Preparation and properties of electrically conductive film nanocomposites

I. Makarova[1*], *M.* Buzaeva[1], and *V.* Segeev[2]

[1]Ulyanovsk State Technical University, Severny Venets str., 32, 432027 Ulyanovsk, Russia
[2]Ulyanovsk Branch of Kotelnikov Institute of Radioengineering and Electronics of Russian Academy of Sciences, 432011 Ulyanovsk, Russia

Abstract. This paper presents methods of obtaining film structures based on polyvinyl alcohol, polymethylmethacrylate with multi-walled carbon nanotubes on various substrates by pulling out of solution and drying with subsequent application of metal contacts. Test samples of polymer film structures with carbon nanotubes with curing in strong electric and magnetic fields for the orientation of with multi-walled carbon nanotubes in the polymer were prepared. The topography of the film surface was studied by atomic force microscopy. By treating nanotubes in a solution of iron chloride (III) and NaOH in diethylene glycol, their magnetic susceptibility is significantly increased, which makes it possible to equalize such "magnetic" carbon nanotubes in the polymer in magnetic fields with an induction of less than 0,5 T. The volt-ampere, C-V and noise characteristics of film structures at temperatures from – 60 ° C to 100 ° C and pressures up to 2 MPa were studied. Key words: nanocomposites, carbon nanotubes, modification, orientation in a magnetic field, topology, electrical properties.

1 Introduction

Polymer composites containing carbon nanotubes (CNTs) are characterized by special physical and mechanical properties, a unique combination of electrical, optical, mechanical and sorption properties. Such materials are used in various fields of technology. CNTs as reinforcing and structure-forming fillers can be introduced into various polymer matrices. The properties of such composites depend on the properties of the matrix and filler, the concentration of nanoparticles in the matrix, and the preparation method [1-4]. The use of CNTs as the main component in the creation of polymer composites, when nanotubes are introduced into polar media, the problem of nanotube aggregation, as well as weak interaction with the medium, arises. Modification of their surface by grafting functional groups makes it possible to solve these problems and form stable dispersions of CNTs in a monomer or solvent before polymerization [5-7].

Various efforts have been devoted to rational design and construction of high-quality conductive network within polymer matrices with carbon nanotubes (CNTs), carbon black (CB) nanoparticles, reduced graphene oxide (RGO), and other conductive nanomaterials. For example, Mondal et al. fabricated a chlorinated polyethylene (CPE) composite with 30 wt%

* Corresponding author: gorlovskaya.irin@bk.ru

of CB, exhibiting an EMI shielding effectiveness (SE) of 38.4 dB in the X-band. Jia et al. reported a flexible natural rubber (NR) nanocomposite with a high EMI shielding efficiency of 43.7 dB at 5.0 wt% of CNT content by forming a segregated conductive network. Shen et al. prepared a flexible sandwich film by coating a nonwoven fabric with a RGO/polyurethane suspension, which exhibits a qualified shielding performance of ~20 dB over a broadband frequency range. Note that some complicated but necessary chemical modification and reduction processes are usually required for fabrication of these conductive polymer nanocomposites filled with RGO and CNTs. [21]
Compared to carbon nanomaterials, transition metal carbide/nitride/carbonitride (MXene) sheets are promising for improving EMI shielding performances of polymers because of their rich surface chemistry and remarkable electrical conductivity, such as 57 dB for a Ti3C2Tx/sodium alginate film with 90 wt% of Ti3C2Tx at a thickness of 8 μm, 62 dB for the polystyrene nanocomposite with 1.9 vol% of Ti3C2Tx at a thickness of 2 mm , and over 50 dB for the 2 mm-thick epoxy nanocomposite with 0.74 vol% of Ti3C2Tx . However, these rigid bulk materials cannot be suitable for stretchable electronics. [21]

Doping of polymers with carbon nanotubes affects their electrophysical properties. The processes of orientation of carbon nanotubes in polymer binders using electric and magnetic fields and mechanically are a promising direction for regulating their microstructure and properties. Nanocomposites and film nanocomposite structures with ordered CNT inclusions can serve as the basis for the development and production of new types of unique sensors (temperature, radiation, bending, pressure sensors, etc.) with improved metrological characteristics in electronics Film structures based on polymer nanocomposites are the most promising for creating new elements of microelectronic sensors; however, the relationship between the characteristics of such film structures and the distribution and orientation of CNTs in a polymer matrix remains insufficiently studied [8-10].

The use of electrically conductive polymer composites continues to attract the attention of researchers and technologists in many countries of the world as the basis of a material for the manufacture of light and durable conductive elements, antistatic coatings, as well as materials that absorb electromagnetic radiation in various wavelength ranges. Due to their electrochemical and ion-exchange properties, they can be used as battery electrodes, ion-exchange materials and ion-selective electrodes. Such materials are capable of changing volume under the action of an electric potential [11-14].

2 The methodology of the experiment

2.1 Materials

Toluene (C_7H_8) and ferrocene $Fe(C_5H_5)_2$, sulfuric (H_2SO_4), nitric acids (HNO_3), iron(III) chloride ($FeCl_3$), sodium hydroxide (NaOH), diethylene glycol (DEG). Ultrapure water use throughout all experiments was purified by distillation. All chemicals were used without further purification.

2.2 Preparation of functionalized MWCNTs

The synthesis of multi-walled carbon nanotubes (MWCNTs) was carried out in an argon stream by chemical vapor deposition using organometallic and carbon-containing compounds (MOCVD method). Ferrocene and toluene were used as precursors [15]. The surface of carbon nanotubes is chemically inert and is activated in various ways. The most common method of surface functionalization is annealing in air and treatment with strong acids, for which we used a mixture of sulfuric and nitric acids [16].

MWCNTs coated with magnetic nanoparticles were obtained according to the procedure described in [17]. a solution of NaOH in diethylene glycol (DEG) (10 mg/ml) was prepared at 120°C for 1 h, then the solution was cooled to 70°C. MWCNTs (10 mg) were dispersed in 10 ml of DEG using an ultrasonic disperser. To this mixture was added 50 mg of anhydrous iron(III) chloride, and stirred at 220°C for 30 minutes. NaOH/DEG solution was added to the mixture and stirring was continued for 1 hour. The mixture was cooled, washed with ethanol and deionized water. The resulting MWNTs (M-MWNTs) were dried at 80°C for 12 h.

Film structures based on polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA), polypyrrole, polyaniline with multi-walled carbon nanotubes (MWNTs) on various substrates were obtained by drawing from solution and drying, followed by deposition of metal contacts.

2.3 Characterization

The topographic features of the surface of film PMMA composites were studied using NANOEDUCATOR (NT-VTD) atomic force microscope.

Capacitance and noise spectroscopy methods were used to study the dielectric and noise characteristics of test film structures. [19, 20].

3 The results of experiments and discussion

The surface of carbon nanotubes is chemically inert and is activated in various ways. The most common method of surface functionalization is annealing in air and treatment with strong acids, for which we used a mixture of sulfuric and nitric acids. Moreover, oxygen-containing groups (-OH, -C = O, -COOH) with a concentration of carboxyl groups of 4.0-5.0 wt.% are formed on the surface of MWCNTs. The formation of these groups in the amount of 0.6 wt. % occurs already during annealing of nanotubes in air. The ends of the nanotubes when exposed to acids are opened, the diameter decreases to 40-50 nm. When MWNTs are introduced into the material matrix, it is necessary to obtain a stable disperse system with a uniform distribution of nanoparticles in the bulk. The compatibility of carbon nanotubes with a binder depends on the type of nanotubes, their size, and their ability to agglomerate.

The study of the surface topography of poly (methyl methacrylate) films showed that the addition of nanotubes promotes structuring of the polymer matrix and leveling of the surface as shown in figure 1. Changes in the surface structure can affect the electrophysical properties of polymer composites.

After acid treatment, magnetic nanoparticles were deposited on the surface of MWCNTs, allowing them to be oriented in a magnetic field. The resulting magnetic mounts were used to obtain polymer nanocomposite films and study their electrophysical properties. Suspensions of MWCNTs in carbon tetrachloride were prepared by ultrasonic mixing (ultrasonic disperser UZD2-0.1/22, frequency 22 kHz). To obtain samples with different content of carbon nanotubes, the necessary volumes of a suspension of MWCNTs in carbon tetrachloride were introduced into PMMA solutions and mechanical stirring was carried out for 2 min. Thin films of a PMMA+MWCNT composite and pure PMMA were deposited on glass substrates with a conductive ITO coating by dip-coating as control samples.

The rate of drawing the substrate out of the solution was chosen in the range of 1–5 cm/min. Due to the high viscosity of the resulting suspension, it can be used to obtain polymer film structures, while maintaining a uniform distribution of MWCNTs during the evaporation of solvents. To study the electrophysical properties, aluminum contacts were deposited on the surface of the films by thermal evaporation in vacuum.

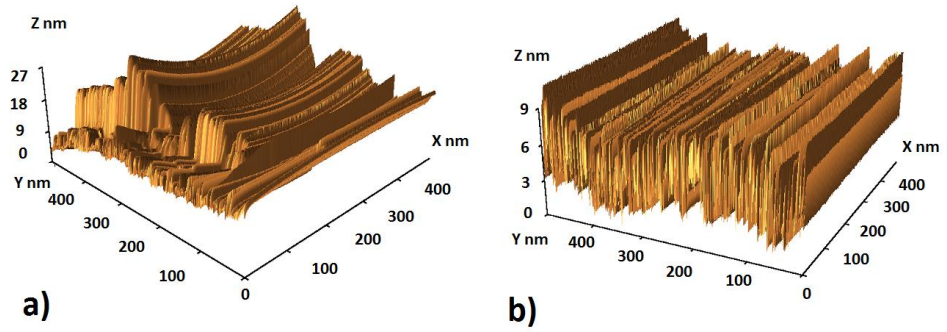

Fig. 1. Topographic image of polymethyl methacrylate film surface: a – without the addition of MWCNTs, b – with MWCNT content of 0,005%.

The volt-ampere (VAC), C-V and noise characteristics of film structures at temperatures from – 60 ° C to 100 ° C and pressures up to 2 MPa were studied. The reuslts showed that the conductivity of PVA and PMMA films with MWCNT has a barrier character, monotonically increases with increasing pressure, and on the frequency dependences of the tangent of the loss angle at small concentrations of MWCNT, a maximum was observed at frequencies of 30-40 kHz. When films with "magnetic" MWCNT are cured in a magnetic field, their conductivity increases by 2 orders of magnitude. The LF noise spectra of the studied films have the form

$S_i \sim 1/ f^{\gamma}$

and the current dependences of the noise level are I^{α}, while the index of the shape of the spectrum of γ films cured in a magnetic field is 0,9, and in the absence of a field – 1,4; and the indicator α of the current dependence is 1,1 and 0,7, respectively.

On the C-V characteristics of PVA films with MWCNT cured in a magnetic field, a maximum was observed at a field strength of about $0{,}5 \cdot 10^6$ V/m.

Measurements of the impedance and dielectric loss tangent of composites with different contents of MWCNTs were carried out in the frequency range of 20 Hz - 200 kHz. Films of pure PVA in the specified frequency range have tgδ close to zero, which indicates a high dielectric quality of PVA.

The addition of 2.5% MWCNT leads to an increase in tgδ by more than 2 orders of magnitude, while the frequency dependence of tgδ acquires a nonmonotonic character with a maximum at about 30 kHz. A further increase in the concentration of MWCNTs leads to a decrease in tgδ to values close to the initial PVA, while the maximum of tgδ is shifted towards higher frequencies. When the film is heated, the maximum of tgδ also shifts to the right, and the value of tgδ at the maximum decreases.

4 Conclusion

The topography of the surface of polymer nanocomposites with carbon nanotubes has been studied, and their effect on polymer structuring has been confirmed. It is shown that for polymer films with MWCNTs cured in a strong magnetic field, the electrical conductivity in the direction perpendicular to the film surface is approximately 2 orders of magnitude higher than for films with MWCNTs cured in the absence of a magnetic field, without measuring the nature of the conductivity.

Acknowledgement

The research results were partially obtained within the framework of the Russian Foundation for Basic Research (RFBR) grant No. 19-42-730011 r-a "Synthesis and study of the properties of film structures of polymer nanocomposites with carbon nanotubes for use in microelectronic sensors"

References

1. M. Farbod, Colloids and Surfaces A: Physicochemical and Engineering Aspects **384(1)**, 685-690 (2011)
2. D. Schaefer, R. Justice, Macromolecules **40(24)**, 8501–8517 (2007)
3. F. Smail, A. Boies, A. Windle, Carbon **152**, 218–232 (2010)
4. A. Blanch, J. Phys. Chem. B **114**, 9805-9811 (2010)
5. G. Kozlov et al, Condensed Matter and Interphases **23(2)**, 223–228 (2021)
6. S. Vasin, M. Efimov, V. Sergeev, I. Frolov, Journal of Physics: Conference Series **1697**, 012104 (2020)
7. A. Chebil et al, Adv. Technol. Elsevier **243(April)**, 125–130 (2019)
8. B. Kraabel et al, Chem. Phys. Lett. **213(3-4)**, 389-394 (1993)
9. N. Sariciftci et al, Science **258(5087)**, 1474-1476 (1992)
10. N. Hu, Carbon **48**, 680-687 (2010)
11. V. Smirnov, E. Korolev, N. Al'bakasov, Nanotekhnologii v stroitel'stve **4**, 17-27 (2011)
12. O. Dyshin, I. Habibov, V. Shamilov, K. Rustamova, PNRPU Mechanics Bulletin **3**, 140-148 (2019)
13. S. Vasin, M. Efimov, V. Sergeev, Technical Physics Letters **46(6)**, 595–598 (2020)
14. V. Sergey, A. Nizametdinov, M. Efimov, Informacionnye Tehnologii **13(4)**, 458-462 (2021)
15. E. Klimov, M. Buzaeva, O. Davydova et al, Russian Journal of Applied Chemistry **87(10)**,1109–1113 (2014)
16. E. Klimov, M. Buzaeva, O. Davydova et al, Russian Journal of Applied Chemistry **88(8)**, 1229–1234 (2015)
17. H. He, J. Gao, Nanomater **3**, 1–10 (2011)
18. A. Nizametdinov, S. Vasin, V. Sergeev et al, Information Technology and Nanotechnology (ITNT) 2021 International Conference, 1-4 (2021)
19. V. Sergeev, S. Rezchikov, Automation of Control Processes **2(52)**, 68-75 (2018)
20. M. Gorlov, V. Sergeev, *Modern Diagnostic Techniques of Semiconductor Devices Quality and Reliability Control* (UlSTU Publ., Ulyanovsk, 2015)
21. Jia-Qi Luo, Sai Zhao, Hao-Bin Zhang, Zhiming Deng, Lulu Li, Zhong-Zhen Yu, Flexible, stretchable and electrically conductive MXene/natural rubber nanocomposite films for efficient electromagnetic interference shielding, Composites Science and Technology, **182**, 107754 (2019)