STRUCTURE AND PROPERTIES OF NANOSCALE AND MESOSCOPIC MATERIALS

PACS numbers: 72.80.Tm, 77.22.Ch, 77.84.Lf, 81.05.U-, 81.07.Bc, 81.40.Tv

Electrophysical Properties of Polymeric Nanocomposites Based on Ferrite/Carbon Nanotube/Copper Iodide


O. O. Chukho Institute of Surface Chemistry, N.A.S. of Ukraine
17 General Naumov Str., UA-03164 Kyiv, Ukraine

The nanocomposites barium ferrite/carbon nanotubes modified with copper iodide are synthesized by the sol-gel autocombustion method. Electrophysical properties in the microwave range and at low frequencies at room temperature of barium ferrite composites/carbon nanotubes/CuI-polychlorotrifluoroethylene (PCTFE) are studied. As shown, the insertion of composites into PCTFE leads to an increase of the values of complex dielectric permittivity of 5–7 times and electrical conductivity by 2 orders of magnitude in comparison with a system that contains unmodified components.

Key words: ferrites, carbon nanotubes, disperse fillers, interfacial interaction.

Методом золь-гель автогоріння синтезовано нанокомпозит ферит ба-рію/вуглецеві нанотрубки, модифіковані йодидом міді. Вивчено електро-фізичні властивості в надвисокочастотному діапазоні та на низьких часто-тах при кімнатній температурі композитів ферит барію/вуглецеві нанотру-бки/CuI-поліхлоротріфлуроетилен (PХТФЕ). Показано, що при введені композитів у ПХТФЕ відбувається збільшення значень комплексної діелек-тричної сприйнятливості у 5–7 разів та електропровідності на 2 порядки величини в порівнянні з системою, яка містить немодифіковані компонен-ти.

Ключові слова: ферити, вуглецеві нанотрубки, дисперсні наповнювачі,
1. INTRODUCTION

Nowadays, development of electronic devices that led to electromagnetic pollution of the environment has caused to the search of new materials that absorb electromagnetic radiation (EMR). Typically, ‘monomaterial’ is unlikely to fully respond the requirement such as a small specific weight and significant adsorption of EMR in a wide range of frequency. The above problems can be solved by developing functional composite materials. More attention is focus on to the combination of magnetic and electrical components due to the possibility of regulating their electromagnetic characteristics, which can be used in the absorption of EMR [1–3]. Therefore, there is a need to optimize the compound of composites and develop new methods for their obtaining. Ferrimagnets and their solid solutions can be promising in terms of the magnetic components of composites. The relevance of research of ferrite is due to their special functional properties. Barium ferrite with hexagonal molecular structure is a promising material for permanent magnet, advanced recording, and microwave absorbing because of its fairly large magnetocrystalline anisotropy, relatively large magnetization, excellent chemical stability, and corrosion resistivity, whereas its magnetic and electric properties should be modulated to satisfy different applications [4]. A promising electroconductive component may be copper iodide, which had been widely using in catalysis, photonics, as well as in piezoelectric and other dielectric devices [5, 6]. However, high performance characteristics of composites are usually achieved by high values of the content of ‘traditional’ fillers (up to 70% by weight), which negatively affects of the physical, mechanical and thermal properties. The solution of this problem can be the introduction of nanodispersed fillers, especially quasi-one-dimensional nano-
particles, for example, carbon nanotubes (CNT), since they have significant advantages, namely, low specific gravity, controlled conductivity, high aspect ratio etc. [7, 8]. The aim of the work is to obtain and study of the electrophysical properties of macro-disordered polymer-filled systems based on polychlorotrifluoroethylene and barium ferrite/CNT with chemically deposited copper iodide on the surface.

2. EXPERIMENTAL

The nanocomposites CNT/ferrite were synthesized by the sol-gel auto-combustion method to create the newest nanomaterials that effectively interact with electromagnetic radiation. The volume content of CNTs was $\varphi \leq 0.11$. For the synthesis of ferrite was used Fe(NO$_3$)$_3$·9H$_2$O (TU 6-09-02-553-96), Ba(NO$_3$)$_2$ (GOST 3777-76) and citric acid (GOST 3652-69).

Fe(NO$_3$)$_3$·9H$_2$O and Ba(NO$_3$)$_2$ were dissolved in distilled water, the molar ratio of Fe$^{3+}$ to Ba$^{2+}$ was 12:1. The reaction of polycondensation occurred in nitrates aqueous solution with presence of citric acid in a molar ratio of 1:1. Ammonia solution NH$_4$OH (GOST 3760-79) was then added dropwise to the resulting mixture under constant stirring to adjust pH to 7.

Nanotubes (TU Y-03291669-009: 2009), that dispersed by ultrasound in distilled water were added to the above solution. The volume content ($\varphi$) of CNT was from 0.001 to 0.11 parts by volume. To evaporate the water content in the solution, the mixture was heated in a magnetic stirrer with a hot plate at 353 K and it became a viscous gel. With an increase the gel temperature to 473 K, the auto-combustion reaction occurred. After the reaction, a high-dispersion powder (barium ferrite precursor-BFP) and also annealed (BFP-a) at 673 K for 8 hours to removal of organic impurities.

The surface of CNT/BFP and CNT/BFP-a composites was modified of copper iodide (CuI-volume content 0.26 < $\varphi$ < 0.4). Modification of the composite by copper iodide was carried out during the coprecipitation of CuI from aqueous solutions of CuSO$_4$, KI and Na$_2$S$_2$O$_3$ in the presence of the obtained composites according to [9]:

$$2\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{KI} + 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \rightarrow 2\text{CuI} + \text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_6 + 20\text{H}_2\text{O}.$$

Polymeric composite materials were prepared by mixing polychlorotrifluoroethylene (PCTFE) with the powder of CuI/CNT/BFP and CuI/CNT/BFP-a by grinding in the mechanical mill to form a homogeneous mixture, which thereafter was compressed at the polymer melt temperature of 513 K and a pressure of 2 MPa.
The real ($\varepsilon'$) and imaginary ($\varepsilon''$) components of the complex dielectric permittivity and the electrical conductivity ($\sigma$) of the conducting composites at microwave frequencies (range 8–12 GHz) were measured using the interferometer that based on RFK 2-18 to measure the phase difference and the standing wave meter P2-60 by an electrodeless method [10]. The electrical conductivity ($\sigma$) at low frequencies (0.1, 1 and 10 kHz) were measured using the immittance meter E7-14 by two-contacts method [11]. The error in determining $\varepsilon'$, $\varepsilon''$ and $\sigma$ did not exceed 5%.

Crystal structure was determined using X-ray analysis (DRON-4-07, Lomo, USSR) in the emission of cobalt cathode with nickel filter in Bragg–Brentano geometry. The size of the crystallites was determined from the width of the most intense line according to the Scherer equation [12].

Images were obtained using transmission electron microscope JEM-1230 (Jeol, Japan).

3. RESULTS AND DISCUSSION

Transmission electron microscopy was used to study the size and shape of nanocomposites 0.011CNT/BFP and 0.32CuI/0.011CNT/BFP-a (i.e., 0.011CNT/BFP modified of copper iodide) (Fig. 1). The micrographs show carbon nanotubes covered with nanoparticles of both copper iodide and ferrite, those sizes are ~20–30 nm.

Analysis of the obtained diffractograms (Fig. 2) of not annealed nanocomposites 0.011CNT/BFP (curve 1) indicates the presence of the cubic phase of Fe$_3$O$_4$ (JCPDS 88-315) and the orthorhombic BaCO$_3$ phase (JCPDS 71-2394). For samples modified of copper iodide, the diffraction patterns show reflections that refer to the cubic phase of CuI (JCPDS 83-1105) and low-intensity reflexes of the hexagonal CuI-phase (curve 2). For all these samples a reflex at $2\theta = 38.51^\circ$ which refers to the hexagonal phase of Fe$_2$O$_3$ (JCPDS 33-664) is observed.

![Fig. 1. TEM images of synthesized nanocomposites: a—0.011CNT/BFP; b, c—0.32CuI/0.011CNT/BFP-a.](image-url)
In the case of annealed samples at 673 K changes in the composition of the phases are not observed, namely, Fe\(_3\)O\(_4\), BaCO\(_3\), Fe\(_2\)O\(_3\) since this temperature is insufficient for the formation of barium monoferrite. Modification of annealed composites (0.11CNT/BFP-a) with copper iodide leads to the appearance of reflexes, both cubic and hexagonal CuI-phases. It should be noted that on the X-ray diffraction patterns for composites 0.11CNT/BFP modified with iodide copper (annealed and not annealed), BaCO\(_3\) reflexes was not observed, probably due to insignificant dissolution of BaCO\(_3\) in water during the process of modifying its surface by copper iodide. The crystallite size of copper iodide for all samples is ~25 nm.

Figure 3 shows the results of thermogravimetric analysis of synthesized CNT/BFP nanocomposites. It can be seen that the process of thermal decomposition of samples consists of three stages. The first stage is observed in the temperature range from 320 to 470 K with a slight loss of mass (from 2% for a sample not containing CNT and up to 7% for samples 2–4 containing CNT), which can be attributed to the evaporation of adsorbed water. The second stage is observed in the region from 570 to 670 K, accompanied by a significant loss of mass and refers to the partial burnout of CNT. In particular, when the CNT volume content in the composite increase from 0.011 to 0.11, then the weight loss changing from 4 to 16%. The third stage (from 670 to 1070 K) refers to the decomposition of BaCO\(_3\) with the formation first of monoferrite and subsequently barium hexaferite [13]. At temperatures above 1070 K there is almost no loss of mass, which indicates the completion of thermal decomposition and the final formation of the BaFe\(_{12}\)O\(_{19}\)-phase.

Electrophysical studies have experimentally established the opti-
mum concentrations of CuI (0.4 vol. parts) of CuI/CNT/PSF composites which the values of the real ($\varepsilon'$) and imaginary ($\varepsilon''$) components of the complex dielectric permittivity in the microwave range and the electrical conductivity ($\sigma$) at low frequencies have the maximum values.

When CuI/CNT/BFP-a is introduced into polychlorotrifluoroethylene, $\varepsilon'$, $\varepsilon''$ and $\sigma$ are nonlinearly depends on the content of copper iodide. The modification of the BFP surface by copper iodide leads to an increase in the values of $\varepsilon'$ and $\varepsilon''$ of polymer composites (0.32CuI/0.11CNT/BFP-PVDF) in the microwave range as compared to the system, does not contain modified components (CuI-PCTFE) (Figs. 4, 5).

![Fig. 3](image)

**Fig. 3.** Thermogravimetric analysis curves of synthesized nanocomposites of CNT/BFP. The volume content of CNT: 1—0, 2—0.011, 3—0.065, 4—0.11.

![Fig. 4](image)

**Fig. 4.** Dependences of $\varepsilon'$ (a) and $\varepsilon''$ (b) at 9 GHz on the volume content ($\varphi$) of copper iodide in nanocomposites for polymer systems with polychlorotrifluoroethylene: 1—0.32CuI/0.11CNT/BFP, 2—0.32CuI/0.11 CNT/BFP-a, 3—CuI, 4—0.32CuI/0.011 CNT/BFP.
This effect is related to the peculiarities of structuring of particles 0.32CuI/CNT/BFP in a polymer matrix, as well as the effect of polymer boundary layers on the electrophysical properties of this composites.

The value of the complex dielectric constant and electrical conductivity in the case of 0.32CuI/CNT/BFP-a composites much below (Fig. 4, 5) than for the system CNT/BFP. This is probably due to the increase of the size of the crystallites of the BFP on the surface of CNT during annealing and also partial destruction of CNT due to the increase in the catalytic activity of iron with increasing temperature. Since CNT is the center of crystallization for copper iodide, with the growth of the size of BFP nanoparticles is the cause of the destruction of CuI conductivity channels on the surface of CNT. It should be noted that for composites containing 0.011 vol. parts of CNT (curve 4), the value of $\varepsilon'$ and $\varepsilon''$ is 2 times larger than for composites containing 0.11 vol. parts of CNT (curve 2). This indicates the destruction of conductivity channels of copper iodide and CNT during annealing.

The introduction of CuI/CNT/BFP into polychlorotrifluoroethylene leads to an increase in the electrical conductivity, by almost two orders of magnitude compared to a system CuI-PVDF that does not contain modified components (Fig. 5). It can be seen from the figure that the main contribution to the electrical conductivity of composites is made by CNT.

In addition, the percolation threshold is shifted to low concentrations at a volumetric content of copper iodide of 0.4. Such a character of the concentration dependences is probably associated with a change in both the particle sizes of copper iodide and the structure of their clusters on the CNT/BFP surface.

Fig. 5. Dependences of the logarithm of electrical conductivity at a frequency of 100 Hz on the volumetric content ($\phi$) of copper iodide in nanocomposites for polymer systems with polychlorotrifluoroethylene: 1—0.32CuI/0.11CNT/BFP, 2—0.32CuI/0.11CNT/BFP-a, 3—CuI; 4—0.32CuI/0.011CNT/BFP.
4. CONCLUSIONS

The nanocomposites CNT/BFP were synthesized by the sol-gel auto-combustion method. The volume content of CNTs was $\varphi \leq 0.11$. The modification of the surface of CNT/BFP composites by copper iodide was carried out. The crystallite size of copper iodide for all samples is $\sim 25$ nm.

It is shown that insertion of CuI/CNT/BFP in polychlorotrifluoroethylene leads to an increase in the values of $\varepsilon'$, $\varepsilon''$ by almost 5 to 7 times in the microwave range. The values of the electrical conductivity is increased by almost two orders of magnitude and a percolation threshold significantly shift to the region of low concentrations of CuI compared to a system that does not contain modified components.

REFERENCES