Continuous wave THz imaging of multi-walled carbon nanotubes polymer composites

A I Berdyugin, A V Badin, G E Kuleshov, E A Trofimow, P P Smygalina, K V Dorozhkin, T N Schematilo and R P Gursky

Faculty of Radiophysics, National Research Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russia

a.berdyugin@mail.tsu.ru

Abstract. In this paper, the problem of creating homogeneous composites with on carbon nanotubes is described. To control the quality of the manufactured composites, a system of terahertz visualization of material inhomogeneity using a continuous radiation source is used. An increase in the homogeneity of the composite based on multi-walled carbon nanotubes with an increase in the time of ultrasonic processing during polymerization is noted. The advantages of THz imaging in comparison with optical microscopy are shown.

1. Introduction

Currently, composite materials with various fillers from cermet inclusions [1] to ferromagnets [2] are actively studied. Multi-walled carbon nanotubes (MWCNTs) are promising nanostructured materials for use as a filler in composites. MWCNTs-based composites have unique mechanical properties [3], such as high strength and rigidity and a huge aspect ratio (the ratio of length to diameter) [4]. These properties are used in micro-and nanoelectronics as dielectrics, sensors [5]; in the chemical industry as heterodyne catalysts of chemical processes [6]; in the light industry – as heavy-duty filaments [7], components of bitumen (asphalt) [8]. These unique properties are achieved by the homogeneous allocation of MWCNTs in the composite and depend on the manufacturing technology. Monitoring of the localization of MWCNTs in manufactured samples can allow assessing the homogeneity of the composite material at different manufacturing technologies.

The progress of visualization technologies today makes it possible to apply them in the art [9], archeology [10], medicine [11], food [12] and electronic industries [13]. Over the last decades, material defectoscopy at terahertz (THz) frequency range became popular [14]. The prospects for the use of THz radiation are primarily because the photon energy of radiation in the submillimeter frequency range is 0.1-0.001 eV (non-ionizing) [15]. The submillimeter-wave radiation has a high penetrating power through thin dielectric media [16]. THz imaging has a number of advantages over long-used methods of non-destructive control, such as optical [17] and X-ray [18] diagnostics. Among the advantages, low measurement error due to the simplicity of processing the results; high compatibility with biological objects [15]; technical implementation of THz systems provides usability and relatively low cost of components relative to more precise X-ray systems. The purpose of this research is to evaluate the heterogeneity of composites based on MWCNTs and determine its dependence on the time of ultrasonic treatment.
2. Experiment
Defectoscopy of MWCNTs composite samples was carried out using the THz imaging system [19]. This system recording of the intensity distribution of the transmitted radiation through the composite sample in a 2D plane. THz imaging system consist of the 2D positioning mechanism of investigated object placed in the quasi-optical path of the interferometer Mach-Zehnder. The functionality of the system provides the ability to identify the characteristics of the material included in the object by analyzing the frequency properties. Automation of the non-destructive visualization system allows to exclude the influence of human factor on the measuring process, as well as to reduce the need for operator's participation.

2.1. Materials
In this research, we used MWCNTs manufactured by the method of catalytic gas-phase deposition of ethylene. The nanotube diameter ranged from 4 to 21 nm, and ED-20 epoxy was used as the binding material.

The technology of production of composite materials samples included 5 stages. Firstly, the epoxy was mechanically mixed with 1 wt. % MWCNTs during 5 minutes. Then, influence for composites samples by 75 W power ultrasonic treatment with frequency of 28 kHz to enhance its homogeneity was performed. Then to obtain the polymer mixtures was dried at room temperature for 48 hours. Finally, the 4 composite samples were mechanically grinded until they were flat-parallel. Sample No. 1 was without ultrasonic treatment, while samples No. 2-4 were ultrasonic treatment for 1, 2, and 5 minutes, accordingly. Table 1 shows the main technological procedures for processing the manufactured samples based on MWCNTs.

| Sample | Mixing by ultrasonic (min) | Thickness (mm) |
|--------|---------------------------|----------------|
| 1      | -                         | 0.77           |
| 2      | 1                         | 1.39           |
| 3      | 2                         | 0.81           |
| 4      | 5                         | 0.60           |

The optical photos of the manufactured samples No. 1 and No. 4 are presented at figures 1-2, respectively.

**Figure 1.** Photo of sample No. 1 based on MWCNTs without ultrasonic processing.

**Figure 2.** Photo of sample No. 4 based on MWCNTs processed by ultrasonic for 5 min.
2.2. Methods

Principle scheme of the THz imaging system [19] for heterogeneous materials with a placed planar positioning mechanism in quasi-optical path of the Mach-Zehnder interferometer is shown in figure 3.

![Figure 3](image1)

**Figure 3.** Scheme of the THz imaging system based on the Mach-Zehnder interferometer.

The source of THz radiation was a backward wave oscillator (BWO). The object under research was placed in sample holder of the planar positioning mechanism. The sample was moved in a 2D-plane by the point to point method relative to a quasi-optical diaphragmatic beam with a diameter of 2 mm. By BWO with a wavelength of 343 µm and with an average power supply of 2 mW continuous THz wave was generated. An optoacoustic sensor based on a Golay cell recorded the power of the electromagnetic response of the transmitted radiation. Control of the measurement procedure, as well as image visualization in real-time, was performed via the L-Card E154 digital input/output module with using software created in the LabVIEW.

To analyze degree of homogeneity of samples, the evaluation of filtered areas of the obtained THz image by intensity was used. The evaluation method is to measure the mean amplitude of the electromagnetic response. Then the localization of areas of the composite sample with the amplitude of the electromagnetic response differs from the mean value was carried out. Finally, the ratio of localized areas in relation to the area in question was estimated.

2.3. Results

To analyze the uniformity of the samples and to compare the evaluation methods the optical microscopy was used. Simultaneously with the illumination from below, the microscope objective was directed at the sample from above. The microscopy result (figures 4 and 5) is shown only for two samples for clarity.

![Figure 4](image2)

**Figure 4.** Optical microphotography of sample No. 1 (without ultrasonic processing).

![Figure 5](image3)

**Figure 5.** Optical microphotography of sample No. 4 (processed by ultrasonic for 5 min).
Obtained results of optical microscopy insufficiently determine the degree of uniformity of composite samples treated with ultrasonic. Due to the inapplicability of optical methods for imaging samples with MWCNTs, it became necessary to use penetrating radiation.

Figure 6 presents the THz image of the two-dimensional matrix of amplitude radiation at 874 GHz that passed through sample No. 1 based on MWCNTs, which was not ultrasonic processed. And also figures 7, 8 and 9 illustrate THz images of sample No. 2, sample No. 3 and sample No. 4 based on MWCNTs, which were additionally mixed with an ultrasonic dispersant for 1, 2, and 5 minutes, respectively.

Figure 6. THz image of sample No. 1 based on MWCNTs, which was not ultrasonic processed.

Figure 7. THz image of sample No. 2 based on MWCNTs with ultrasonic treatment for 1 min.

Figure 8. THz image of sample No. 3 based on MWCNTs with ultrasonic treatment for 2 min.

Figure 9. THz image of sample No. 4 based on MWCNTs with ultrasonic treatment for 5 min.

Figure 10 presents images of localized areas of 4 composite samples, where: a - sample without ultrasonic treatment before polymerization; and samples with ultrasonic treatment before polymerization (b - 1 minute, c - 2 minute, d - 5 minutes).
Figure 10. THz-image of localized areas of 4 composite samples made by various manufacturing processes: (a) - sample No. 1, which was not ultrasonic processed; (b) - sample No. 2 treated by ultrasonic for 1 min; (d) - sample No. 3 treated by ultrasonic for 2 min; (c) - sample No. 4 treated by ultrasonic for 5 min. The blue areas in the figures are MWCNTs agglomerates, and the white areas in the sample are epoxy without MWCNTs.

The results in figure 10 indicate that the area of the heterogeneity distribution (agglomerates of MWCNTs and epoxy without MWCNTs) in sample No. 1 (a) is 24.4 %, in sample No. 2 (b) – 19.4 %, in sample No. 3 (c) – 11.1%, and in sample No. 4 (d) – 7.7% of the viewed area in the sample. The edge areas were not included in the estimates because of the mechanical treatment of the samples and the grinding of the edges. Figure 11 shows the ultrasonic treatment time dependence of heterogeneity areas of the composites.

Figure 11. Ultrasonic treatment time dependence of the areas of heterogeneity of composites based on epoxy and MWCNTs.

3. Conclusion
The research showed that the uniformity of MWCNTs distribution in composites depends on the ultrasonic treatment time. Long-term ultrasonic treatment improves material homogeneity. However, as was shown in [20], when the ultrasonic treatment time was increased over 3 minutes, the fact of MWCNTs shortening due to their destruction, as well as a decrease in the dielectric permittivity of the material, was observed. Based on these observations, it was decided to limit the maximum time of ultrasonic treatment to 5 minutes. Thus, this research shows (figure 11) that if ultrasonic treatment time up to 2 minutes, the reduction rate of inhomogeneous areas is 6.65 %/min, and from 2 to 5 minutes it is 1.13 %/min. The possibility of using a BWO-based continuous wave THz imaging system to evaluate homogeneity in composite manufacturing is also shown. Optical microscopy is inferior to THz imaging methods in assessing the homogeneity of composites based on MWCNTs.

Acknowledgments
The reported study was funded by RFBR according to the research project No. 20-32-90125.
References

[1] Ivanov O, Yaprintsev M, Vasil'ev A, Zhezhu M and Novikov V 2022 Features of microstructure and thermoelectric properties of the cermet composites based on grained Bi2Te3 matrix with locally-gradient Ni@NiTe2 inclusions Chin. J. Phys. 77 24-35.

[2] Haldar T and Kumar V R K 2021 Coexistence of ferromagnetism and superconductivity in MWCNT/Bi2SiO5 nanocomposites Phys. Scr. 96 125859.

[3] Kumar J, Kumar K, Jaiswal B, Kumar K and Verma R K 2022 Investigation on the physico-mechanical properties of carpet waste polymer composites incorporated with multi-wall carbon nanotube (MWCNT) J. Text. Inst. 1-10.

[4] Thostenson E T, Ren Z and Chou T W 2001 Advances in the science and technology of carbon nanotubes and their composites: a review Compos. Sci. Technol. 61 1899-912.

[5] Rao R K and Sasmal S 2022 Development of Smart Cementitious Composite Sensors for Ambient Vibration-Based Continuous Health Monitoring of Structures Advances in Non Destructive Evaluation 203-18.

[6] Moghadam M T T, Seifi M, Askari M B and Azizi S 2022 ZnO-MWCNT@Fe3O4 as a novel catalyst for methanol and ethanol oxidation J. Phys. Chem. Solids. 165 110688.

[7] Yousefi N, Fisher S J, Burgstaller C, Shaffer M S and Bismarck A 2022 Hierarchical carbon fibre composites incorporating high loadings of carbon nanotubes Compos. Sci. Technol. 222 109369.

[8] Shah P M and Mir M S 2021 Investigating the influence of carbon nanotube on the performance of asphalt binder Prog. Rubber Plast. Recycl. Technol. 37 422-40.

[9] Odlyanitskiy E L, Smolyanskaya O A, Sirro S, Guillet J P, Detalle V and Menu M 2021 Terahertz data processing for imaging and spectroscopy of artwork Optics for Arts, Architecture, and Archaeology VIII 11784 117840D.

[10] Artesani A, Ljubenovic M, Bonetti S and Traviglia A 2021 Processing and analysis of THz time-domain spectroscopy imaging applied to cultural heritage Optics for Arts, Architecture, and Archaeology VIII 11784 117840E.

[11] Tarabichi S, Al-Raeel M and Solieva O 2022 Improving the accuracy of tumor surgery by THz imaging and making the results of pathological anatomy faster by THz spectroscopy beni-Seuf univ. j. Basic appl. sci. 11 1-21.

[12] Zappia S, Crocco L and Catapano I 2021 THz Imaging for Food Inspections: A Technology Review and Future Trends Terahertz Technology 1-18.

[13] Berdyugin A I and Badin A V 2021 Continuous terahertz wave imaging of microelectronics objects J. Phys. Conf. Ser. 1862 012030.

[14] Tretiakov S A, Molchanov S V, Kaplanov I A and Ivanova A I 2021 Influence of roughness parameters of surface on the emissivity of germanium single crystals J. Phys. Conf. Ser. 2103 012230.

[15] Guo Y, Wu S, Liu X, Yang L and Zhang C 2021 The Application of Microplasma in the Terahertz Field: A Review Appl. Sci. 11 11858.

[16] Smolyanskaya O A et al. 2018 Prog. Quantum Electron. 62 1-77.

[17] Luker G D and Luker K E 2008 Optical imaging: current applications and future directions J. Nucl. Med. 49 1-4.

[18] Russo P (Ed.). 2017 Handbook of X-ray imaging: physics and technology CRC press.

[19] Zhakupov S N, Badin A V and Berdugin A I 2019 Automated Quasioptical System for EHF Imaging of Heterogeneous Materials with Subwavelength Resolution 2019 International Siberian Conference on Control and Communications (SIBCON) 1-4.

[20] Dotsenko O and Kachusova A 2016 Influence of Ultrasonic Treatment on Electromagnetic Characteristics of Composites Based on Multiwall Carbon Nanotubes at Microwave Frequencies Key Eng. Mater 683 65-70.