Method of manufacturing of composite for 3D printing and the electrophysical properties of the obtained material

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Abstract. The present paper presents the technology for the manufacture of filaments based on ABS plastic and Taunit-M nanomaterial for use in 3D printing. A test sample was printed from this filament on a 3D printer using the layered overlap method at 15% Taunit-M content. The transmittance spectra for the printed sample were obtained using a Mach-Zander interferometer in the frequency range 120-260 GHz. The complex dielectric constant of the studied composite was calculated.

1. Introduction

Currently, there is an increasing need for shielding materials for high-frequency electronics [1], for ecology and medicine, for antenna technology and for military purposes [2]. The problem of electromagnetic compatibility is relevant [3] and requires new technologies for designing small-sized matching devices of different geometric shapes. Additive technologies (3D printing), which are currently successfully used in various fields of science and technology, can be used in this case. A distinctive advantage of 3D printing is the production of individual products, which, if necessary, can be easily converted into mass customization [4]. Most often, 3D printing technology uses a single source material, such as plastic. However, composites based on polymers filled with active phase inclusions are promising for shielding. Polymers: polylactic acid (PLA) [5], Acrylonitrile butadiene styrene (ABS) [4], polycarbonate (PC) [6], polybutylene terephthalate (PBT) [7] provide strength characteristics, flexibility, adhesion, resistance to external influences. The active component of the composites provides the required electromagnetic parameters. Carbon nanostructures: single-and multi-layer carbon nanotubes, graphenes and their combinations are successfully used in reducing the level of electromagnetic radiation in free space [8-9]. Magnetic materials: ferrites, carbonyl iron [9], effectively interact with electromagnetic radiation when composites based on them are located on a conductive surface. New materials are required in connection with the miniaturization of electronic devices, with the expansion of the operating frequency band.

The following technologies are used to implement 3D printing: inkjet printing, where a powder bound with a liquid binder is used [10], stereolithography (SL), laminated object fabrication (LOM), fused deposition modeling (FDM), selective laser sintering (SLS), and extrusion [4]. The FDM method is the most common 3D printing method in the world. Millions of 3D printers work on the
basis of FDM, from the cheapest to industrial three-dimensional printing systems. FDM printers work with various types of plastics, the most popular and affordable of which is ABS. Plastic products are characterized by high strength, flexibility, perfect for product testing, prototyping, as well as for the manufacture of ready-to-use objects.

Additive technologies offer unlimited possibilities in the manufacture of objects of any geometry. The popular FDM printing technology is replenished with threads having unique mechanical and electrophysical properties. These radio-absorbing and electrically conductive filaments containing dielectric matrices with nanoscale carbon inclusions, such as carbon nanotubes [11,12], multi-wall carbon nanotubes (MWCNT) of the "Taunit" series [13], graphene [14], can serve for these purposes.

This paper presents a description of the methodology for manufacturing a polymer filament from ABS and the results of studying the electromagnetic response and electrophysical parameters of flat samples from carbon nanomaterials and ABS polymer.

2. Materials and methods

2.1. Starting material
Carbon nanomaterials of the company NanoTechCenter (Tambov, Russia) of the Taunit-M series (specification No. 2166-001-77074291-2012) [15,16] were selected for the manufacture of composite filaments. The material is a stable aqueous colloidal solution containing 20 wt.% MCNT “Taunit-M”. These are coaxial multilayer carbon nanotubes (MCNT) with an external diameter of 8–15 nm (inner diameter of 4–8 nm) and a length of more than 2 μm. The number of layers of one tube is about 6–10. The amount of non-carbon impurities is not more than 1 wt.%. The specific geometric surface is 300–320 m²/g. The bulk density is 0.03–0.05 g/cm³.

2.2. Method of manufacturing of radio-filament for 3D printing
The thermal technology of mixing and extruding was used in the overwhelming majority of studies for the production of radiofilaments. The chemical method of composite material manufacturing for the extruder filament was the most successful.

Block-scheme of the technological process of manufacture of the samples based on ABS with nanomaterial “Taunit-M” is shown in figure 1.

Figure 1. Block-scheme of the technological process of manufacture of the samples based on ABS with nanomaterial “Taunit-M”.

![Block-scheme of the technological process of manufacture of the samples based on ABS with nanomaterial “Taunit-M”](image-url)
ABS plastic was used to conduct an experiment to create a filament from Taunit-M, since this polymer is the most affordable. Its mechanical strength in the scientific literature is noted as excellent. The authors of the article have experience using ABS plastic earlier to create 3D filaments from multi-walled carbon nanotubes.

The process of making of composite filament involves several steps.
1. At the first stage necessary quantity of ABS granules or small pieces of pure ABS were carefully weighed on an electronic scale Shimazu (accuracy ~ 1 mg).
2. The obtained material is dissolved by solvent acetone or V-646 and pours it into glass containers.
3. The next stage is adding carbon nanomaterial “Taunit-M” to the dissolved mixture and mix thoroughly by ultrasonic disperser during for 10 minutes at a power of 75 W.
4. The composite is removed from the mold after complete polymerization of the resulting mixture composition.
5. Then the polymerized mixture is grinded (figure 2). Further, this raw material was used for extruding, when manufacturing filament.

The extruder is a device for continuous processing of polymeric raw materials. Because squeezing, mixing and contact with a heated cylinder, the polymer raw material melts and turns into a homogeneous mass - the melt. The assembled extruder is shown in figure 3.

![Figure 2. This material (ABS/15%"Taunit-M" composite) is prepared for extrusion.](image1)

![Figure 3. Extrusion head of computerized system for the manufacturing of test filaments.](image2)

The production technology of the filament provides for at least 10 iterations of extrusion to form a homogeneous structure of the filament. Increase the number of iterations (N) leads to a decrease in the size of air pores inside the filament (figure 4). It should be noted that the porosity negatively effects on flexibility of the filament, increasing the probability of breaking during the 3D printing process.

The uniformity of filaments is a prerequisite for successful use in 3D-printers based on FDM technology. The filament is heated in the nozzle until it reaches a semi-liquid state, and then is extruded on a platform or over a previously printed layer.

2.3. Experimental equipment

The Mach-Zender interferometer for measuring transmission and phase shift was used [17,18]. Interferometer consists of two arms: working “Arm II” (with ABS/15%“Taunit-M” composite – “Sample”) and reference “Arm I”. Backward-wave oscillator (BWO) with water cooling was used as a source of monochromatic electromagnetic wave. Focusing of quasi-optical beam is carried out by Teflon lenses. As a detector of terahertz radiation optoacoustic converter (Golay cell) was used. “Amplitude modulator” was used for setting the amplitude modulation.
3. Results and discussion

The reflection coefficients $R$ and transmission $T$ of a flat sample 1.99 mm thick made from the obtained filament were measured in the frequency range 120-260 GHz (figure 5). It is seen that the transmitted signal decreased by 30-40% when the reflection coefficient is relatively small (of the order of 10%). A composite material manufactured by the same technique based on MCNT was used to evaluate the effectiveness of the interaction of the new material with microwaves. Carbon nanotubes were obtained by catalytic gas-phase deposition of ethylene in the presence of a FeCo/Al$_2$O$_3$ catalyst at the Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences. The prepared nanotubes were purified by refluxing in HCl, filtered, washed to a neutral pH and dried for 24 hours at 40 °C. It is a light, downy black powder containing individual nanotubes, bundles and aggregates of nanotubes, impurity metal particles that were enclosed in nanotubes, particles of an oxide carrier. The average nanotube diameter is 9.4 nm.
The concentration of MCNT was 1%, which approximately corresponds to the mass of carbon material in 15% liquid MCNT Taunit-M. This material is well known and well studied. The power of the transmitted signal through the test sample of the same thickness as the newly created one turned out to be lower (figure 5). Perhaps this is due to the inaccuracy in determining the mass of the active phase in the new material.

The dielectric permittivity (DP) spectra of materials (figure 6), calculated from the measured components of the electromagnetic response of the samples (figure 5), indicate another reason for the difference.

![Figure 6. Frequency dependence of real and image parts of permittivity for 3D-printed composites based on 15% carbon nanomaterial “Taunit” and 1% MWCNTs.](image)

The frequency dependence of the DP composite from MWCNTs shows the presence of conductivity, which occurs when the tubes contact. The conductivity of the MCNT Taunit-M composite is much lower, the frequency dispersion of the DP is not observed in this range. This means that the contacts between the particles of the conductive fraction are negligible.

It was not possible to increase the concentration of the liquid fraction to ensure electrical contacts in the new material. ABS plastic quickly solidified with increasing mass of liquid MCNT Taunit-M during mixing, which was caused by a conflict of acetone with the liquid fraction of the new material. It is likely that the effective use of this promising material requires a change in the method of mixing the components or replacement of the polymer. This issue will be resolved soon.

4. Conclusion
Filaments made according to the developed technology for 3D printing, based on “Taunit-M” nanomaterial in a polymer ABC matrix, can be used for the manufacture of low-reflectance screens in the terahertz range. For the manufacture of threads with a high content (more than 15%) of the active phase, a change in manufacturing technology or a change in the substance of the polymer matrix is required.

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References
[1] Batrakov K, Kuzhir P, Maksimenko S, Volynets N, Voronovich S, Paddubskaya A, Valusis G, Kaplas T, Svirko Y and Lambin P 2016 Enhanced microwave-to-terahertz absorption in graphene. *Appl. Phys. Lett.* 108 123101 DOI:10.1063/1.4944531
[2] He J, Luo H, He L, Yan S, Shan D, Huang S and Deng L 2018 Investigation on microwave dielectric behavior of flaky carbonyl iron composites. J. Mater. Sci. Mater. Electron. 29 15112 https://doi.org/10.1007/s10585-019-00959-0

[3] Kuzhir P P, Letellier M, Bychanok D S, Paddubskaya O G, Suslyaev V I, Korovin E Y, Baturkin S A, Fierro V and Celzard A 2017 Electrical Properties of Carbon Foam in the Microwave Range. Russ. Phys. J. 59 1703 DOI:10.1182-017-0964-3

[4] Ngo T D, Kashani A, Imbalzano G, Nguyen K T Q and Hui D 2018 Additive manufacturing (3D printing): A review of materials, methods, applications and challenges Compos. Part B Eng. 143 172 DOI: 10.1016/j.compositesb.2018.02.012

[5] Zhang D, Chi B, Li B, Gao Z, Du Y, Guo J and Wei J 2016 Fabrication of highly conductive graphene flexible circuits by 3D printing Synth. Met. 217 79 https://doi.org/10.1016/j.carbon.2014.10.080

[6] Postiglione G, Natale G, Griffini G, Levi M and Turri S 2015 Conductive 3D microstructures by direct 3D printing of polymer/carbon nanotube nanocomposites via liquid deposition modeling Compos. Part A Appl. Sci. Manuf. 76 110 http://dx.doi.org/10.1016/j.compositesa.2015.05.014

[7] Gnanasekaran K, Heijmans T, van Bennekom S, Woldhuis H, Wijnia S, de With G and Friedrich H 2017 3D printing of CNT- and graphene-based conductive polymer nanocomposites by fused deposition modeling Appl. Mater. Today 9 21 https://doi.org/10.1016/j.amattoday.2017.04.003

[8] Shuba M V, Yuko D I, Kuzhir P P, Maksimenko S A, Kanygin M A, Okotrub A V, Tenne R, Lambin Ph 2017 How effectively do carbon nanotube inclusions contribute to the electromagnetic performance of a composite material? Estimation criteria from microwave and terahertz measurements. Carbon 129 688 DOI:10.1016/j.carbon.2017.12.067

[9] Shuba M V, Melnikov A V, Paddubskaya A G, Kuzhir P P and Maksimenko S A 2013 Role of finite-size effects in the microwave and subterahertz electromagnetic response of a multiwall carbon-nanotube-based composite: Theory and interpretation of experiments. Physical Review B 88 045436 DOI: 10.1103

[10] Naiden E P, Zhuravlev V A, Suslyaev V I, Minin R V and Itin V I 2011 Structure parameters and magnetic properties of Me2W1 cobalt-containing hexaferrite systems synthesized by the SHS method. Russian Physics J. 53(9) 87 https://doi.org/10.1007/s11182-011-9519-1

[11] Czyzewski J, Burzyński P, Gawel K and Meissner J 2009 Rapid prototyping of electrically conductive components using 3D printing technology J. Mater. Process. Technol. 209 5281 DOI 10.1007/s40964-017-0019-x

[12] Schmitz D P, Ecco, L G, Dul S, Pereira E C, Soares B G, Barra G M, Pegoretti A 2018 Electromagnetic interference shielding effectiveness of ABS carbon-based composites manufactured via fused deposition modelling. Materials Today Communications 15 70 https://doi.org/10.1016/j.mtcomm.2018.02.034

[13] Kotsilkova R, Ivanov E, Todorov P, Petrova I, Volynets N, Paddubskaya A, Kuzhir P, Uglov V, Biró I, Kertész K, Márk G I and Biró L P 2017 Mechanical and electromagnetic properties of 3D printed hot pressed nanocarbon/poly (lactic) acid thin films. J. Appl. Phys. 121 064105 http://dx.doi.org/10.1063/1.4975820

[14] Sweeney C B, Lackey B A, Pospisil M J, Achee T C, Hicks V K, Moran A G, Teipel B R, Saed M A, Green M J 2017 Welding of 3D-printed carbon nanotube–polymer composites by locally induced microwave heating. Science Advances 3 1700262 DOI: 10.1126/sciadv.1700262

[15] Polyakov V, Mukhin V, Abramova I, Morozova S, Shubina N, Voropaeva N, Tkachev A, Burakov A, Romantsova I, Karpachev V, Figovsky O 2017 Sorption Activity of “Taunit”-Series Carbon Nanomaterials. Int. Letters of Chemistry, Physics and Astronomy 74 1 doi: 10.1016/j.proche.2012.10.043

[16] Terukov E I, Babaev A A, Tkachev A G, Zhilina D V 2018 Radio-wave absorbing properties of
polymer composites on the basis of shungite and carbon nanomaterial Taunit-M. Technical Physics 63 1044 https://doi.org/10.1134/S1063784218070289

[17] Badin A V, Dorozhkin K V, Suslyaev V I, Berdyugin A I, Vigovskiy V Y 2017 Quasi-optical 2D system for non-contact non-destructive testing of defects in natural and artificial crystals. Proceedings of SPIE - The Int. Society for Optical Eng. 10466 1046625 https://doi.org/10.1117/12.2291960

[18] Dunaevskii G E, Suslyaev V I, Zhuravlev V A, Badin A V, Dorozhkin K V 2016 Ferromagnetic resonance in hexagonal ferrite $\text{Ba}_3\text{Co}_2\text{Fe}_2\text{O}_{11}$ at the THz frequency range. Int. Conf. on Infrared, Millimeter, and Terahertz Waves, IRMMW-THz 7758771 DOI: 10.1109/IRMMW-THz.2016.7758771