Electromagnetic characteristics of coatings based on graphene oxide- and multi-walled carbon nanotubes Taunit-M in a wide range of frequencies

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Abstract. The frequency dependences of the reflection, transmission, and absorption coefficients of samples of materials based on graphene oxide and Taunit-M multi-walled carbon nanotubes were measured. Graphene oxide and carbon nanotubes are glued with acrylic adhesive to a double-sided sheet of plastic. The method of free space is used to measure in the frequency range 35 - 260 GHz. It is shown that the addition of MWCNT of 30 weight percent reduces the transmission coefficient by more than ten times.

1. Introduction

Carbon nanostructures (multi-walled and single-walled nanotubes, graphene, fullerenes) are highly conductive [1] and effectively interact with electromagnetic (EM) radiation [2, 3]. Composites based on them have a strong shielding effect in the microwave and radio frequency ranges [4, 5]. 2D structure - graphene oxide (GO) attracts interest from specialists in the field of development and application of radio absorbers in connection with the ability to control its dielectric properties. So, in [6, 7], a method is described for obtaining an effective absorber based on GO in the frequency range from 10 to 18 GHz with sample thicknesses of 3-4 mm.

Currently, the possibility of creating light thin protective screens is being actively studied. Screens should protect biological objects from the harmful effects of microwaves, reduce the radio visibility of military objects and solve the problems of electromagnetic compatibility. This can be done by developing multilayer multielement structures.

It should be noted that carbon nanostructures and carbon-filled composites are promising for detecting terahertz radiation [8, 9] and for creating passive elements (attenuators, polarizers, matched loads) in this frequency range [10-13].

In this paper, we study the high-frequency electromagnetic parameters of a thin screen based on GO obtained by the new technology. The degree of influence of MWNTs is studied.
2. Experimental part

2.1. Sampling technique

The samples were made from aqueous dispersions of MWCNTs Taunit-M (diameter 10-30 nm, length more than 2 μm) (figure 1a) and 0.5 wt.% Graphene oxide (GO (figure 1 b), (both manufactured by NanoTechCenter Ltd, Tambov, Russia). The plastic sheet was covered with an acrylic adhesive base 3M 468MP 200MP Adhesive (China). This is the first time this technology has been used. The elemental composition of the GO is presented in table 1.

After adding the MWCNTs, the solution was stirred on a mechanical stirrer (Witeg HT-50AX) for 5 min at 800 rpm. To improve the distribution of the nanotubes in the graphene oxide, the resulting mixture was processed on a three-roll machine (Exakt - 80E) in 2 stages: 1 - gaps between the rolls – 30-15 μm, rotation speed - 120 rpm, and 2 - gaps between the rollers –15-5 microns, rotation speed - 120 rpm. Next, the mixture was subjected to a 10-minute ultrasonic (US) processing (I-10 ultrasonic generator) with direct mixing at 300 rpm. The resulting composition was poured on a double-sided acrylic adhesive sheet and dried at room temperature.

![Figure 1. SEM images of the MWCNTs Taunit-M (a) and the GO (b).](image)

| Table 1. The elemental composition of the GO. |
|---------------------------------------------|
| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| C       | 57.54      | 64.97      |
| O       | 40.21      | 34.08      |
| S       | 2.24       | 0.94       |
| Sum     | 99.99      | 99.99      |

The MWCNTs were introduced into the GO aqueous solution at the concentrations shown in table 2.

| Table 2. Characteristics of coatings. |
|--------------------------------------|
| Sample (No) | Composition (wt.%) | Size (mm) | Thickness (μm) |
|-------------|-------------------|-----------|----------------|
| 1           | Coating base      |           | 123            |
| 2           | GO                |           | 107            |
| 3           | GO/MWCNTs 95/5    | 200x200   | 94             |
| 4           | GO/MWCNTs 90/10   |           | 100            |
| 5           | GO/MWCNTs 80/20   |           | 101            |
| 6           | GO/MWCNTs 70/30   |           | 111            |
The structure of a slice of a nanocomposite of graphene oxide and carbon nanotubes is shown in figure 2. The design has a layered, porous structure with inclusions of carbon nanotubes. Carbon nanotubes are evenly distributed in the graphene oxide matrix. However, agglomerates are present in the structure. The size of the agglomerates corresponds to the size set between the rolls on a three-roll machine Exakt-80E.

![SEM image of the cross-sectional structure of a nanocomposite of carbon nanotubes and graphene oxide (CNT concentration of -30% mass).](image)

**Figure 2.** SEM image of the cross-sectional structure of a nanocomposite of carbon nanotubes and graphene oxide (CNT concentration of -30% mass).

### 2.2. Measurement of electromagnetic parameters

The efficiency of interaction of the fabricated material with electromagnetic radiation of the gigahertz and terahertz ranges was estimated by the reflection $R$ and transmission $T$ coefficients, which were obtained in the experiment, and the absorption coefficient $A$, which is $A = 1 - R - T$.

The coefficients $R$ and $T$ are mainly determined by the magnitudes of the magnetic and dielectric constant at a given frequency. The relationship is described by the following relationships for a plane wave that normally falls on a flat surface:

\[ R = \rho(1 - e^{-2\gamma d})/(1 - \rho^2 e^{-2\gamma d}), \]
\[ T = (1 - \rho^2) e^{-2\gamma d}(1 - \rho^2 e^{-2\gamma d}), \]

where $\rho = (Z - 1)/(Z + 1)$ is the coefficient of reflection from the front surface of the sample with respect to the incident electromagnetic wave; $Z = (\mu / \varepsilon)^{1/2}$ is the wave impedance of the medium, $\gamma = k_0 (\mu \varepsilon)^{1/2}$ is the propagation constant, $c$ is the speed of light, $d$ is the thickness of the flat layer.

The free space method is used to experimentally determine the coefficients. This non-destructive method allows you to study samples of a large area. The measurements were carried out at three frequency sections: 30-56 GHz, 40 -120 GHz and 120-260 GHz.

The horn measurement method was used in the range of 30 - 56 GHz. This method modified to study the electromagnetic characteristics of materials with large losses in this range. The modification made it possible to increase the sensitivity of the horn method and preserve the plane-wave approximation, which is usually used to calculate the dielectric constant spectra [14]. The vector network analyzer PNA X N5247A (Agilent Technologies) was used for the generation, reception of electromagnetic radiation and the primary processing of measurement results.
The terahertz spectrometer of the Russian production of STD-21 was used to measure the electromagnetic response in the frequency range of 40 -120 and 120-260 GHz. The set of backward wave tubes was used to generate a continuous harmonic signal in these ranges. The spectrometer allows to measure the modules of the transmission and reflection coefficients and their phases [15].

The equipment of the Center for Collective Use "Center for Radio Measurement TSU" was used to measure the frequency dependencies of the listed coefficients [16].

3. Results
Coefficients $R$ and $T$ were measured on flat samples, the geometric characteristics of which are shown in table 2.

Figures 3-5 show the frequency dependences of the $R$, $T$, $A$ coefficients of the samples (table 1). Electromagnetic energy almost completely passes through a layer of pure GO (figure 3), decreasing at high frequencies due to the increase in reflectivity (figure 4).

![Graph of transmission coefficient vs frequency](image)

**Figure 3.** Frequency dependences of transmission coefficients.
An increase in the concentration of MWCNTs leads to an increase in the screening effect due to an increase in absorption (figure 5). The increase in coefficient $A$ is caused by: 1- an increase in the hopping conductivity characteristic of MWCNTs; 2- by the layered structure that was formed during manufacture (figure 2), which provides polarization losses.

The sample (at 30 percent aqueous dispersion of MWCNTs) shields 90 percent of the incident energy, which is a high indicator for the selected thickness.
A high reflection coefficient is noted. It can be reduced by using an additional matching layer on the side of the incident electromagnetic wave.

The created structure surpasses the other composite in its shielding properties - epoxy resin+MWCNTs Taunit-M described in [17].

4. Conclusion
As a result of studying the electromagnetic response spectra (reflection coefficients R, transmittance T, absorption coefficient A) of graphene oxide material samples with different contents of Taunit-M MWCNTs, it is seen that an increase in MWCNT concentration leads to a significant increase in the protective qualities of the developed material, a relatively small increase reflection coefficient. A sample containing 30 wt.% aqueous dispersion of MWCNTs Taunit-M showed the greatest shielding property.

We can conclude that this material is promising for solving the problems of electromagnetic compatibility, protecting personnel from the harmful effects of electromagnetic radiation, and other practical applications.

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