Electromagnetic Properties of Composite Materials Based on ABS Plastic with Carbon Nanotubes Obtained by the Additive Technology in the SHF and EHF Bands

G E Kuleshov\textsuperscript{1,2}, A V Badin\textsuperscript{1,2} and M O Gering\textsuperscript{2}

\textsuperscript{1}Laboratory of radiophysical and optical methods of exploring the surrounding environment, National Research Tomsk State University, Tomsk, Russia
\textsuperscript{2}Department of Radioelectronics, Faculty of Radiophysics, National Research Tomsk State University, Tomsk, Russia

E-mail: grigorij-kge@sibmail.com

Abstract. The results of study of the electromagnetic characteristics of polymer composite materials containing multwall carbon nanotubes are presented. New radio filaments for 3D printing with MWCNTs have been created. Experimental samples were obtained from composite filaments by 3D printing. Also investigated is the ABS plastic brand Conductive with carbon fibers. Studies of electromagnetic characteristics were carried out in the SHF and EHF ranges. The frequency dependences of the complex permittivity for these materials are shown. The results show that ABS Conductive plastic has the best absorbing properties on microwave frequency, and composite plastics with MWCNTs of 2\% or more on EHF.

1. Introduction
The rapidly developing 3D printing technologies today offer unlimited possibilities in the manufacture of structures and objects of any geometry for radioelectronic devices. Additive technologies have several advantages over traditional technologies, such as reducing the number of technological operations and time spent, waste-free use of source components, ease of development, optimization and modernization of products in engineering CAD-programs, high automation and manufacturability [1, 2]. Recently, it has been very common to manufacture composite materials based on plastics for 3D printing with the addition of fillers that effectively interact with electromagnetic radiation [3, 4]. Using of additive technology with radio filaments can significantly speed up and reduce the cost of the production of radio materials and protective coatings for end devices, and also makes it possible to create completely new elements and composite structures [5].

2. Materials and methods of measurement
Composition and structure of the materials was determined by X-ray diffraction analysis. Shimadzu XRD 6000 X-ray diffractometer and XRF-1800 wavelength dispersion X-ray fluorescence spectrometer were used. The samples of powders were studied.

The study of the structure of the material was carried out using an optical microscope, as well as by transmission electron microscopy. Electron-microscopic measurements were carried out with a transmission electron microscope Philips CM 30 with electronic image recording.
2.1. Materials
Various polymeric filaments can act as the basis of a composite filament for 3D printing. The characteristics of the final sample can vary greatly from the choice of binder. Plastics are divided into several main types: ABS, PLA, HIPS, RUBBER, FLEX, CRYSTAL and etc.

In our case, the acrylonitrile-butadiene-styrene (ABS plastic) acted as the base polymer of the composite filament for 3D printing. Powders of multi-walled carbon nanotubes (MWCNTs) were used as filler [4]. They were obtained by catalytic gas-phase deposition of ethylene and contained more than 97.5% of the main phase with an average nanotube diameter \( d = 9.4 \) nm. TEM images of carbon materials are shown in Figure 1. MWCNT agglomerates in the form of tangles are observed.

| Characteristics                        | Value of                                      |
|----------------------------------------|-----------------------------------------------|
| Synthesis method                       | Catalytic gas-phase deposition of ethylene    |
|                                        | with FeCo catalysts                            |
| Average nanotubes diameter             | 9.4 nm (4 – 21 nm)                            |
| Filler content MWCNT, wt.%             | more than 97.5                                |
| Impurities                             | particles FeCo/Al\(_2\)O\(_3\)                 |
| Ash content, wt.%                      | < 2.4                                        |
| Metal impurities (Fe, Co, Ca), wt.%    | < 1.7                                        |
| External specific surface, m\(^2\)/g  | 320                                          |
| Wall thickness of nanotubes            | 4.0 nm; 7-9 layers                            |

Figure 1. TEM images of the powders of MWCNT.

2.2. Obtaining experimental samples
Methodology for producing composite radiofilaments can be divided into several stages (Figure 2), each of which has an important role and will be described. For the production of composite plastic, the chemical method of mixing the components of the material was used. At the first stage, the required number of ABS granules (pieces of pure ABS) and filler were carefully weighed on an electronic balance with an accuracy of 0.001 g. At the next stage, the components are mixed, while the plastic used is previously dissolved to a homogeneous liquid state in acetone. The next step is the ultrasonic treatment of the unpolymerized mixture of ABS plastic with a filler. The processing was carried out on an ultrasonic device of the “Alena” series, model UZTA-0,1/28-O. The ultrasound power was 75 watts. This treatment allows to achieve greater uniformity and also breaks down the agglomerates of the filler, which is no less important. Since a dimethiketone solution was used to make the radiofilament, special attention had to be paid to the polymerization of the sample. After ultrasonic treatment, the liquid was placed in a container, where it solidified at room temperature. However, the
evaporation of acetone vapor at room temperature occurs rather quickly, therefore, in order to avoid the appearance of empty cavities inside the sample, which will lead to anisotropy of properties, it is necessary to periodically stir the resulting mixture. After complete polymerization of the composite mixture, the resulting material was ground and hot extruded to create a filament. At least 20 iterations of extrusion are necessary to form a uniform filament structure. Resulting homogeneous filament was placed in the clip of 3D printer for further printing.

The diameter of the printer nozzle is 1 mm. As a result, experimental samples were printed in the form of coaxial washers (inner diameter of \( d_{in} = 3 \) mm, an external \( d_{out} = 7 \) mm and a thickness of about \( h = 2.25 \) mm) for microwave research and in the form of flat cylinders for research in the UHF range. This allows you to cover the largest possible frequency band. The thickness of the fabricated samples is about 1 mm, and the diameter is about 2 cm.

Table 2 below shows the main parameters of the manufactured experimental samples for microwave measurements.

A total of twelve samples were made. Ten samples based on ABS plastic with the addition of 1, 2, 3, 4, and 5 wt.% MWCNTs (five for microwave measurements and five measurements for EHF), as well as an additional sample based on the industrially produced ABS-Conductive “Mellow” filament (China) containing carbon fibers (resistivity \( 10^3-10^5 \) Ohm /cm). EHF measurement samples are shown in Figure 3.
Table 2. Parameters of manufactured samples for a coaxial cell.

| Sample No. | Binder, wt.% | Content of the filler, wt.% | Sample Thickness, mm |
|------------|--------------|----------------------------|----------------------|
| 1          | 99 ABS       | 1 of MWCNT                 | 2.26                 |
| 2          | 98 ABS       | 2 of MWCNT                 | 2.26                 |
| 3          | 97 ABS       | 3 of MWCNT                 | 2.25                 |
| 4          | 96 ABS       | 4 of MWCNT                 | 2.25                 |
| 5          | 95 ABS       | 5 of MWCNT                 | 2.24                 |

2.3. Measuring equipment
The electromagnetic properties of the materials were measured by the waveguide method on a “Mikran” R4M-18 vector network analyzer in a coaxial cell according to the “transmission” schemes and on the STD-21 terahertz spectrometer.

Vector network analyzer allows you to measure S-parameters (transmission and reflection coefficients) with phase when placing the sample in the measuring cell. The frequency range is from 1 to 18 GHz. Further, using the obtained values of the transmission coefficients ($T$) and reflection ($R$) with their phase, one can find the spectra of complex magnetic and dielectric permittivity using the modified Becker–Jarvis method [6].

The electromagnetic characteristics of radio materials in the EHF range were studied using the free space method using the STD-21 terahertz spectrometer according to the standard “transmission” scheme in the frequency range 115–265 GHz. Backward wave lamps (BWT) were used as a radiation source, and a Galea cell was used as a receiver. The frequency dependences of the complex transmission coefficient were measured, which were further used in calculating the complex permittivity.

3. Results and discussion
Figure 4 shows the frequency dependences of the complex permittivity for samples based on composite radiofilaments.

It can be seen from the above dependences that with an increase in the concentration of carbon nanotubes in ABS plastic from 2 to 5 wt.%, An increase in the values of both real (from 3.5 to 7 rel.units) and imaginary (from 0.1 to 0, 7 rel.units) parts of the complex permittivity. The ABS Conductive plastic has $\varepsilon'$ values comparable to ABS + 5% MWCNTs, but much larger $\varepsilon''$ values, which is probably due to conductivity losses, which decrease with increasing frequency. Thus, filaments with MWCNTs are suitable for creating shielding or narrow-band absorbing coatings at microwave, since they have high permittivity values.
Figure 4. Frequency dependences of the real (a) and imaginary (b) parts of the complex permittivity for composite materials based on ABS plastic with carbon fillers.

Figures 5, 6 show the complex permittivity of the samples with MWCNTs, as well as the aforementioned ABS-Conductive Mellow sample. Figure 5 shows that in the considered frequency range, the ABS-Conductive «Mellow» sample has a linear frequency dependence of the real part of the complex permittivity. The samples with MWCNTs are characterized by a decrease in the real part of the permittivity with increasing frequency. It is also seen that for samples with a higher filler concentration, the decline is more avalanche. This is due to the polarization properties of the material and significant dielectric losses. In composites with a high concentration of MWCNTs, they are large (reach 2.4 rel.units at a concentration of 5 wt.%), and in plastic ABS Conductive ε" are small (0.9 rel.units), therefore, it has an almost linear frequency dependence. Figure 6 shows an almost linear frequency dependence of the imaginary part of the complex permittivity for all the samples studied.

For the ABS-Conductive sample, the imaginary part of permittivity takes values close to 0.8 rel. units, and for plastic samples with MWCNTs, dielectric losses linearly increase with increasing filler concentration. Already at a concentration of 2 wt.% MWCNT ε" is greater than that of ABS-Conductive, and at a concentration of 5 wt.% It reaches 2.4 rel.

Figure 5. Frequency dependence of the real part of permittivity.
Figure 6. Frequency dependence of the imaginary part of permittivity.

4. Conclusions
New composite radiofilaments with multi-walled carbon nanotubes for 3D printing have been created. The measured dielectric constant of the samples showed a good agreement between the results in the SHF and EHF ranges. The results show that ABS Conductive plastic has the best absorbing properties on microwave frequency, and composite plastics with MWCNTs of 2% or more on EHF.

Acknowledgment
The research was supported by The Tomsk State University competitiveness improvement programme.

References
[1] Laur V, Kaissar Abboud M, Maalouf A, Palessonga D, Chevalier A and Ville J 2019 30th Asia-Pacific Microwave Conference Proceedings (APMC) 1318–1320
[2] Pa P, Larimore Z, Parsons P and Miroztnik M 2015 Multi-material additive manufacturing of embedded low-profile antennas Electronics Letters 51 (20) 1561–1562
[3] Wu Y, Isakov D and Grant P S 2017 Fabrication of Composite Filaments with High Dielectric Permittivity for Fused Deposition 3D Printing Materials 10 1–12
[4] Badin A V, Kuleshov G E, Dorozhkin K V, Dunaevskii G E, Suslyaev V I and Zhuravlev V A 2018 43rd International Conference on Infrared, Millimeter, and Terahertz Waves, IRMMW-THz 8509938
[5] Grant P S, Castles F, Lei Q, Wang Y, Janurudin J M, Isakov D, Speller S, Dancer C and Grovenor C R M 2015 Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 373(2049) 20140353
[6] Chalapat K, Sarvala K, Li J and Paraoanu G 2009 IEEE Transactions on 57 2257–2267