Investigation of the dielectric properties of composites based on silicon dioxide with carbon nanotubes

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Abstract. The aim of this work is an experimental study of the dielectric properties of nanocomposites with a matrix of silica reinforced with multi-walled CNTs at different concentrations and to determine the role of the CNT in the scattering and absorption of electromagnetic radiation in the range of extra-long and medium radio waves (25 Hz-1 MHz). The study found that in addition to the standard behavior of the electrical characteristics of nanocomposites with increasing concentration there was an optimum concentration of carbon nanotubes at which conductivity and absorption of electromagnetic radiation in the material greatly increased. This can be used to enhance the functionality of nanocomposites.

1. Introduction
Recently, active research of composite materials is being conducted which include nanostructures, in particular, carbon nanotubes (CNTs) as filler. Due to the large surface area of the CNT, as well as significant differences of the physical properties of nanoobjects from macrostate material properties of the nanocomposites its properties are not additive characteristics of each phase and can be radically different from those of each of its components [1]. In the review [2] data is provided on the study of the electrical properties of nanocomposites with CNT. Particularly urgent task is to study the strongly nonlinear dependence of properties of the composite on the concentration of the filler, which is necessary for the selection of the optimum functional properties of materials (strength, thermal, dielectric and other characteristics). In the literature [3] data is presented on the influence of impurities on the dielectric properties of CNTs of different composites at microwave frequencies associated with the search for promising materials for "stealth"-technologies [3]. This paper [4, 5] investigates the microwave characteristics at a controlled modification of carbon nanotubes and the nanocomposite materials based on them.

2. Obtaining nanocomposite material
Our composite consist of SiO2 (matrix). It is reinforced with multi-walled CNTs at different concentrations – 0%, 0.05%, 0.1%, 0.5% (by weight of silica + water), with an aspect ratio of 10-10^2 (see Figure 1), obtained by CVD-method.
Silicon were obtained from silicate glue (see Figure 2). The chemical reaction is shown below.

\[ \text{Na}_2\text{SiO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{SiO}_3, \]
\[ \text{H}_2\text{SiO}_3 \rightarrow \text{H}_2\text{O} + \text{SiO}_2. \]

**3. The frequency dependence of the nanocomposite electrical properties**

Electrical characteristics of the samples were studied by dielectric relaxation spectroscopy method [2], according to which the sample is placed between the plates of the capacitor (area of \( S = 16 \text{ cm}^2 \) and the distance between the plates \( d = 3.3 \text{mm} \)). The sample was exposed to an alternating electric field with a frequency varying in the range of 25Hz -1MHz. The measured values were electrical capacitance \( C \), the quality factor \( Q \), and the resistance \( R \). Study of electrical properties of the composites in electric fields were produced using immittance meter E7-20.

Microwave properties of the composite are described by the frequency electrical field \( f \) dependence of the complex permittivity:

\[ \varepsilon = \varepsilon' - i\varepsilon'', \]
\[ \varepsilon'(f) = \frac{(C(f) - C_0) d}{\varepsilon_0 S}, \quad \varepsilon''(f) = \frac{d}{\varepsilon_0 S} \left( \frac{C(f)}{Q(f)} - \frac{C_0}{Q_0} \right), \]
\[ \sigma(f) = 2\pi f \varepsilon''(f) \varepsilon_0. \]
Where the real and imaginary parts characterize the dielectric polarization and losses in the composite respectively. Where $C, C_0$ - capacitance of the cell with the composite and empty cell respectively and $Q, Q_0$ - quality factor of the filled and empty cells.

4. Results of experiment

According to the table it can be argued, that there is an optimum concentration at which maximum absorption and scattering of electromagnetic waves at low frequencies occurs. It is known that the change of CNTs concentration leads to a nonlinear modification of the nanomaterials functional properties. In [6] this dependence is noted for the mechanical properties. The dependence of the electrical properties (1), (2) of the silicon dioxide powder on concentration of carbon nanotubes at different frequencies in Table 1.

| Composition, CNT, n% | Frequencies of electrical field | 50 Hz | 500 Hz |
|----------------------|---------------------------------|-------|-------|
|                      | $\varepsilon', 10^4$           | $\varepsilon'', 10^4$ | $\varepsilon', 10^4$ | $\varepsilon'', 10^4$ |
| Natural, no CNT      | 59.4                            | 283    | 0.95  | 23.8  |
| 0.01                 | 53.6                            | 31.5   | 18.4  | 13    |
| 0.05                 | 326.3                           | 2331   | 22.8  | 243   |
| 0.1                  | 41.9                            | 72.3   | 13.3  | 12.3  |
| 0.5                  | 8.8                             | 8      | 2.3   | 2.4   |

Based on the data (see Figure 3) it can be concluded that there is a sharp increase in the absorption properties of the sample at a concentration $\sim 0.05\%$ at low frequencies. There is also strongly marked maximum in dispersion of electromagnetic waves for all concentrations in the range of $\sim 10$kHz.

![Figure 3](image.png)

**Figure 3.** Depenence of the electrical properties (the imaginary (a), and real (b) part of the permittivity (2), conductivity (c), (3)) on the frequency of the electromagnetic field at different concentrations of CNTs: 0.5\% 0.1\% 0.05\% 0.01\% 0\%.

The behavior of $\varepsilon'$ is associated with a decrease of electromagnetic field change rate compared to the typical recharge time (relaxation time) of effective capacitor formed of adjacent conductive particles. At high frequencies the capacitor does not have time to recharge, and the value of the dielectric permittivity tends to the same value of the composite permittivity with zero concentration of CNTs.

Dependence of the imaginary part of permittivity and conductivity on the frequency also shows a clear concentrational nonlinearity. When $n = 0.5\%$ apparently occurs the transition into the zone of agglomerate conductivity where there is deterioration in the conductivity of the sample. With increase
of the electromagnetic field frequency the conductivity is caused by the bias current and increasing for all samples.

5. Model of agglomerates
These nonlinear dependence suggests the restructuring of a complex system fine powder SiO₂ + multiwalled CNTs + H₂O (free and bound). With the increase of concentration structures are formed (agglomerates). Dielectric properties of samples support this hypothesis. Their surface area is less than the summary surface area of their components (see Figure 4a,4b). The Figure 4c shows an equivalent circuit a electrical rechargeable capacitor nanosystem. The reason of the formation of this structures is the great difference between silicon and CNTs surface energy.

Figure 4. Model representation of the CNT polarization in an alternating electromagnetic field and percolation conductivity (a), the formation of agglomerates with increasing concentration of CNTs (b), rechargeable capacitor system (c).

6. Conclusions
We formulate the main conclusions and results.
- The obtained results allow to judge about the essentially nonlinear dependence of dielectric properties (conductivity and permittivity) on the CNT concentration in this frequency range. There is an optimum concentration of CNTs (~ 0.05%) at which the absorption and dispersion of electromagnetic waves increase sharply. At this concentration even distribution of CNTs by volume of the sample is achieved.
- There is an opportunity to create a nanomaterial with desired dielectric functional properties ε ′, ε ″.
- Such features of dielectric properties of the sample possibly relate to the formation of agglomerates, which surface is less than the total surface of the constituent nanotubes.
- Verification of the hypothesis of agglomerates formation with the increase of CNTs concentration is possible by means of positron annihilation microscopy [7, 8, 9], which is in contrast to the AFM and electron microscopy allows to investigate internal structure of the sample.

Acknowledgements
This work was supported by the project the Ministry of Education and Science of the Russian Federation №3635 "Investigation of the properties nanocomposites with controlled modification of the structure reinforced with carbon nanotubes".

The research was done using the equipment of Core Facility Center "Arktika" of Northern (Arctic) Federal University under financial support of Ministry of Education and Science of the Russian Federation (project RFMEFI59414X0004).

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