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ABSORPTION AND REFLECTANCE SPECTRA OF MICROWAVE RADIATION BY AN EPOXY RESIN COMPOSITE WITH MULTI-WALLED CARBON NANOTUBES

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A procedure for dispersing multi-walled carbon nanotubes in the two-component polymer SpeciFix-20 (epoxy resin + hardener) using combined hydromechanical and ultrasonic mixing was developed. New composites with carbon nanotubes were produced. Their structures and optical and electrophysical characteristics were studied. The propagation of microwave radiation (26–38 GHz) in experimental composite samples was investigated. It was shown that the strong absorption of the composites appeared only with significant additions of multi-walled carbon nanotubes and was caused by the resulting electrical conductivity of the composites. A size effect of the additive on the optical characteristics of the produced composites was established. Equal absorption coefficients for microwave radiation could be achieved by using a smaller amount of carbon nanotubes with smaller diameters and greater specific surface areas in the composite.

Keywords: *multi-walled carbon nanotubes, epoxy resin, composite, electromagnetic radiation absorption, Raman scattering.*

Introduction. The first detailed description of the structure of hollow carbon fibers focused on the synthesis of the new carbon allotrope using an electric arc [1]. This discovery drew the attention of researchers around the world. Studies of the unique physical properties of carbon nanotubes (CNTs) remain a popular scientific topic. The discovery and synthesis of CNTs stimulated extensive research on their potential applications because of their unique mechanical and electrical properties [2, 3]. CNTs are known to possess extremely high mechanical strength (Young′s modulus ~2 TPa) and elasticity, thermal conductivity (2000 W/m·K), electrical strength and the ability to pass currents up to 10^{10} A/cm^2, and high electron mobility. CNTs can be semiconducting or metallic depending on their diameter and structural chirality. These features are scientifically interesting and may provide a basis for effective application of CNTs to various sectors of science and technology.

However, CNTs alone are difficult to work with because of their small sizes and strong interaction with electric and magnetic fields. Such difficulties can be obviated by creating macroscopic materials based on CNTs. Therefore, the creation of new composites containing carbon nanomaterials in their matrix has recently been developing rapidly. Work on this topic is broadly conducted on various composites, especially those based on polymers containing 1–10 mass % CNTs [4–13]. Even small additions of CNTs can significantly change the properties of polymers by increasing the strength and thermal conductivity and producing electrical conductivity. Producing electrical conductivity in polymers, which are almost always good electrical insulators, by adding CNTs is very attractive. It is noteworthy that the percolation threshold at which the composite electrical conductivity increased after adding single-walled CNTs (SWCNTs) was very low (~0.1 mass %). All other properties of the polymer were unchanged or changed insignificantly at these CNT concentrations. Such materials are interesting for application as protective coatings for shielding unique electronic systems from microwave radiation [4], including aerospace apparatuses. Absorption and reflection of electromagnetic radiation in polymers with CNTs over a broad wavelength range are interesting [5, 14, 15]. Transparent and conductive coatings, electrostatic protection, electrostatic

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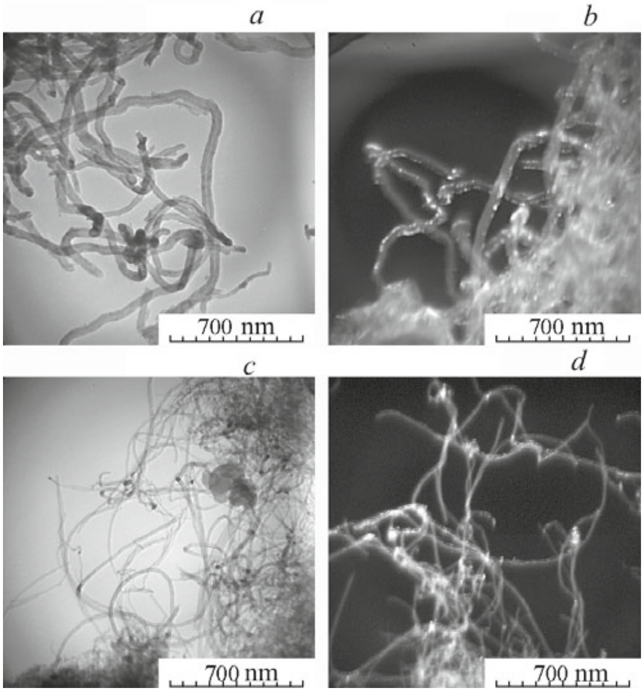

Fig. 1. Light-field (a, c) and dark-field (b, d) TEM photomicrographs of Taunit (a, b) and Taunit-M (c, d).

TABLE 1. Dimensional Characteristics of Multi-Walled Carbon Nanotubes

Parameter	Taunit	Taunit-M
Outer diameter, nm	20–70	8–15
Inner diameter, nm	5–10	4–8
Inner diameter, nm	>2	>2
Specific surface area, m^2/g	>120–130	>300–320

paints, coatings for shielding electrical noise and absorption of microwave power can also be fabricated. The creation of new multifunctional composites with carbon nanostructures, including composite radiomaterials capable of attenuating significantly electromagnetic radiation, was reported [16–19]. The increasing level of microwave radiation and so-called electromagnetic environmental contamination explain the interest in developing such materials. Furthermore, physicomechanical properties of shielding materials such as elasticity and resistance to external factors can be significantly improved by using polymers as matrices for CNTs while preserving the shielding properties as compared with material consisting of only CNTs [7, 13].

Several requirements must be considered in creating new composites with unique optical and physicomechanical characteristics for applications in modern technologies. On one hand, this ensures the composites have the necessary properties and characteristics. On the other, the composite production technology should be inexpensive, easily reproducible, and flexible for rapid modification of the properties of the produced composites according to the required technical parameters of the items. SWCNT production technologies are currently rather expensive. The yields of material from these technologies are low. The cost per gram of SWCNTs is tens to hundreds of USD. Therefore, it seemed advisable to use inexpensive materials that were available in large quantities for mass production of composites containing nano-sized carbon materials. Multi-walled carbon nanotubes (MWCNTs) and polygraphene materials, which are manufactured on industrial scales, can be considered as such materials.

Experimental. The starting polymer matrix for preparing the composites was SpeciFix-20 (epoxy resin + hardener), an optically transparent shrink-proof two-component polymer. The filler was MWCNTs (OOO Nanotekhtsentr, Tambov) under

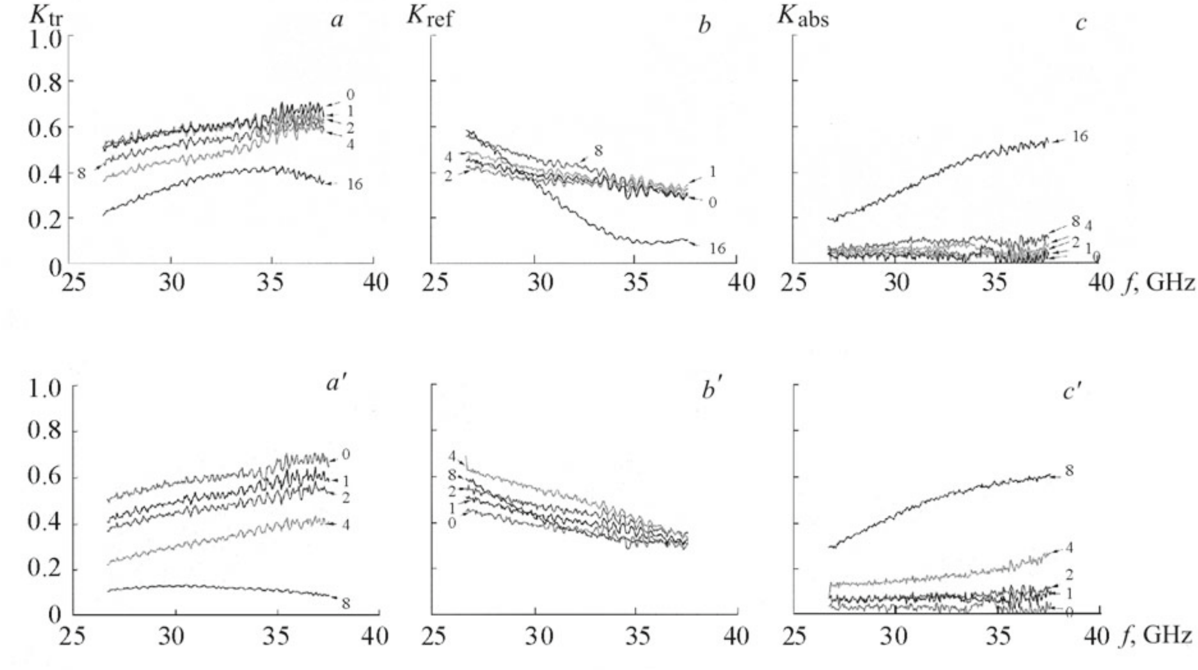

Fig. 2. Coefficients of transmission (a, a′), reflectance (b, b′), and absorption (c, c′) of electromagnetic radiation by composites based on epoxy resin with added MWCNT Taunit (a–c) and Taunit-M (a′–c′) (sample thickness 1.5 mm).

the trade names Taunit and Taunit-M. Two types of MWCNTs with different geometric parameters (diameter, number of layers in walls, bulk density, specific surface area) that should affect the dispersion in the polymer matrix and the characteristics of the produced composites were selected as the additives (Fig. 1). Table 1 presents the dimensional characteristics of the used MWCNTs. Transmission electron microscopy (TEM) structural studies agreed well with the manufacturer′s certificate. This indicated that Taunit MWCNTs were produced with good reproducibility.

The carbon nanomaterials were dispersed in the epoxy resin at elevated temperature (65°C) for 2–4 h. The process consisted of rapid hydromechanical stirring (up to 2000 rpm) of the components with simultaneous ultrasonic irradiation at 35 kHz of the mixture. Composites were prepared with various MWCNT contents. The maximum amount of Taunit CNT additive in the SpeciFix-20 matrix was 16 mass %; of Taunit-M, 8 mass %. The samples were (15 ± 1)-mm thick. The structures of the MWCNTs used as the polymer additives were investigated by TEM.

An R2-408R scalar network analyzer was used to determine the optical characteristics of the composites in the microwave region (effects of transmission, reflection, and absorption of electromagnetic radiation). It was constructed from a sweep generator, waveguide reflectometer, analyzer unit, and signal processing system. The apparatus was described in detail before [20]. Measurements were made in the frequency range 26–38 GHz. Composite samples were cut into parallelepipeds 7.2 × 3.4 × 1.5 mm, which corresponded to the waveguide reflectometer dimensions. The *S*-parameters for transmission S_{21} and reflection S_{11} were used as input data. The coefficients of transmission (K_{tr}), reflection (K_{refl}), and absorption (K_{abs}) were calculated from the formulas:

$$K_{tr} = S_{21}^2 , \quad K_{refl} = S_{11}^2 , \quad K_{abs} = 1 - S_{21}^2 - S_{11}^2 .$$

The composite structural homogeneity was evaluated using an optical microscope in combination with Raman scattering (RS) using a Nanofinder®HE high end Raman microspectrometry system (LOTIS TII). Raman studies were made at room temperature in reverse scattering geometry. The radiation source was a solid-state laser with $\lambda = 473$ nm. The laser radiation was focused to a spot ~1 μm in diameter. Diffraction gratings (600 lines/mm, spectral resolution 0.01 nm) and a high-sensitivity CCD detector chilled to –80°C were used for the recording.

Results and Discussion. Figure 2 compares the coefficients of transmission, reflection, and absorption from composites based on SpeciFix-20 with various contents of Taunit (from 1 to 16 mass%) and Taunit-M (from 1 to 8 mass %).

Composites with Taunit concentrations of 1–8 mass % were characterized by a smooth drop of the reflection and increase of the transmission function. The transmission function with the maximum Taunit concentration (16 mass %) in the polymer increased in the frequency range ≤34 GHz and then fell. The reflection function for this sample decreased more sharply, up to <10%, at frequencies of 33–38 GHz. As a result, the composite with 16 mass% Taunit had a high absorption coefficient. It is noteworthy that the absorption coefficient of this sample changed drastically in the studied frequency range, increasing smoothly from 20% at 26.5 GHz to 53% at 37.5 GHz.

Composites containing Taunit-M showed a smoothly decreasing transmission coefficient with increasing MWCNT concentration. The curves for the transmission and absorption coefficients followed paths analogous to those for Taunit, i.e., transmission increased smoothly with increasing frequency whereas absorption decreased. The reflection function for the composite with 8 mass % Taunit-M dropped. Transmission was strongly weakened (~10% throughout the whole frequency range) and depended little on frequency. The absorption coefficients of the composites increased noticeably as the Taunit-M concentration increased. The composite with 8 mass % had the greatest absorption coefficient. The absorption coefficient changed from 30% at 26.5 GHz to 60% at 37.5 GHz, like for the composite with 16 mass % Taunit.

Thus, the absorption coefficients for microwave radiation increased considerably (up to 50–60%) in composites with the maximum additive concentrations (Fig. 2c and 2c′). The transmission, reflection, and absorption functions of the composites changed little at lower additive concentrations as compared with the starting polymer. An analysis of the optical characteristics of the composites with various CNT additions taking into account their structural characteristics led to the conclusion that a size effect from the type of additive on the composite characteristics occurred. A smaller amount (almost half) of MWCNTs of smaller diameter and larger specific surface area (Taunit-M) was required to achieve comparable absorption coefficients.

Raman spectra were recorded in combination with optical microscopy of various sample cross sections to investigate the morphology and assess the quality of MWCNT dispersion in the prepared composites. Raman spectra of starting polymer SpeciFix-20 (not shown) contained narrow bands characteristic of atomic vibrational modes in epoxide rings. Thus, distinct peaks at 2930 and 2880 (aliphatic C–H) and 3073 cm^{-1} (aromatic C–H) were identified [21]. Weaker lines associated with breathing modes of epoxide rings and bending of covalent bonds (aromatic C=C stretching and C–H bending vibrations) in rings appeared in the range 600–1600 cm^{-1} [21, 22]. Figure 3 shows Raman spectra of composites containing large amounts of CNTs for which the absorption behavior for electromagnetic radiation changed considerably. It was found that regions free of MWCNTs were present even in cross sections of samples with the maximum (16 mass %) concentrations of Taunit. Regions of light and dark contrast were visible in the optical photographs. Spectra taken from the light regions were identical to those of the pure epoxy composite that were described above. These light regions in the sample cross sections extended up to 100 μm. Strong bands at ~1350 and ~1580 cm^{-1} that were characteristic only of MWCNTs were recorded in Raman spectra taken from the dark regions [23–27]. A band near 1580 cm^{-1} corresponded to lattice vibrations of symmetry E_{2g} in the planes of the graphene layers with sp^2-hybridized bonds [27]. This band could have different frequencies and shapes depending on the structural perfection of the materials. A band at 1350 cm^{-1} corresponded to the *D*-band that is usually associated with small ordered regions and carbon crystallites with distinct boundaries that cause violation of the selection rules for the wave vector in RS. It is present in spectra of all carbon materials and characterizes the defectiveness of the materials [28]. A weaker band at ~2700 cm^{-1} was attributed to two-phonon scattering (second-order scattering) and was designated as the *G*′-band (or 2*D*-band) [29].

Regions of light contrast in optical photographs of cross sections were also found for composites with Taunit-M at concentrations up to 8 mass % (Fig. 3c). However, they were much smaller, from hundreds of nanometers to several micrometers. The composite with 8 mass % Taunit-M was characterized by homogeneous contrast in the photographs of the sections. In this instance, the *D*- and *G*-bands were clearly visible in Raman spectra of the cross sections at all points. This indicated that this nanomaterial was dispersed rather well in the matrix.

The composites were confirmed to be three-dimensional (3D) networks of regions with high MWCNT concentrations, despite the presence of regions free of MWCNTs. As a rule, prepared MWCNT materials have mixed-type conductivity, i.e., both metallic and semiconducting. It was thought that 3D conducting channels formed and interacted with each other through nano-sized parts of the dielectric matrix to make the whole composite highly conductive at high MWCNT concentrations even considering that the nanotubes lay within the matrix as bulky clusters and did not fill the whole volume. This was confirmed by electrophysical studies. Table 2 presents the measured specific electrical conductivity of the composites on the test station for frequency-domain dielectric spectroscopy [30].

The conductivity of the composites increased smoothly as the concentration of the MWCNT additive was increased. It is noteworthy that composites with Taunit-M had higher (by almost an order of magnitude) conductivity than those with

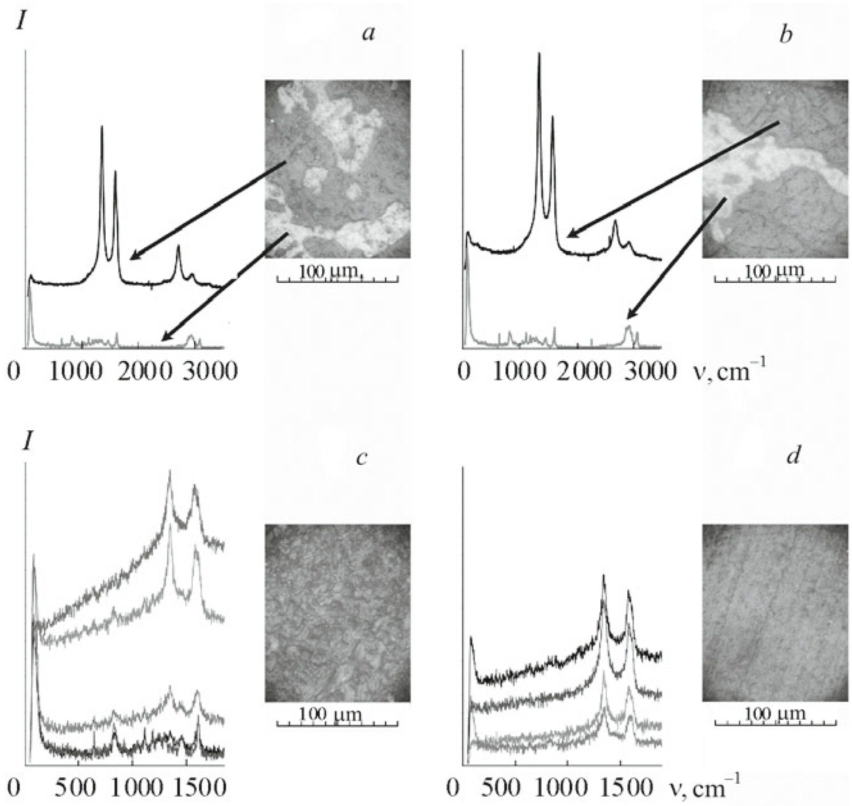

Fig. 3. Raman spectra of SpeciFix-20 composite with added MWCNT Taunit at 8 (a) and 16 mass % (b) and Taunit-M at 4 (c) and 8 mass % (d) that were obtained from various sample cross sections; in the insets, optical photographs of polished polymer cross sections.

TABLE 2. Specific Conductivity (S/cm) of Composites at Room Temperature as Measured with Alternating Current (50 Hz for Measurements)

MWCNT additive, mass %	Taunit	Taunit-M
0 (starting polymer)	10^{-13}	10^{-13}
1	4.83×10^{-11}	2.1×10^{-10}
2	3.19×10^{-11}	1.6×10^{-9}
4	2.77×10^{-10}	1.1×10^{-9}
8	1.71×10^{-9}	1.17×10^{-7}
16	3.7×10^{-5}	–

Taunit at the same additive concentrations. The conductivity of composites with 16 mass % Taunit increased by more than seven orders of magnitude as compared with the pure epoxy resin. The conductivity of the composite with 8 mass% Taunit-M increased by almost six orders of magnitude. It is noteworthy that the strong absorption of electromagnetic radiation by composites with high MWCNT concentrations (8 mass % Taunit-M and 16 mass % Taunit) was consistent with their sharp conductivity increase due to the formation of a 3D network of conducting channels.

Conclusions. An effective procedure for dispersing MWCNTs in an epoxy resin matrix that allowed the preparation of composites capable of attenuating considerably microwave radiation was developed. The optical properties of the prepared composites were studied. Coefficients of transmission, reflection, and absorption of electromagnetic radiation were determined in the frequency range 26–38 GHz. It was found that the absorption coefficient of composites with

16 mass % of the MWCNT additive Taunit reached 55% at 38 GHz. An analogous situation occurred for composites with the MWCNT additive Taunit-M at a concentration of 8 mass %, i.e., the absorption coefficient increased up to 60% at 38 GHz. It was established that the geometric dimensions of the MWCNTs (smaller tube diameter and larger specific surface area) affected considerably the absorption characteristics of the prepared composites because a smaller amount of MWCNTs was required to reach the same composite absorption. The absorption coefficient in composites with the maximum amount of Taunit increased (up to 55%) whereas the reflection coefficient decreased sharply (<8%). The absorption coefficient in composites with Taunit-M increased up to 60% as the transmission coefficient for electromagnetic radiation through the sample decreased greatly (<10%). It was shown that 3D conductive channels formed and interacted through nano-sized parts of the dielectric matrix to produce electrical conductivity in the whole composite at high MWCNT concentrations, even though the nanotubes formed clusters within the matrix. This was explained by the appearance of strong absorption of electromagnetic radiation in the range 26–38 GHz by composites with the highest concentrations of the MWCNT additives (8 mass % Taunit-M and 16 mass % Taunit).

REFERENCES

1. S. Ijima. *Nature*, **354**, 56–58 (1991).
2. P. N. D′yachkov, *Carbon Nanotubes. Structure, Properties, Application* [in Russian], Binom, Moscow (2006).
3. A. G. Tkachev and I. V. Zolotukhin, *Apparatus and Synthetic Method for Carbon Nanostructures* [in Russian], Mashinostroenie-1, Moscow (2007).
4. B. Hornbostel, U. Leute, P. Potschke, J. Kotz, D. Kornfeld, P.-W. Chiu, and S. Roth, *Physica E*, **40**, No. 7, 2425–2429 (2008).
5. R. Lv, F. Kang, J. Gu, X. Gui, J. Wei, K. Wang, and D. Wu, *Appl. Phys. Lett.*, **93**, No. 22, 223105 (1–3) (2008).
6. S. H. Park, P. Thielemann, P. Asbeck, and P. R. Bandaru, *Appl. Phys. Lett.*, **94**, No. 24, 243111 (1–3) (2009).
7. F. F. Komarov, A. G. Tkachev, E. Munoz, O. V. Milchanin, R. M. Krivosheev, I. N. Parkhomenko, and P. Zhukovskii, in: *Proc. 1st Int. Scientific-Practical Conf. on Graphene and Related Structures: Synthesis, Production and Application* [in Russian], Nov. 11–13, 2015, Tambov, TSTU (2015), pp. 50–52.
8. F. F. Komarov, A. G. Tkachev, R. M. Krivosheev, and O. V. Milchanin, in: *Proc. 1st Int. Scientific-Practical Conf. on Graphene and Related Structures: Synthesis, Production and Application* [in Russian], Nov. 11–13, 2015, Tambov, TSTU (2015), pp. 200–202.
9. H. Zhang, G. Zeng, Y. Ge, T. Chen, and L. Hu, *J. Appl. Phys.*, **105**, No. 5, 054314 (1–4) (2009).
10. F. F. Komarov, R. M. Krivosheev, M. A. Ksenofontov, T. N. Koltunovich, Kh. A. Abdulin, L. E. Ostrovskaya, and A. K. Togombaeva, *Inzh.-Fiz. Zh.*, **88**, No. 2, 344–349 (2015).
11. F. F. Komarov, M. A. Ksenofontov, A. G. Tkachev, R. M. Krivosheev, L. E. Ostrovskaya, V. N. Rodionova, and A. K. Togombaeva, *Dokl. Nats. Akad. Nauk Belarusi*, **58**, No. 4, 2–46 (2014).
12. V. E. Muradyan, E. A. Sokolov, S. D. Babenko, and A. G. Moravskii, *Zh. Tekh. Fiz.*, **80**, 83–87 (2010).
13. F. F. Komarov, P. Zukowski, R. M. Kryvasheyeu, E. Munoz, T. N. Koltunowicz, V. N. Rodionova, and A. K. Togambaeva, *Phys. Status Solidi A*, **212**, No. 2, 425–432 (2014); doi: 10.1002/pssa.201431493.
14. O. S. Ostrovskii, E. N. Odarenko, and A. A. Shmat′ko, *Fiz. Inzh. Poverkhn.*, **1**, No. 2, 161–173 (2003).
15. D. Bychanok, P. Kuzhir, S. Maksimenko, S. Bellucci, and C. Brosseau, *J. Appl. Phys.*, **113**, No. 12, 124103 (1–6) (2013).
16. F. F. Komarov, O. V. Milchanin, E. Munoz, V. N. Rodionova, V. B. Karpovich, and R. M. Krivosheev, *Zh. Tekh. Fiz.*, **81**, No. 11, 140–145 (2011).
17. K. L. Vinoy and R. M. Jha, *Radar Absorbing Materials from Theory to Design and Characterization*, Kluwer Acad., Boston (1996).
18. J. A. Roberts, T. Imholt, Z. Ye, C. A. Dyke, D. W. Price, Jr., and J. M. Tour, *J. Appl. Phys.*, **95**, No. 8, 4352–4356 (2004).
19. D. Bychanok, G. Gorokhov, D. Meisak, P. Kuzhir, S. A. Maksimenko, Y. Wang, Z. Han, X. Gao, and H. Yue, *Prog. Electromagn. Res. M*, **53**, 9–16 (2017).
20. D. Bychanok, G. Gorokhov, D. Meisak, A. Plyushch, P. Kuzhir, A. Sokal, L. Lapko, A. Sanchez-Sanchez, V. Fierro, A. Celzard, C. Gallagher, A. P. Hibbins, F. Y. Ogrin, and C. Brosseau, *Prog. Electromagn. Res. C*, **66**, 77–85 (2016).
21. T. Miyake, T. Yamakawa, and N. Ohno, *J. Mater. Sci.*, **33**, No. 21, 5177–5183 (1998).
22. T. M. Brooks Brinton II, Condition Assessment of Kevlar Composite Materials Using Raman Spectroscopy, Candidate Dissertation for the degree of Master of Science, Columbia, Missouri (2007), pp. 78
23. R. J. Nemanich and S. A. Solin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, **20**, No. 2, 392–401 (1979).

24. V. I. Ivanov-Omskii and E. A. Smorgonskaya, *Fiz. Tekh. Poluprovodn.*, **39**, No. 8, 970–975 (2005).
25. H. Vaskova and V. Kresalek, *Int. J. Math. Models Methods Appl. Sci.*, **5**, No. 7, 1197–1204 (2011).
26. E. Vajaiac, S. Palade, A. Pantazi, A. Stefan, G. Pelin, D. Baran, C. Ban, M. Purica, V. Meltzer, E. Pincu, C. Berbecaru, and D. Dragoman, *Dig. J. Nanomater. Biostructures*, **10**, No. 2, 359–369 (2015).
27. E. Ivanov, R. Kotsilkova, and E. Krusteya, *J. Nanopart. Res.*, **13**, No. 8, 3393–3403 (2011).
28. W. Ma, L. Liu, Zh. Zhang, R. Yang, G. Liu, T. Zhang, X. An, X. Yi, Y. Ren, Zh. Niu, J. Li, H. Dong, W. Zhou, P. M. Ajayan, and S. Xie, *Nano Lett.*, **9**, No. 8, 2855–2861 (2009).
29. S. Osswald, E. Flahaut, H. Ye, and Y. Gogotsi, *Chem. Phys. Lett.*, **402**, Nos. 4–6, 422–427 (2005).
30. T. N. Koltunovich, *Zh. Prikl. Spektrosk.*, **82**, No. 4, 616–621 (2015) [T. N. Koltunowicz, *J. Appl. Spectrosc.*, **82**, No. 4, 653–658 (2015)].