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Electromagnetic Properties of Cold-Cure Silicone Mixtures Containing Multi-Walled Carbon Nanotubes

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Abstract

Nanocomposite materials based on a cold-cure silicone mixture containing multi-walled carbon nanotubes were obtained. The concentration dependences of the radio-physical properties of materials were investigated. An increase in the efficiency of shielding electromagnetic radiation in the radio frequency range of wavelengths with increasing concentrations of multi-walled carbon nanotubes up to 10 wt. % was verified.

Keywords

Polymer radar absorbing materials; multi-walled carbon nanotubes; radiophysical properties.

Introduction

At present, an interest in the research and application of new polymer nanocomposite materials that are effective for shielding electromagnetic radiation is increasing [1], and studies are actively conducted in many global research centers and laboratories. Carbon nanomaterials are introduced into polymer matrices as functional components. Among the most promising are multi-walled carbon nanotubes (MWCNTs) [2–8] since the transformation of their structure leads to a change in the electromagnetic characteristics [1], and they are much cheaper than single-walled ones. Silicone materials occupy a special place among polymer matrices, since they have good mechanical properties, chemical resistance, and convenient fabrication, but they are practically transparent to electromagnetic radiation. It is possible to improve the shielding properties of silicones using MCNT. Moreover, the shielding properties of silicone composites are insufficiently explored, and the available information is rather scarce.

Therefore, in the present work, nanocomposite silicone materials with different concentrations of MCNTs were chosen as the object of study for electromagnetic properties. The influence of the concentration of MCNTs on the radiophysical properties of the obtained nanocomposite materials has been studied.

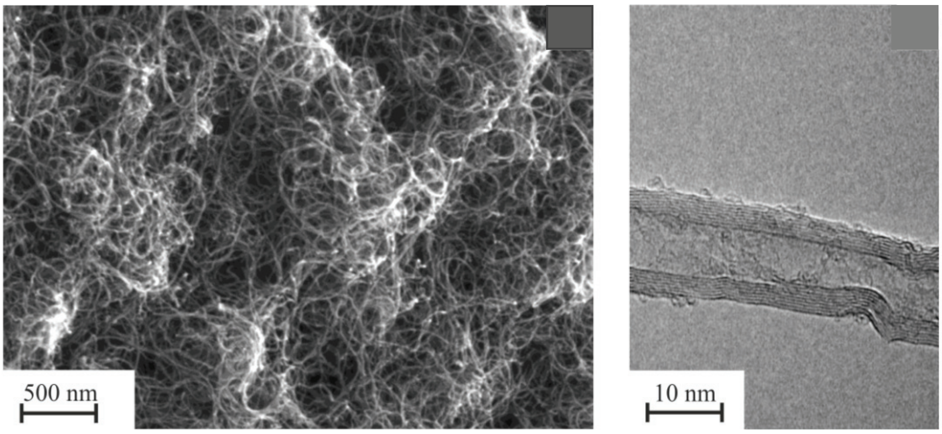
Materials and methods

Materials

Carbon nanomaterial "Taunit-M" consists of multi-walled carbon nanotubes (MWCNTs) with a diameter of from 10 nm to 30 nm and a length up to 2 μm (Fig. 1).

MWCNTs "Taunit-M" were synthesized by the method of catalytic pyrolysis of natural gas in "NanoTechCenter" (Tambov).

In this paper, cold cure silicone mixture, a two-component injection molding silicone rubber mixture of additive crosslinking, was chosen as a polymer matrix. Polydimethylsiloxane with functional groups and auxiliary substances to create a network was used for additive crosslinking. This material allows for obtaining flexible and chemically resistant non-toxic



a) *b*)

Fig. 1. SEM (*a*) and TEM (*b*) images of the "Taunit-M" MWCNTs

materials. The polymer mixture used in the work was a cold cure silicone mixture of the brand Elastomould 115 of the company BMP Technology Co. Ltd. (Moscow), the dielectric constant values were ε' = 2.8, ε'' = 0.1.

Coatings

MWCNTs were introduced into the silicone base at the concentrations shown in Table 1.

After adding the MWCNTs, the mixture was blended on a mechanical stirrer (Witeg HT-50AX) for 10 minutes. Next, the resulting material was uniformly applied to the polyethylene substrate and maintained at room temperature until complete curing.

Characterization

The TEM studies of the material obtained were performed using a JEM-2010 high-resolution transmission electron microscope. The study of the morphology and microstructure of the surface of the MWCNTs was carried out using a scanning electron microscope (SEM) "Merlin" (Carl Zeiss, Germany).

Table 1

Characteristics of materials

Sample, No.	Composition, wt. %	Size, mm	Thickness, mm
1	Silicone/ MWCNTs, 98/2		1.2
2	Silicone/ MWCNTs, 95/5	200×200	1.9
3	Silicone/ MWCNTs, 90/10		1.3

The electrical conductivity of nanomaterials was measured using impedance spectroscopy using the Alpha AN impedance meter (NovoControl, Germany). The measurements were carried out with the samples placed and pressed at a pressure of about 100 MPa between titanium electrodes with a diameter of 8 mm.

Electromagnetic characteristics of the samples were measured using a Rohde & Schwarz vector ZVA67 electrical circuit analyzer in the near-field ultra-wideband diaphragm lens horn antennas in the wavelength range from 3 to 40 GHz: in the low-frequency wavelength range from 3 to 24 GHz and in the high-frequency wavelength range from 23 to 40 GHz. This measurement method is based on measuring the reflection coefficients of a quasi-flat electromagnetic wave at a normal angle of incidence for samples of materials in the form of flat sheets. When measuring, a sample of the material is placed in a window of a round metal radio absorbing diaphragm located in the near zone of horn antennas in order to minimize the contribution of diffraction processes at the edges of the sample and edges of horn antennas. In the process of measuring the reflection coefficient of samples in the area behind the diaphragm, a matched load is set – a volumetric radio-absorbing unit with a low reflection coefficient in the working frequency band (no higher than minus 50 dB) to eliminate additional parasitic reflections from the surrounding space.

Results and discussion

Power losses of electromagnetic radiation during passage through a material result from the following phenomena: reflections (and / or multiple reflections) and absorption [1]. The absorption coefficient A, the reflection coefficient R and the transmission coefficient T are related by:

$$A = 1 - R^2 - T^2. \quad (1)$$

The sum of all losses is called the shielding efficiency (**SE**). It is measured in units of dB and is determined using the following expressions:

$$\mathrm{SE}_{\mathrm{TOTAL}}(dB) = \mathrm{SE}_{\mathrm{A}} + \mathrm{SE}_{\mathrm{R}}; \quad (2)$$

$$\mathrm{SE}_{\mathrm{TOTAL}}(dB) = 10\log 10\left(1/T^2\right); \quad (3)$$

$$\mathrm{SE}_{\mathrm{R}}(dB) = 10\log 10\left(1 - R^2\right); \quad (4)$$

$$\mathrm{SE}_{\mathrm{A}}(dB) = 10\log 10\left(T^2/\left(1 - R^2\right)\right), \quad (5)$$

where SE_{A} is absorption loss, SE_{R} is reflection loss.

Fig. 2 shows the frequency dependences of radio-physical parameters (reflection coefficient R, shielding efficiency $\mathrm{SE}_{\mathrm{TOTAL}}$ and permittivity ε) for materials with different component composition. Increasing the MWCNT concentration slightly affects the value of the reflection coefficient and increases the screening efficiency of the material. When introducing more than 2 wt. % of the MWCNTs into the polymer matrix, the SE magnitude significantly increases (Table 2).

The graphs in Fig. 2 represent the result of measurements at the test bench for measuring the electrodynamic parameters of materials using a Rohde & Schwarz vector network analyzer, which allows determining the S-parameters of the sample, that is, the spectral dependences of the reflection coefficients $R_{\mathrm{exp}} = S_{11}(f)$ and the transmission coefficients $T_{\mathrm{exp}} = S_{21}(f)$ flat sheets arbitrary thickness.

To determine the specific shielding parameters $\mathrm{SE}_{\mathrm{TOTAL}}$, attenuation of radiation (in dB) with a material of 1 mm thickness, the reflection and transmission coefficients for the layer thickness of 1 mm were recalculated after the electrodynamic parameters of the material ε′, ε″ were recovered from the initial measurement results of the studied flat sheets of material arbitrary thickness. The calculation of the electrodynamic parameters of materials ε′, ε″ was performed for each frequency point of the spectrum in the range from 3 to 40 GHz, in which measurements were carried out using the minimization procedure of the objective function of two variables ε′ and δ, where $\delta = \mathrm{arctg}(\varepsilon''/\varepsilon')$ is the dielectric loss angle.

Table 2 shows the values of the radiophysical parameters of the materials obtained herein.

The material of sample No. 3, containing 10 wt. % of the MWCNTs, possesses the maximum SE value 12.3 dB/mm.

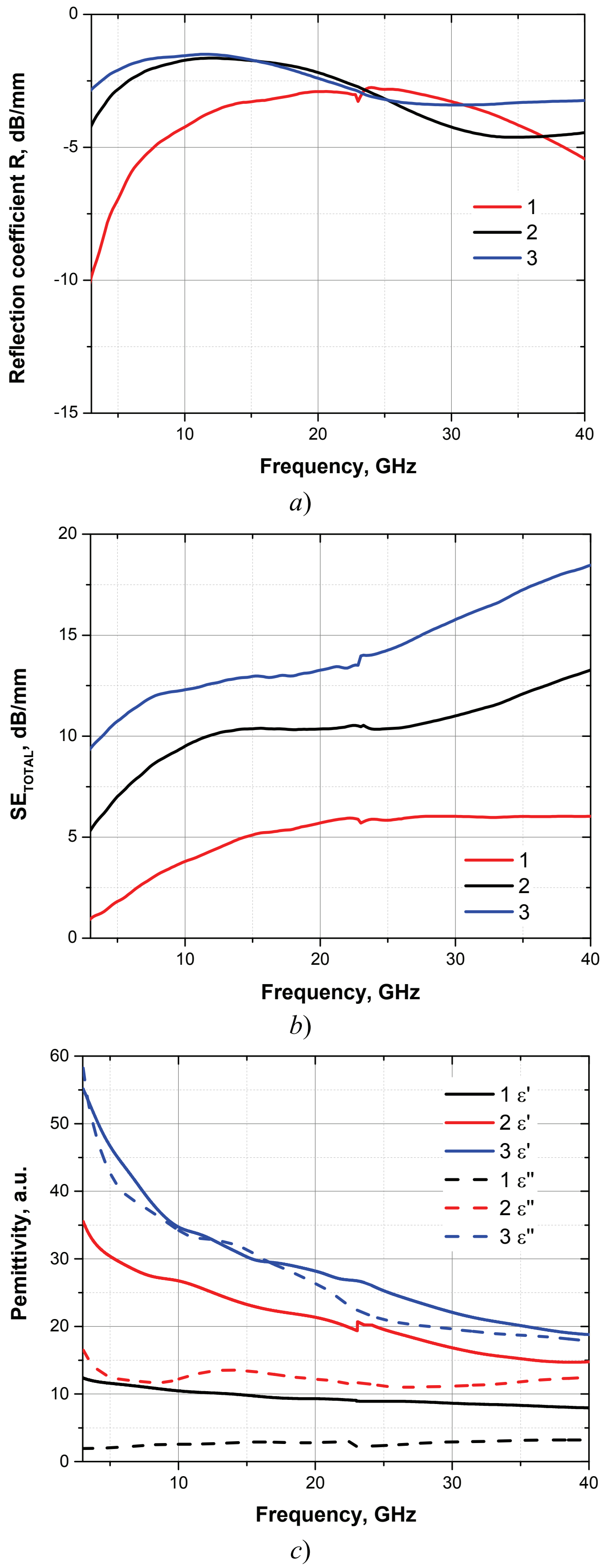


Fig. 2. Frequency dependence of the parameters of materials:
a – reflection coefficient R; *b* – $\mathrm{SE}_{\mathrm{TOTAL}}$; *c* – Permittivity

Table 2

Electromagnetic properties of polymer composites containing MWCNTs

Sample, No.	Matrix	Component	Concentration, wt. %	Frequency, GHz	SE_{TOTAL}, dB mm^{-1}	SE_A, dB	SE_R, dB
1	Silicone	MWCNTs	2	8–12	3.77	1.71	2.07
2			5		9.47	4.69	4.78
3			10		12.31	7.10	5.21

Conclusion

Polymer nanocomposite materials containing multi-walled carbon nanotubes were obtained. The concentration dependences of the radio-physical properties of the materials in the frequency range from 3 to 40 GHz were investigated. The maximum value of the shielding efficiency was found to be 12.3 dB in the range from 8 to 12 GHz at the MCNT concentration of 10 wt. %.

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