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ELECTROPHYSICAL PROPERTIES OF POLYMERIC NANOCOMPOSITES BASED ON TIN DIOXIDE MODIFIED WITH NICKEL FERRITE

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The creation of new nanomaterials for absorbtion of electromagnetic radiation microwave range is an important direction in consequence of electromagnetic pollution of the environment. The aim of the paper was to develop and synthesize the polymer-filled systems based on the polychlorotrifluoroethylene and tin dioxide modified by nickel ferrite in order to study their electrophysical properties as potential materials absorbing electromagnetic radiation. $NiFe_2O_4/SnO_2$ nanocomposites with a volume content of nickel ferrite on the surface of tin dioxide from 0.62 to 0.8 were synthesized by co-precipitation. Size of SnO_2 and $NiFe_2O_4$ nanoparticles was determined by a transmission electron microscope and its about 30–50 nm and 15–30 nm, respectively. For the $NiFe_2O_4/SnO_2$ nanocomposites the values of complex permittivity and complex permeability in the microwave range, values of conductivity at low frequencies were investigated. Maximum values of complex permittivity and complex permeability were found for $NiFe_2O_4/SnO_2$ nanocomposites at the volume content of nickel ferrite 0.62. An increase was observed in the complex permittivity for the $NiFe_2O_4/SnO_2$–polychlorotrifluoroethylene system, 2–3 times greater than the values related to the $NiFe_2O_4/SnO_2$ nanocomposites. The electrical conductivity at low frequencies (100 Hz) of polymer composites increases by an order of magnitude with a decrease of the concentration of nickel ferrite on the surface of tin dioxide. It was found that the calculated absorption coefficient of an electromagnetic wave in the frequency range 1–41 GHz for $NiFe_2O_4/SnO_2$ nanocomposites is about 2 times greater than that for nickel ferrite. It is shown that the creation of nanocomposites based on a conductive component modified by a magnetic component is more efficient for the processes of absorption of electromagnetic waves in the microwave range at optimal ratios of the values of the permittivity and permeability than pure ferrite.

***Keywords**: nanocomposite, nickel ferrite, tin dioxide, complex permeability, complex permittivity, electrical conductivity, absorption coefficient*

INTRODUCTION

The rapid development of science and technology, as well as the use of electronic and communication equipment have caused electromagnetic pollution of the environment. Electromagnetic (EM) radiation is a threat not only to information security, the use of high-precision electronic equipment, but also to human health [1]. Therefore, nowadays, the creation of new materials for absorbing of EM radiation is an important direction. Nevertheless, the development of such materials is a serious problem, since it is necessary to combine simultaneously in materials such parameters as a wide range of absorption frequencies, strong absorption, light weight, thin thickness *etc*. [2]. Traditional absorbing materials are mainly divided into dielectric loss materials and magnetic loss materials, and they are generally limited to one loss mechanism. This makes it impossible to use such absorbing materials with parameters listed above. For intensification of the EM wave adsorption use of combination of different electromagnetic properties of materials (permittivity and permeability *etc*.) [3], different morphology (sheet, linear, spherical, core-shell structure *etc*.) and different sizes [4, 5]. This approach makes it possible to provide multiple loss mechanisms in composite materials in an EM field.

Spinel-type ferrites ($MeFe_2O_4$, where Me = Co, Ni, Fe, Zn, Cu *etc*.) and various conductive components (carbon and semiconductor materials (CuS, $BaTiO_3$, SnO_2) metallic particles *etc*.) are often used to create such composite materials [6–8]. The spinel ferrite $NiFe_2O_4$ feature a moderate saturation magnetization, low toxicity, high mechanical hardness, excellent chemical stability, large electrical resistivity, which is a promising candidate as a microwave absorbers [9].

There are numerous articles describing the structures of core-shell particles (Ni/SnO_2), porous core-void-shell nanocomposites (Fe_3O_4-

SnO_2), Fe_3O_4@SnO_2/graphene oxide nanocomposites with good absorption of EM microwave radiation [10–12]. The authors note that the improvement in absorbing properties is possibly due to an effective combination of dielectric losses and magnetic losses, but the effect of SnO_2 content on microwave absorption properties was not illustrated systematically. Nonetheless, the articles noted that the microwave absorption properties of nanocomposite can be tuned by control of SnO_2 contents.

The aim of the paper was to develop and synthesize the polymer-filled systems based on the polychlorotrifluoroethylene and tin dioxide modified by nickel ferrite in order to study their electrophysical properties as potential EM radiation absorbing materials.

MATERIALS AND METHODS

To create materials that effectively interact with EM radiation, nanocomposites $NiFe_2O_4/SnO_2$ were synthesized. First, tin dioxide nanoparticles were synthesized accordingly to the procedure described elsewhere [13]:

$$Sn + 4HNO_{3(\text{conc.})} = SnO_2 + 4NO_2 + 2H_2O. \quad (1)$$

The powder SnO_2 was washed by deionized (DI) water and heat treated at 923 K in air for 4 h. Then SnO_2 nanoparticles were modified with nickel ferrite by coprecipitation method in the presence of a reducing agent (hydrazine hydrate). For this, the stoichiometric amounts (2:1) of iron nitrate $Fe(NO_3)_3\cdot 9H_2O$ (pure grade), nickel nitrate $Ni(NO_3)_2\cdot 6H_2O$ (pure grade) were dissolved in DI water. The appropriate amount of SnO_2 nanoparticles was added to nitrate solution with continuous stirring for 2 h and 293 K. Then appropriate amount of hydrazine hydrate was added to solution with continuous stirring till the pH was adjusted to 7.0 and boiled for 2 h. The powder was separated by magnetic separation and dried at 100 °C for 6 h. The concentration of $NiFe_2O_4$ on a surface of SnO_2 was from 0.62 to 0.8 vol. fractions (ϕ).

Polymer filled composites were prepared by mechanical milling of the polychlorotrifluoroethylene (PCTFE) powder with modified powders ($NiFe_2O_4/SnO_2$) until homogeneous mixture, which thereafter was compressed at the polymer melt temperature of 513 K and a pressure of 2 MPa.

The real (ε′) and imaginary (ε″) components of the complex permittivity, the real (μ′) and imaginary (μ″) components of the complex permeability of composites at microwave frequencies (9 GHz) were measured using an interferometer (RFK 2-18, USSR, for measuring thet phase difference) and a standing wave meter (R2-60, USSR) by an electrodeless method [14]. The samples of the composites had a rectangular shape of 10×23 mm with a thickness of 2 mm. The immittance meter (E7-14, USSR) is used to measure the electrical conductivity (σ) at low frequencies (100 Hz) by two-contacts method [15]. The samples of the composites had a square shape of 10×10 mm with a thickness of 2 mm. For measurements of electrical conductivity graphite electrodes were used and the experimental error did not exceed 5 %.

Crystalline structure of the samples was characterized by an X-ray diffractometer DRON-4-07 (Lomo, USSR) with CoK_α radiation. Scherrer's equation (Eq. (2)) [16] was used to determine the crystal sizes of the samples from the width of the most intense line in XRD patterns.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

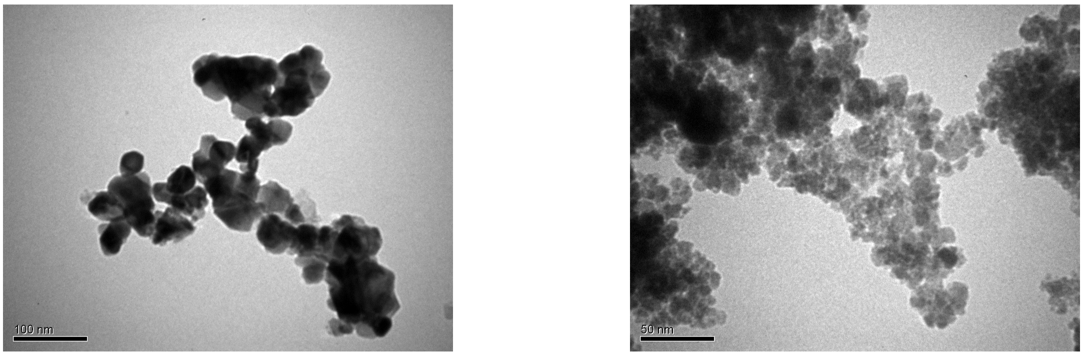
where λ is the X-ray wavelength (0.1789 nm), θ is the Bragg diffraction angle, β is the full width at half maxima of the peak [17].

Information about the morphologies and microstructures of composites was determined using transmission electron microscope (TEM) (JEOL-1200 EX, Jeol, Japan) images of the as-synthesized samples.

RESULTS AND DISCUSSION

The TEM images of the synthesized SnO_2 nanoparticles and after their modification by nickel ferrite are presented in Fig. 1. All TEM images show moderately agglomerated and individual particles. The results of a TEM study indicated that nanoparticles of SnO_2 were a size of about 30–50 nm (Fig. 2 *a*). The size of $NiFe_2O_4$ nanoparticles on the surface of tin dioxide was 15–30 nm (Fig. 2 *b*).

Crystalline structure of the as-synthesized nickel ferrite and SnO_2 modified by nickel ferrite were studied with X-ray analysis (Fig. 2). The diffraction pattern of SnO_2 modified with nickel ferrite (Fig. 2, curve *2*) contains all reflections corresponding to $NiFe_2O_4$ (JCPDS 86-2267) and SnO_2 (JCPDS 88-0287). The main reflections synthesized ferrite corresponded to the cubic structure and to the (111), (220), (222), (311), (400), (422), (440), (511) crystalline planes. The main reflections tin dioxide corresponded to the tetragonal structure and to the (110), (101), (200), (211), (220) crystalline planes. The average size of crystallites of nickel ferrite and tin dioxide is 27 and 25 nm, respectively.



a *b*

Fig. 1. TEM images of synthesized tin dioxide nanoparticles (*a*) and 0.68 $NiFe_2O_4/SnO_2$ (*b*)

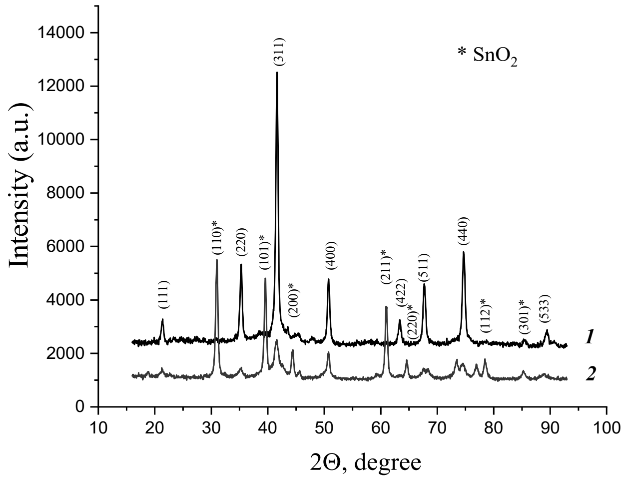


Fig. 2. X-ray diffraction patterns of synthesized samples: *1* – $NiFe_2O_4$, *2* – 0.68 $NiFe_2O_4/SnO_2$

The values of ε′, ε″ and μ′, μ″ in the microwave range as well as values of σ at 100 Hz nonlinearly depend on the concentration of – $NiFe_2O_4$ for modified $NiFe_2O_4/SnO_2$ composites and reaches a maximum values ε′, ε″ μ′, μ″ at ϕ = 0.62. The formation of branched non-conducting clusters of nickel ferrite ($\sigma = 1\cdot10^{-8}$ $Om^{-1}\cdot cm^{-1}$) on the surface of tin dioxide leads to a decrease in the interaction of the electromagnetic field and, accordingly, to a decrease in the values ε′ and ε″. It was found that the main contribution to the electrical conductivity of the $NiFe_2O_4/SnO_2$ composites is caused by tin dioxide, but the main influence on the σ is exerted by nickel ferrite on the surface SnO_2. The values of the real and imaginary component of complex permeability and complex permittivity at 9 GHz for the synthesized nickel ferrite and modified SnO_2 by nickel ferrite are presented (Table). It was also determined that an increase of the nickel ferrite concentration on the surface of SnO_2 leads to a decrease in the values of complex permeability. This is due to natural ferromagnetic resonance [18] and an increase in the degree of defectiveness of the surface of magnetic nanoparticles, due to an increase in the surface of interaction between the magnetic component and the conductive component (SnO_2).

The experimental results of the complex permittivity for the systems $NiFe_2O_4/SnO_2$–PCTFE are presented in Fig. 3. An introduction of

$NiFe_2O_4/SnO_2$ composites in PCTFE leads to an increase ε′ and ε″ in all concentration range, at room temperature. The maximum values of complex permittivity for $0.62NiFe_2O_4/SnO_2$–PCTFE composites were observed. The nonlinear character of the increase of the values of ε', ε" in three-component systems with an increase of the volume content of the nickel ferrite was observed.

Table. Complex permeability and complex permittivity of synthesized nickel ferrite and nanocomposites

Sample	μ'	μ''	ε′	ε″
$NiFe_2O_4$	1.01	0.02	2.1	0.5
$0.8NiFe_2O_4/SnO_2$	1.09	0.05	4.1	2.9
$0.68NiFe_2O_4/SnO_2$	1.09	0.06	4.2	3.4
$0.62NiFe_2O_4/SnO_2$	1.11	0.06	4.4	3.6

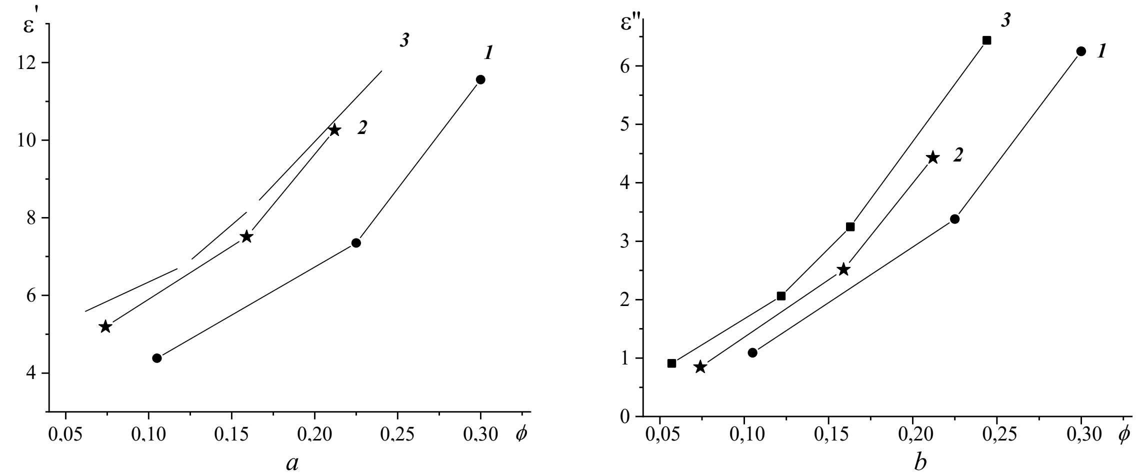


Fig. 3. Dependences of the ε′ (*a*) and ε″ (*b*) at 9 GHz of the nickel ferrite volume fractions (ϕ) in polymer composite systems: *1* – $0.8NiFe_2O_4/SnO_2$–PCTFE, *2* – $0.68NiFe_2O_4/SnO_2$–PCTFE, *3* – $0.62NiFe_2O_4/SnO_2$–PCTFE

The dependences of the electrical conductivity at a low frequency on the volumetric content of nickel ferrite for three-component systems are shown in Fig. 4. Since the main contribution to the electrical conductivity of nanocomposites $NiFe_2O_4/SnO_2$ is tin dioxide, but the main influence on the σ is exerted by nickel ferrite on the surface SnO_2, with an increase in the volume fraction of ferrite, a decrease in conductivity values is also observed in three-component systems $NiFe_2O_4/SnO_2$–PCTFE. This can be explained by a decrease in the formation of conductive clusters interacting with the microwave field, as well as direct contacts between conductive tin dioxide nanoparticles.

The calculated dependences of the absorption coefficient of EM waves by $NiFe_2O_4/SnO_2$ nanocomposites and nickel ferrite in the microwave range are shown in Fig. 5. The absorption coefficient (A) was calculated according to Eq.:

$$A = 1 - R - T \, , \quad (3)$$

where R - reflection coefficient of EM wave, T - transmission coefficient of EM wave, which were determined by equations in a complex form, using the experimental values of ε′, ε″ and μ′, μ″ according to [19].

The figure shows that the absorption of EM waves by nanocomposites is more efficient than by nickel ferrite. The frequency curves (*2*, *4*) of nanocomposites have minima in the frequency range of 10 and 25 GHz, which is due to changes in the reflection coefficient, namely, increasing its values. For nanocomposites $0.68NiFe_2O_4/SnO_2$ (curves *3*) in the frequency range up to 20 GHz, a decrease in the values of the absorption coefficient of the EM wave was observed, due to an increase in the reflection coefficient, which occurs due to the summation of the reflected EM waves from the front and back sides of the measured sample. After 20 GHz, an increase in the absorption coefficient of the EM wave was observed, due to a decrease in the reflection coefficient, since there was a subtraction of the reflected EM waves from the front and back sides of the measured sample.

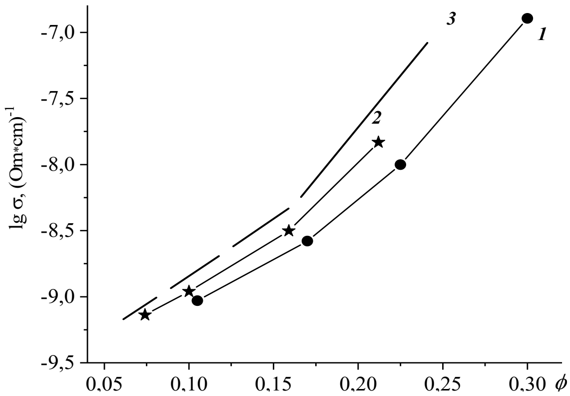


Fig. 4. Dependences of the electrical conductivity logarithms of the nickel ferrite volume fractions (ϕ) in polymer composite systems: *1* – $0.8NiFe_2O_4/SnO_2$–PCTFE, *2* – $0.68NiFe_2O_4/SnO_2$–PCTFE, *3* – $0.62NiFe_2O_4/SnO_2$–PCTFE

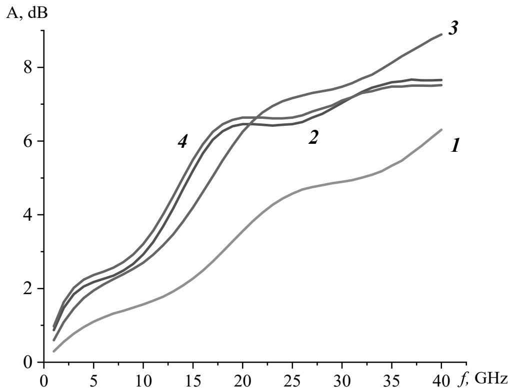


Fig. 5. Frequency dependence of absorption coefficient (*A*) for nanocomposites: *1* – $NiFe_2O_4$, *2* – $0.8NiFe_2O_4/SnO_2$, *3* – $0.68NiFe_2O_4/SnO_2$, *4* – $0.62NiFe_2O_4/SnO_2$. The thickness of the samples was 4 mm

CONCLUSIONS

$NiFe_2O_4/SnO_2$ nanocomposites were obtained by modifying tin dioxide with nickel ferrite with its volume fraction from 0.62 to 0.8. The size of SnO_2 and $NiFe_2O_4$ nanoparticles were 30–50 and 15–30 nm, respectively.

The values of ε′, ε″ and μ′, μ″ in the microwave range as well as values of conductivity at 100 Hz nonlinearly depend on the concentration of $NiFe_2O_4$ for modified $NiFe_2O_4/SnO_2$ nanocomposites and reaches a maximum value at $\phi = 0.62$.

An introduction of $NiFe_2O_4/SnO_2$ nanocomposites in PCTFE leads to an increase ε′ and ε″ in 2–3 times in all concentration range in 2–3 times at room temperature. The complex permittivity for $0.62NiFe_2O_4/SnO_2$–PCTFE composites is 2 times higher compared to the same for $0.8NiFe_2O_4/SnO_2$–PCTFE. The electrical conductivity for $0.62NiFe_2O_4/SnO_2$–PCTFE composites is 1 orders of magnitude higher compared to the same for $0.8NiFe_2O_4/SnO_2$–PCTFE, presumably due to formation more branched cluster of tin dioxide modified by nickel ferrite.

The obtained experimental values of the complex permittivity and complex permeability of $NiFe_2O_4/SnO_2$ nanocomposites made it possible to calculate the absorption coefficient of EM waves for the frequency range 1-40 GHz. It is shown that for $NiFe_2O_4/SnO_2$ nanocomposites the value of the absorption coefficient of EM waves is almost 2 times higher compared to nickel ferrite.

Електрофізичні властивості полімерних нанокомпозитів на основі діоксиду олова, модифікованого феритом нікелю

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Створення нових наноматеріалів для поглинання електромагнітного випромінювання мікрохвильового діапазону є важливим напрямом у зв'язку з електромагнітним забрудненням навколишнього середовища. Метою роботи була розробка та синтез полімерно-наповнених систем на основі поліхлортрифторетилену та діоксиду олова, модифікованих феритом нікелю, з метою дослідження їхніх електрофізичних властивостей як матеріалів, що поглинають електромагнітне випромінювання. Методом співосадження синтезовано нанокомпозити $NiFe_2O_4/SnO_2$ з об'ємним вмістом фериту нікелю на поверхні діоксиду олова від 0.62 до 0.8. Розміри наночастинок SnO_2 та $NiFe_2O_4$ визначали за допомогою трансмісійного електронного мікроскопа, які становили близько 30–50 та 15–30 нм відповідно. Для нанокомпозитів $NiFe_2O_4/SnO_2$ проведено дослідження комплексної діелектричної та комплексної магнітної проникності в мікрохвильовому діапазоні, а також електропровідності на низьких частотах. Встановлено максимальні значення комплексної діелектричної та комплексної магнітної проникності для нанокомпозитів $NiFe_2O_4/SnO_2$ при об'ємному вмісті фериту нікелю 0.62. Спостерігалося збільшення комплексної діелектричної проникності для системи $NiFe_2O_4/SnO_2$–поліхлортрифторетилен у 2–3 рази порівняно з нанокомпозитами $NiFe_2O_4/SnO_2$. Електропровідність на низьких частотах (100 Гц) полімерних композитів зростає на порядок зі зменшенням концентрації фериту нікелю на поверхні діоксиду олова. Встановлено, що розрахований коефіцієнт поглинання електромагнітної хвилі в діапазоні частот 1–41 ГГц для нанокомпозитів $NiFe_2O_4/SnO_2$ приблизно в 2 рази більший, ніж для фериту нікелю. Показано, що створення нанокомпозитів на основі провідної компоненти, модифікованої магнітною компонентою, є більш ефективним для процесів поглинання електромагнітних хвиль мікрохвильового діапазону при оптимальних співвідношеннях значень діелектричної та магнітної проникності порівняно з феритом.

***Ключові слова**: нанокомпозит, ферит нікелю, діоксид олова, комплексна магнітна проникність, комплексна діелектрична проникність, електропровідність, коефіцієнт поглинання*

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