 1.0; 2.0 wt. % were made, the rest is color (Table 1).

| Sample No. | Color, % wt. | Composition, % wt. | MWCNT |
|------------|--------------|--------------------|--------|
| 1          | 100.00       |                    | 0.00   |
| 2          | 99.75        | 0.25               |
| 3          | 99.50        | 0.50               |
| 4          | 99.25        | 0.75               |
| 5          | 99.00        | 1.00               |
| 6          | 98.00        | 2.00               |

Two types of samples were made. In the first case, the mixture was applied in layers, and the next layer was applied to the previous one after it was dried to exfoliation. Final polymerization took place within 24 hours. The fabricated samples are rectangular rods with a width of about 2 mm. The thickness of the finished samples is an average of 0.8 mm.

In the second case, a layer of a gas-filled polymer – polyurethane 0.5 cm thick – was steeped with the mixture. After the mixture was soaked, the polyurethane preforms were placed on a flat surface to polymerize the mixture. The complete polymerization of the preforms took place at room temperature for 24 hours. The blanks were turned over every 2 hours to ensure uniform distribution of the mixture over the volume of the samples. Experimental samples were cut from the blanks, which were thin rods 2 × 2 × 70 mm3 in size.

2.2. Measuring equipment
The electrophysical characteristics were investigated by the cavity technique using a measuring cell, a rectangular cavity. The complex permittivity was measured in the frequency range 3 – 13 GHz. The Agilent Technologies E8363B vector network analyzer was used as a measuring device (Figure 1). The measurements were carried out at room temperature.

![Figure 1. Block diagram of the experimental setup](image-url)
For measurements, the samples were placed in the center of a rectangular resonator at the antinode of the electric field.

3. Results and discussion
3.1 The effect of ultrasonication on the permittivity of a composite material

Experiment was carried out for optimal time selection. Results of experiment are shown in Figure 2. In this case it was used 1 % wt. concentration MWCNT for fabrication experimental samples. This choice can be explained that the initial mixture is liquid and mixes well at this concentration. Figure 2 is demonstrated the dependence of the complex permittivity on the time of processing by ultrasonication.

![Figure 2. The dependence of the complex dielectric constant of the sample on the processing time](image)

Measurements were carried out at the frequency of 8.123 GHz. Figure 2 is shown that there is a slight increase real and imaginary part of permittivity. It can be explained that MWCNT evenly distribute into matrix and appear extended conductive inclusions into the binder. In the research work [10] was explored composite where lacquer was used as a binder. The dependence of the complex permittivity in the time had a different character. For this composite observed maximum permittivity at 3 minutes of ultrasonication processing. Probably, maximum of permittivity will be at long processing times for composite material with 1 % wt. concentration of MWCNT. It should be noted that when heated during 5 minutes there is a strong boiling of the mixture, which are lead to evaporation of water.

In this research the relative measurement error of complex permittivity (Figure 3) was identified. For this purpose, we used experimental sample with known characteristics. Measurement error was calculated from accounting results and experiments for samples of rectangular cross section having a real volume, and displacement of the sample from the center of the cavity up to 5 mm along the length of the resonator.
Figure 3. The dependence of the relative error of the dielectric constant of the sample from shift along the z axis

From Figure 3 it follows that, with an allowable relative measurement error of the real and imaginary parts of permittivity not more than 5 % and 20 %, respectively, the displacement of the sample from the center of the cavity should be no more than 2 mm along the length of the resonator.

It can be concluded from the results that minimizing experimental error is required the exact installation of the sample in the center of the cavity.

3.2 Investigation of permittivity of composite samples with multi-walled carbon nanotubes
Based on the results, which is given in section 3.1 and article [10] time of ultrasonication processing was chosen equal 4 minute.

Consider solid samples were obtained from mixtures, the composition of which is given in table 1, according to the procedure described in section 2.1. (Figures 4, 5).

Figure 4. Frequency dependence of the real part of the dielectric constant of continuous carbon nanotube composites

Figure 5. Frequency dependence of the imaginary part of the dielectric constant of continuous carbon nanotube composites

Figures 4, 5 shows that increase concentration of MWCNT lead to increase permittivity of samples. Composite material with 2 % wt. concentration of MWCNT has highest permittivity. Composite materials with 0.25 %; 0.5 % и 0.75 %; 1.0 % wt. concentration of MWCNT have the same permittivity in the frequency range 6 – 9 GHz. However, for these concentrations there is a slight
discrepancy in the permittivity in the low-frequency region. It is shown that at a concentration of nanotubes equal to 0.25; 0.5; 0.75; 1.0; 2.0 % wt., it was not possible to carry out measurements at frequencies 9 – 13 GHz. It can be explained that electrical length of sample for measurement cavity has become comparable with the electric length of the cavity. That is, at these frequencies, the conductive properties of the sample began to appear.

Figures 6, 7 is demonstrated frequency dependence real and imaginary part of permittivity of porous samples.

![Figure 6](image1.png) ![Figure 7](image2.png)

**Figure 6.** Frequency response of the real part of the dielectric constant of porous samples with different concentrations

**Figure 7.** Frequency response of the imaginary part of the dielectric constant of porous samples with different concentrations

The obvious resonance at the region of 7 – 13 GHz can be explained the presence of polar particles in its composition, since it is an aqueous solution of acrylic latex, micrized marble, kaolin, titanium dioxide, rheological, antiseptic and plasticizing additives. The addition carbon nanostructures in the mixture deal with a change structure of mixture and also to a change in the contribution to the effective permittivity of various types of fillers and the «smearing» of this resonance.

In analyzing these dependences, it can be noted that the permittivity decreases with increasing frequency, but rises with increasing concentration of carbon nanotubes for both samples. The frequency changes show that there are the relaxation polarization mechanisms that can occur into the composite due to the presence of regions with an increased number of electrons in nanotubes. The effect of concentration is due to the fact that nanotubes are conductive structure, which increase permittivity.

According to the generalized conductivity theory, the addition filler into binder permittivity should be higher than that of a pure binder. However, as can be seen from Figure 6, the dependence at number 1, which corresponds to a sample containing only water dispersion color, shows that this material has a higher permittivity than samples with MWCNTs in a mass concentration of 0.25 %. The obtained inconsistency with theory can be explained as follows. During the polymerization of a sample soaked with color, a thin film forms on the surface at room temperature, which leads to the combined water inside the sample. At the same time mixture strongly heats during ultrasonication processing and portion of water is evaporation. This effect corresponds to low concentrations of filler.

Permittivity rises with a further increase in the filler concentration, which indicates its contribution to the effective permittivity of the composite.

If it is compared the dependences for solid and porous samples (Figures 4, 6), it can be seen that composite materials with matrix as a color are approximately twice superior to polyurethane composites in permittivity.
4. Conclusion
The influence of the location of the sample in a rectangular cavity on the accuracy of measuring the permittivity was studied. It was shown that the shift of the sample relative to the centre should not exceed 2 mm.

For the composite materials that consist of water dispersion color and MWCNT were shown that concentration dependence has nonlinear character for porous samples. Based on this, it can be concluded that polyurethane composite materials have an inhomogeneous structure, it is impossible to definitely claim how the filler is distributed in the matrix. Consequently, further study of the effect of ultrasonication processing on the properties of the binder is required, because the result has obtained not identical.

Permittivity of solid composite material is approximately twice greater than that of a porous composite.

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