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Radar absorbing properties of carbon nanotubes/polymer composites in the V-band

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Abstract. This research is devoted to the study of radar absorbing properties of the composites, based on the epoxy binder and carbon nanotubes (CNT) in the frequency range of 52–73 GHz. Three species of unmodified multi-walled CNT differing in length and diameter were investigated as fillers. The reflection coefficients (K_{refl}) at the radar absorbing material (RAM)–air interface and the electro-magnetic radiation (EMR) absorption coefficients (K_{abs}) in the materials with the different content of nanotubes were measured (K_{refl} and K_{abs} were calculated using the highest (the worst) value of the voltage standing-wave ratio (VSWR) in the frequency range of 52–73 GHz). It was established that the increase in nanotubes aspect ratio (a ratio of CNT length to its diameter) leads to K_{abs} rising for polymer composites. Also, CNT diameter decrease leads to K_{refl} reduction. CNT of 8–15 nm in diameter and more than 2 μm in length are the most effective from all investigated fillers. The reflection loss values were calculated and CNT optimal concentrations were obtained at different thickness of RAMs.

Keywords. Radar absorbing materials; carbon nanotubes; nanocomposites; reflection loss.

1. Introduction

From year to year, radar absorbing materials (RAMs) become more widely used in the electronic devices development. The bulk of absorbing materials are the composites, consisting of a polymer matrix and electrically-conductive or magnetic fillers. CNTs are one of the most perspective materials for these purposes. Much research in this area are devoted to the study of radar absorbing properties of CNT/polymer composites in the range of frequencies from 2 to 18 GHz [1–8], because the bulk of the modern electronic devices, such as wireless data communication devices, air traffic control systems, meteorological equipment, radar stations, satellite navigation and mapping systems, missile guidance systems, operate in this range. Fewer publications are devoted to the study of RAMs with CNT in the range of frequencies from 25 to 40 GHz [9–12]. Precision mapping systems, air traffic control systems at short distances, systems of high-precision tracking of low-flying targets operate in this range. The RAMs investigations for the range of 40–75 GHz (V-band) are practically absent, in spite of the mainly military and aerospace devices operating in this range, which also shows a great potential in the promising high-speed ultra wideband system data.

This research is devoted to the study of radar absorbing properties of polymer composites based on the epoxy binder and several CNT species in the range of frequencies from 52 to 73 GHz. The purpose of our investigation was to develop the broadband RAMs characterized by the required properties throughout the frequency range.

2. Experimental

2.1 *Materials*

Our experiments were performed with CNT of grades ‘Taunit-M’ (CNT-1), ‘Taunit-MD’ (CNT-2) and ‘Taunit’ (CNT-3) (Technical Specification 2166-001-02069289–2006, NanoTechCenter, Tambov, Russia). The CNT parameters according to the producer’s data are listed in table 1.

KDS-25 epoxy compound was used as a polymeric matrix for radar absorbing materials (RAMs) (Technical Specification ADI 426–93, STEP Research and Production Association, St. Petersburg, Russia). Penta-11 antiadhesive coating (Technical Specification 2257-082-40245042–2004, Penta-91, Moscow, Russia) was used for facilitating the removal of RAMs specimens from a steel mold.

2.2 *Method of RAMs sample preparation*

The weight fraction of CNT in the composite was varied from 0.02 to 6% for CNT-1 and CNT-2 and from 0.2 to 33% for CNT-3. Acetone (10 g) was added to a weighed portion of CNT and the mixture was ultrasonically treated for 5 min.

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Table 1. The parameters of CNT.

Parameter	CNT-1	CNT-2	CNT-3
Outside diameter, nm	8–15	30–80	20–70
Inner diameter, nm	4–8	10–20	5–10
Length, μm	≥2	≥20	≥2
Impurities volume, mass%	<1	<1	<1
Specific surface area, $m^2\ g^{-1}$	300–320	180–200	120–130
Thermal stability, °C	≥600	≥600	≥600

Then, 10 g of the epoxy resin was added and the mixture was ultrasonically treated for an additional 10 min with simultaneous stirring and water cooling. Acetone was evaporated in an oven at 60°C for 6 h and at the same temperature in vacuum for additional 6 h. The curing agent was added, and the components were thoroughly mixed. Then, the mixture was transferred into a steel mould coated with Penta-111, heated to 70°C and compressed at 30–40 kg cm^{-2}.

The curing was interrupted after 1 h at the point of formation of a rubbery material. The plate of size $120 \times 120 \times 3$ mm was taken off from the mould, and disks of 50 mm in diameter were cut and kept in an oven at 70°C for 7 h for complete curing.

2.3 *Methods of investigation*

Electron micrographs of CNT were taken with a scanning electron microscope (SEM) TESCAN VEGA II.

Radar absorbing properties of the samples were measured with panoramic meter R2-69 as it was described in ref. [13]. An antenna was closely attached to the sample (figure 1a) and the VSWR maximum was measured in the range of frequencies from 52 to 73 GHz.

Close to a sample an RTA5 antenna was placed, on which a signal from a sweep frequency generator was translated. A Ya2R-67 indicator was used to measure the maximum of VSWR in the frequency range of 52–73 GHz. The VSWR measurement accuracy by R2-69 instrument is 5%. The reflection coefficient was calculated by the following formula:

$$K = \left(\frac{\text{VSWR} - 1}{\text{VSWR} + 1}\right)^2. \tag{1}$$

For each sample, two measurements of the reflection coefficient were performed: with a metal screen behind a sample (K_2) and without it (K_1).

An electromagnetic wave (EMW) incident on any material is partially reflected, absorbed and passes through it:

$$E_0 = R + A + E_{\text{pass}}, \tag{2}$$

where E_0 is the energy of incident radiation, R the energy of reflected radiation, A the energy of absorbed radiation and E_{pass} the energy of passed radiation.

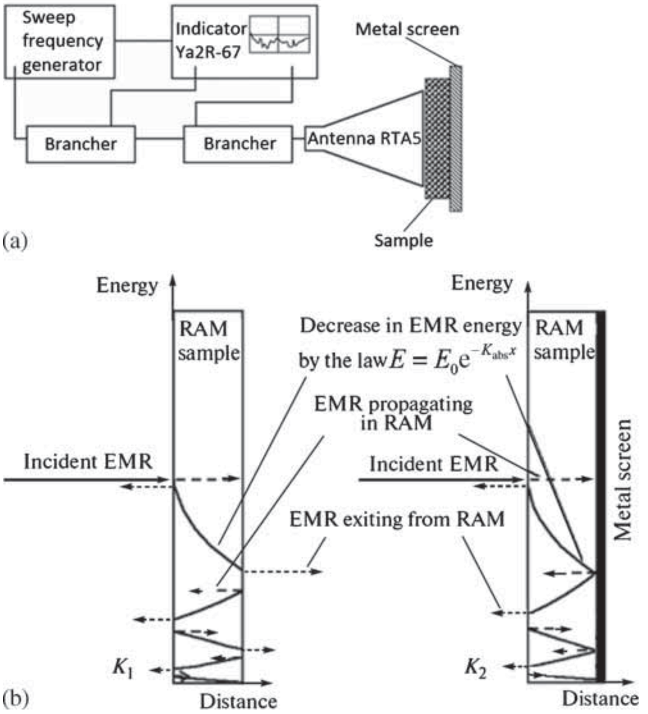

Figure 1. (**a**) Block diagram of R2-69 panoramic device for measuring VSWR and (**b**) schematic of propagation of electromagnetic wave in the material.

An electromagnetic wave reaching the RAM surface is partially reflected at the interface and partially penetrates into the material (figure 1b). Passing through the material, radiation is absorbed exponentially:

$$E = E_0 e^{-K_{\text{abs}}x}, \tag{3}$$

where K_{abs} is the absorption coefficient and x the path travelled by a wave in the material.

On reaching the back wall of a sample, EMW is partially reflected, returning to RAM and partially leaves the material. Thus, several cycles of rereflection occur until EMW is completely absorbed or exits from the material. In the case, where a metal screen is placed behind a RAM sample, EMW is absolutely reflected from it, while on the front surface of the sample there is reflection and passing of radiation through the interface. The reflection coefficients calculated from equation (1) are combined values which account for multiple reflection and absorption of EMW in RAM (figure 1b).

The most informative characteristics of RAM are the reflection coefficient (K_{refl}) at the air–RAM interface (K_{refl} is the ratio of reflected EMW energy to EMW energy incident normally to the interface) and the absorption coefficient (K_{abs}) from equation (3). Taking into account the aforementioned values, we will write the expression for K_1 and K_2. Let us assume that EMW is normally incident to the sample with the energy E_0. On reaching the air–RAM interface, the wave is partially reflected so that the fractions of the reflected and passed waves are equal to, respectively, $K_{\text{refl}} \cdot E_0$ and $(1 - K_{\text{refl}})E_0$. In the RAM, radiation is absorbed exponentially, so that radiation with the energy $(1 - K_{\text{refl}})E_0e^{-K_{\text{abs}}x}$, reaches the back wall, where $x = 3$ mm (the sample thickness). On the back surface of the sample, there is reflection; with a metal screen, the reflection is total, and if there is no screen, the wave with energy $(1 - K_{\mathrm{refl}})^2 E_0 \mathrm{e}^{-K_{\mathrm{abs}}x}$ exits and the wave with the energy $K_{\mathrm{refl}}(1 - K_{\mathrm{refl}}) E_0 \mathrm{e}^{-K_{\mathrm{abs}}x}$ reflects. Thus, the wave is multiplied and reflected in the material, and the expressions for K_1 and K_2 will be expressed as:

$$\begin{cases} K_1 = K_{\mathrm{refl}} + K_{\mathrm{refl}}(1-K_{\mathrm{refl}})^2 \mathrm{e}^{-2K_{\mathrm{abs}}x} + K_{\mathrm{refl}}^3 (1-K_{\mathrm{refl}})^2 \mathrm{e}^{-4K_{\mathrm{abs}}x} \\ \qquad + \cdots + K_{\mathrm{refl}}^{2n+1} (1 - K_{\mathrm{refl}})^2 \mathrm{e}^{-2nK_{\mathrm{abs}}x}, \\ K_2 = K_{\mathrm{refl}} + (1 - K_{\mathrm{refl}})^2 \mathrm{e}^{-2K_{\mathrm{abs}}x} + r(1 - K_{\mathrm{refl}})^2 \mathrm{e}^{-4K_{\mathrm{abs}}x} \\ \qquad + \cdots + K_{\mathrm{refl}}^n (1 - r)^2 \mathrm{e}^{-(2n+2)K_{\mathrm{abs}}x}. \end{cases} \tag{4}$$

This system of equations was solved using the Mathcad 8.0 software program for each measured sample. Thus, the values of K_{refl} and K_{abs} (mm^{-1}) were obtained. For convenience, the K_{abs} value was converted from mm^{-1} to dB cm^{-1}.

The volume resistivity of the composites was measured with an E6-13A mhometer at a constant voltage of 100 V.

3. Results and discussion

The structure of the investigated CNT is presented in figure 2.

Figure 3 shows the optical microscope images of the obtained CNT dispersions in the epoxy resin. CNTs are situated in a polymer matrix as agglomerates of a size upto 120 μm. Such agglomeration is typical for non-functionalized nanotubes.

The measurements in the range of 52–73 GHz indicated that the maximum (the worst) VSWR values for all RAM samples are registered at a frequency of 52 GHz. The reflection coefficients K_1 and K_2 and the coefficients of reflection (K_{refl}) at the RAM–air interface and absorption (K_{abs}) were calculated using the obtained maximum VSWR values. The dependences of K_{refl} and K_{abs} from the nanotubes content in the composites are shown in figure 4.

The absorption coefficient for the composites with CNT-1 content is less than 4%, and for the composites with CNT-2 content is less than 1% is presented in figure 4b. The CNT content is more than the specified values, the absorption in the material is enough to absorb all radiations, passing into the material, during its double pass from RAM surface to a metal screen and back. Thus, above this CNT content K_1 is always equal to K_2, i.e., K_1 and K_2 are determined only by the reflection at the RAM–air interface. So, for CNT content higher than specified value, it is impossible to calculate K_{abs} by solving the equations (4) (this system is solved at any K_{abs} value).

According to figure 4a K_{refl} insignificantly varies at low CNT concentrations and there is a slight K_{refl} decrease which is explained by the incident radiation scattering on the nanotubes, when the permittivity of the composite is practically equal to the same of polymer matrix at low CNT concentrations (lower or closely to the percolation threshold). Such a decrease of the reflection coefficient at low CNT content is also showed in ref. [11]; however, the authors do not discuss this effect. At the higher CNT concentrations, it is impossible to register the effect of radiation scattering on nanotubes, because the reflection and absorption coefficients of the composites were quickly increased due to their conductivity growth.

It is worthwhile to note that the initial parts of CNT-2 and CNT-3 reflection curves are situated closely to each other, but for the similar CNT-1 curve it is situated below. Thereby, it can be suggested that at low CNT concentrations, the scattering radiation effect depends on CNTs' diameter,

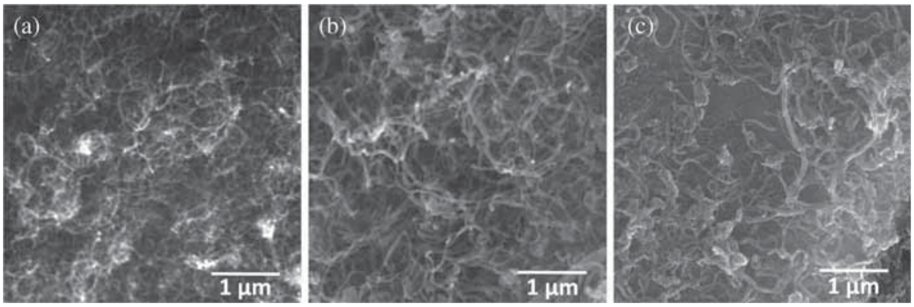

Figure 2. SEM images of (**a**) CNT-1, (**b**) CNT-2 and (**c**) CNT-3.

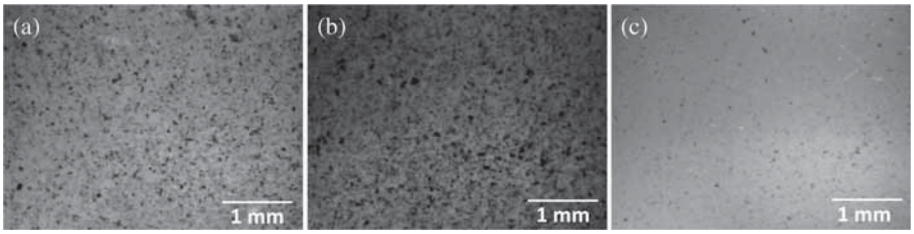

Figure 3. The dispersions of (**a**) CNT-1, (**b**) CNT-2 and (**c**) CNT-3 in the epoxy resin (CNT content is 0.02%).

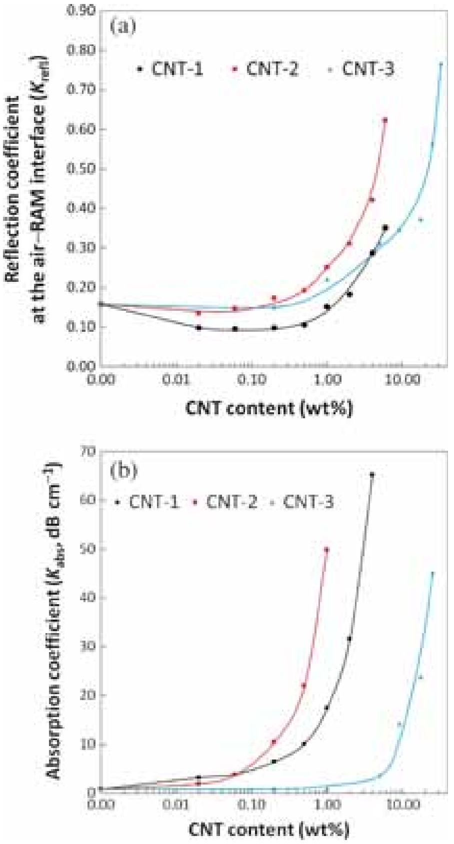

Figure 4. Dependences of (**a**) K_{refl} and (**b**) K_{abs} on the nanotubes content in the composites.

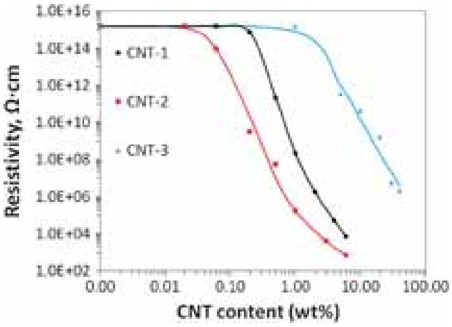

Figure 5. Dependences of volume resistance on CNT content.

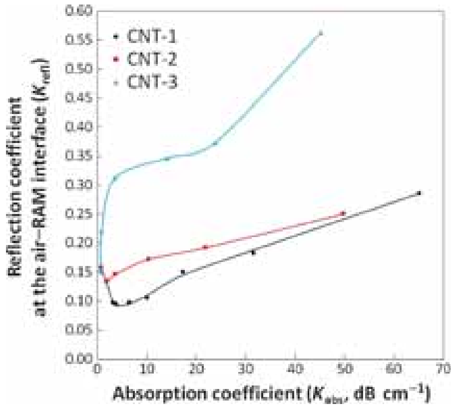

Figure 6. Dependences of K_{refl} on K_{abs}.

because the diameters of CNT-2 and CNT-3 are close to each other, while the diameter of CNT-1 is significantly less. So at the given CNT concentration, the number of nanotube segments, as scatters, increases per unit volume at the decrease of CNT diameter. At low CNT concentrations, K_{abs} also varies insignificantly. The coefficients of reflection and absorption begin to increase rapidly when the CNT content in the composites achieves the certain value. Such growth is due to percolation threshold achievement in the composites and, consequently, the electrical conductivity sharply increases (the resistance decreases), which is confirmed by the dependences of the volume resistance from CNT content (figure 5).

In its turn, the value of percolation threshold for investigated composites correlates very accurately with CNT aspect ratio. So CNT-2, CNT-1 and CNT-3 aspect ratios are 364, 174 and 44 and percolation thresholds are 0.042, 0.2 and 4%, respectively. However, the values of K_{abs} and K_{refl} separately do not allow to conclude that obtained composites are effective as radar absorbing materials. The effective RAM must have an optimal combination of reflecting and absorbing properties, i.e., the absorbing ability must be maximum at the minimal reflection coefficient. Therefore, it is advisable to consider the ratio of reflection coefficient to absorption coefficient (K_{refl}/K_{abs}) for obtained composites (figure 6).

The increase of K_{abs} according to the growth of CNT content in the composite leads to K_{refl} rise in the material (except the initial part of the curve), however, at the same absorbing ability, the composites with CNT-1 characterized by the least reflection coefficient (K_{refl}) (figure 6). CNT-2 have a high aspect ratio and provide the similar absorbing ability at less concentration of nanotubes, but in spite of that, CNT-2 concede to CNT-1 in the effectiveness of its application in RAMs. CNT-3 are significantly less in the effectiveness in comparison with another species of nanotubes and similar to the standard carbon modifications such as graphite and carbon black by the influence on radar absorbing properties of the material [13].

The values of reflection loss at different CNT concentrations and thickness of sheet RAMs were calculated based on the obtained K_{refl} at the RAM–air interface and K_{abs} values (table 2).

The natural phenomenon for the radar absorbing filler is shown in the table 2, when initially the reflection loss grows according to the increase in filler concentration and when the maximum value is achieved, it starts to decrease. The CNT concentration is optimal, when reflection loss is maximal. The further rising of CNT concentration leads to the decrease in reflection loss due to K_{refl} increase at the RAM–air interface. The optimal CNT concentration depends on

Table 2. The minimal reflection loss values (dB) in the frequency range of 52–73 GHz (actually, at the frequency of 52 GHz) when RAM is placed on a steel substrate at the given thickness of the material*.

CNT type	CNT content, %	Material thickness (mm)				
		1	2	3	5	10
CNT-1	0.02	0.6	1.2	1.8	3.0	5.4
	0.06	0.8	1.5	2.2	3.5	6.3
	0.2	1.3	2.4	3.5	5.5	8.6
	0.5	1.9	3.6	5.1	7.3	9.5
	1	3.0	5.2	6.7	7.9	8.2
	2	4.6	6.6	7.2	7.4	7.4
	4	5.1	5.4	5.4	5.4	5.4
	6	4.5	4.6	4.6	4.6	4.6
CNT-2	0.02	0.4	0.8	1.1	1.8	3.4
	0.06	0.7	1.4	2.1	3.2	5.5
	0.2	1.9	3.4	4.7	6.3	7.5
	0.5	3.5	5.5	6.5	7.1	7.2
	1	5.1	5.9	6.0	6.0	6.0
	2	4.9	5.1	5.1	5.1	5.1
	4	3.8	3.8	3.8	3.8	3.8
	6	2.1	2.1	2.1	2.1	2.1
CNT-3	0.2	0.2	0.3	0.5	0.8	1.6
	1	0.2	0.4	0.6	0.9	1.7
	5	0.7	1.2	1.8	2.6	3.9
	9	2.1	3.2	3.9	4.4	4.6
	17	2.8	3.8	4.1	4.3	4.3
	25	2.3	2.5	2.5	2.5	2.5
	33	1.1	1.2	1.2	1.2	1.2

*The reflection loss values were measured when RAM is placed on the metal substrate.

RAMs' thickness. However, it is shown in table 2 that the most effective filler is CNT-1 at all RAMs' thickness.

We have not found another research devoted to the investigations of RAMs with CNT in the same frequency range, so a direct comparison of the obtained results with the similar materials is impossible. The comparison with the characteristics of materials, investigated in the lower frequency range can be done only approximately. So, for example, the papers of [3–5,7,8,14] are devoted to study of the materials, which is similar to ours in the frequency range of 2–18 GHz and there are the width of the absorption bands, where the reflection loss is more than 5 dB, is 4, 13, 9, 5, 6, 8 GHz, respectively, for the best samples. In our case, throughout the frequency range from 52 to 73 GHz, the level of the reflection loss is from 5.1 (for the material of 1 mm in thickness) to 9.5 dB (for the thickness 10 mm) for the most effective RAMs (with CNT-1). Usually, the reflection loss equal to 5–10 dB (from a flat surface) is enough for RAMs, applied for the production of different elements (such as waveguide loads, flat or relief absorbers), provided the electromagnetic compatibility of radio-electronic blocks. Herewith the significant request is the reflection loss of RAMs must not be lower than the specified value throughout the working range of radio-electronic device.

4. Conclusions

In this work, radar absorbing properties of polymer composites with the several CNT species were studied in the frequency range of 52–73 GHz. The investigations showed that radar absorbing properties of polymer composites significantly depend on the CNT species, composed them. The absorbing ability of the composites grows according to the CNT aspect ratio increase. It is supposed that the value of CNT diameter influences on the effectiveness of radiation scattering and, as follows, on the reflecting properties of the composites. It was shown that nanotubes of 8–15 nm in diameter and more than 2 μm in length (i.e., nanotubes having a small diameter and large aspect ratio (174)) are the most effective nanotubes from all the studies. Broadband RAMs were obtained that absorb the electromagnetic radiation at small absorber thickness throughout the range from 52 to 73 GHz.

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