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# Synthesis, Electrical and Magnetic Properties of Composites Copper Iodide/Magnetite-Polychlorotrifluoroethylene

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The structural, magnetic and electrophysical properties of composites based on nanosized magnetite chemically modified of copper iodide and polychlortrifluoroethylene have been studied at temperatures 298 – 450 K and CuI concentrations of from 0 to 0,58 volume. It has been found the optimal volume content of copper iodide (~ 0,4) in the composites $CuI/Fe_3O_4$, when the interfacial interaction shows most intensively and maximum values electrical parameters take place. The value of the coercive force of nanocomposites $CuI/Fe_3O_4$ increases with increasing content copper iodide. It was shown that polymer composites containing $CuI/Fe_3O_4$, have higher values of real and imaginary components of complex permittivity and conductivity compared with a system that contains only copper iodide.

**Keywords:** magnetite, copper iodide, nanocomposites, specific magnetization, interfacial interaction.

## Introduction

Nanotechnologies allow creation, improvement and modification of nanomaterials by controlled method and their implementation in fully functioning systems. Nanoparticles and nanomaterials that comprise them are used in different fields of science due to their new perspective unlike the properties of micro-objects. Namely, nanoparticles of materials and their oxides, semiconductors etc. may be used for creation of the materials used in sensor devices, components of nanoelectronics, microelectronics and separating materials [1-4]. Functionalized magnetic nanoparticles and perspective of their use in biomedicine (contrast materials for diagnostics, magnetic sorbents of biochemical products as carriers of biologically active compounds and medicines) [5-9], construction materials (screening materials and radar-absorbent coatings) etc. [10-12] are increasingly drawing the attention. Today, there are many scientific works devoted to combination of the properties of magnetic and electrically conductive properties components of nanomaterials [13-15]. Such approach allows the solution of important problems, namely in the structures of coatings that suppress electromagnetic radiation, i.e. the combination of dissipation of electromagnetic waves, magnetic and dielectric losses. Due to this fact, the properties of these materials can vary in a wide range of frequencies.

Magnetic nanoparticles of ferric oxide are often used for these materials, namely magnetite ($Fe_3O_4$) [16-17]. CuS [18], ZnO [19-20], MnO [21], $BaTiO_3$ [22] and materials that contain carbon are used as electrically conductive components [23-25]. However, the functionalization of the magnetite surface with respective components affects its characteristics and composites in general.
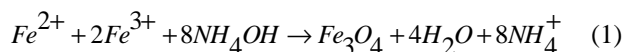
Therefore, the study and obtaining of magnetite chemically modified with electrically conductive components, namely copper iodine, creation of new functional materials on their basis and the study of the effect of chemical nature of the components on physical/chemical and magnetic properties of composites in general are very importantly.

The purpose of this work is a study and obtaining of electrical and magnetic properties of polymer-filled systems based on polychlorotrifluoroethylene and nanosized magnetite with copper iodide that is chemically settled on its surface.

## I. Study object and methods

We used $FeSO_4 \cdot 7H_2O$ of CP (the chemically pure) grade (GOST 4148-66) and $FeCl_3 \cdot 6H_2O$ of CP grade (GOST 4147–74) for synthesis of magnetite. $Fe_3O_4$ was obtained by the method, proposed by Elmor [26], i.e. chemical condensation - quick settling of salts of divalent and trivalent iron, concentrated with 25% ammonia
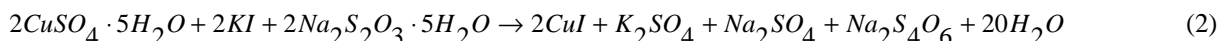
solution:

$$Fe^{2+} + 2Fe^{3+} + 8NH_4OH \rightarrow Fe_3O_4 + 4H_2O + 8NH_4^+ \quad (1)$$

To conduct the reaction, 5 g of $FeSO_4 \cdot 7H_2O$ (molar concentration c = 0.09 M) and 10 g of $FeCl_3 \cdot 6H_2O$ (c = 0.185 M) were dissolved in 20 ml of distilled water. After filtration, the glass with resultant solution was placed in magnetic stirrer. Then aqueous solution of $NH_4OH$ 50 ml was added to ferrous salt solution with the speed of one drop per second. Co-settlement reaction was conducted at temperature of ferrous salt solution of 293 K. The precipitates was removed and washed by distilled water.

$CuSO_4 \cdot 5H_2O$ of PFA (pure for analysis) grade (GOST 4165-78), $Na_2S_2O_3 \cdot 5H_2O$ of PFA grade (GOST 27068-86) and KI of PFA grade (GOST 4232-74) were used for synthesis of copper iodine. The modification of nanosized magnetite with copper iodide (the content up to 0.58 volume ratio) was carried out from aqueous solutions $CuSO_4$, KI and $Na_2S_2O_3$ in the presence of previously synthesized magnetite during the process of CuI settlement according to [27]:

$$2CuSO_4 \cdot 5H_2O + 2KI + 2Na_2S_2O_3 \cdot 5H_2O \rightarrow 2CuI + K_2SO_4 + Na_2SO_4 + Na_2S_4O_6 + 20H_2O \qquad (2)$$

X-ray patterns of obtained samples were acquired by means of X-ray diffraction meter DRON–4–07 ($CuK_\alpha$ radiation - anode lines with nickel filter in reflected beam, the geometry of exposure was according to Bregg-Brentano). The crystallite size was determined by the width of the largest respective intensive line according to Sherrer's equation [28].

Thermogravimetric analysis was carried out by means of derivatograph Q–1500D (Paulik-Erdey, Hungary) within temperature range from 273 to 1273 K at heating speed of 10 K/minute in the air.

The hysteresis loops of magnetic moment of samples were measured by means of vibration magnetometer at room temperature. The descriptions of the device and measurement procedures are shown in [29]. Specially prepared, demagnetized dry materials were used for the study. To prevent dipole-dipole interaction between nanoparticles of resultant magnetite, the latter was divided into paraffin matrixes at mass concentration ≈

3%. The sample with known specific intensity of magnetization was used for comparison: tested sample of nickel and nanoparticles $Fe_3O_4$ (firm 'Nanostructured & Amorphous Materials Inc.', USA). Measurement error doesn't exceed 2.5%.

Polymer composites based on $CuI/Fe_3O_4$ and polychlorotrifluoroethylene (PCTFE) F–3 M were obtained by pressing method at temperature of 513 K and pressure of 2 MPa. The study of real ($\varepsilon'$) and imaginary ($\varepsilon''$) component of complex permittivity of composites was carried out within high-frequency range of 8-12 GHz by means of interferometer based on phase differential meter RFK2-18 and standing wave coefficient meter using electrodes method [30]. The electrical conductivity ($\sigma$) was measured by two-contact method at low frequencies of 0.1, 1 and 10 kHz [31] by means of the immitance mete E7-14. The error of $\varepsilon'$, $\varepsilon''$ and $\sigma$ did not exceed 5%.

Electron-microscopic studies were carried out by
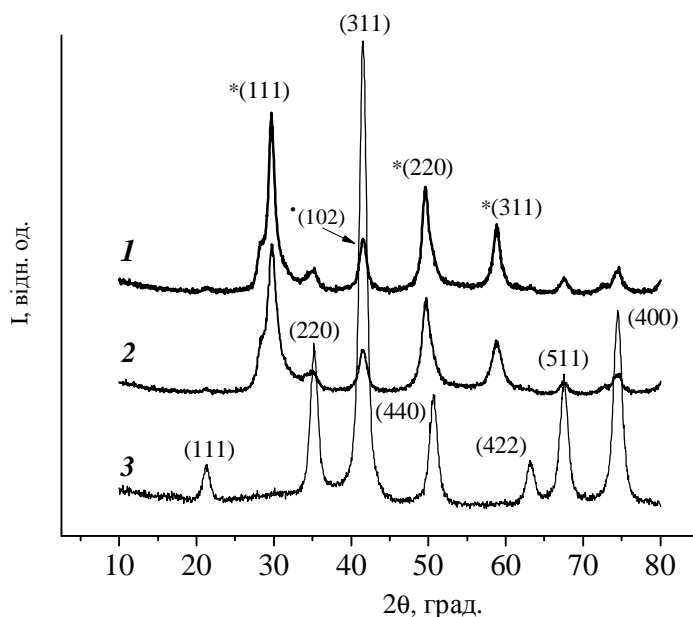


**Fig. 1.** Diffraction patterns of synthesized nanocomposite $CuI/Fe_3O_4$. The volume fraction of CuI: *1* – 0.58; *2* – 0.4; *3* – 0.
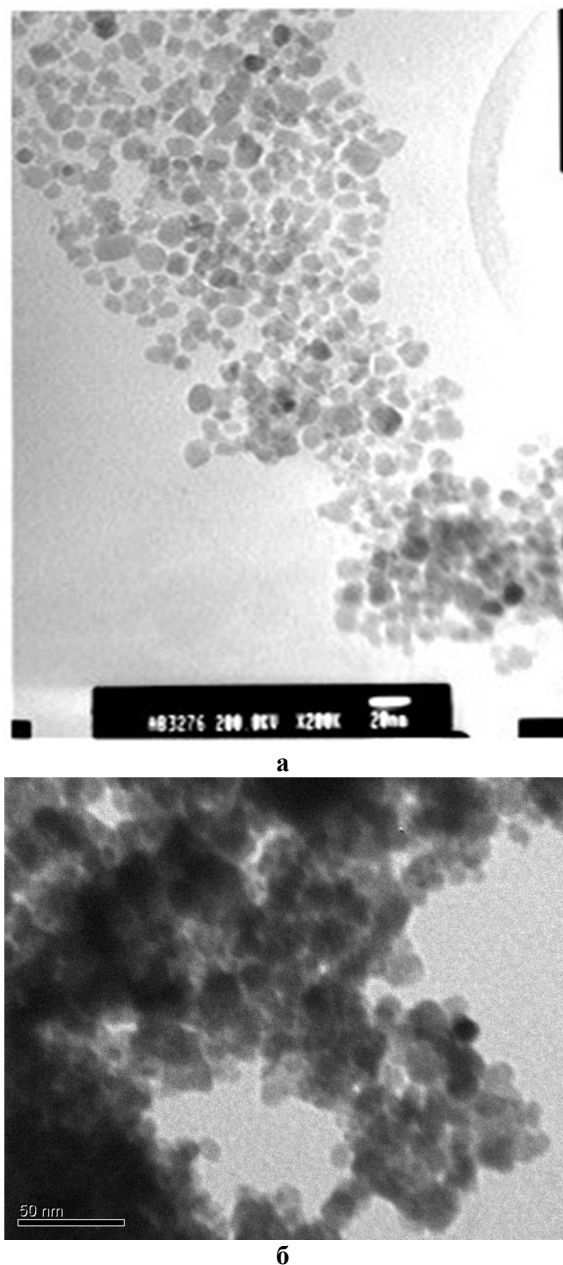
**Fig. 2.** Photomicrographs of synthesized samples of magnetite (*a*) and nanocomposites0.58CuI/Fe$_3$O$_4$ (*b*).

means of transmission electronic microscope JEM-2100F (Jeol, Japan) and Jeol-2010.

## II. Results and their discussion

Figure 1 shows X-ray diffraction spectrums for composites CuI/Fe$_3$O$_4$ and magnetite powder. Nanoparticles of magnetite (curve 3) are characterized by reflexes that meet crystal phase Fe$_3$O$_4$ (JCPDS № 19-629) with cubic crystal syngony. In modified samples CuI/Fe$_3$O$_4$ (curve 1 and 2), main reflexes suggest the availability of cubic and hexagonal structure of copper iodide and their amplitude increases in proportion to CuI content. It should be noted that the reflexes that are peculiar for crystalline lattice of magnetite were not disclosed in CuI/Fe$_3$O$_4$ composites. Therefore it is possible to conclude that volumetric content of copper iodide ($\phi \approx 0.4$) is already enough for creation of the layer on the surface of magnetite. The crystallite size of copper iodide, for CuI/Fe$_3$O$_4$ composites with CuI volumetric content of 0.4 and 0.58, is equal to 9 nm and 10.5 nm respectively. The crystallite size of magnetite is 8.8 nm.

Methods of transmission electronic microscopy were used for study of the sizes and the shape nanoparticles of magnetite and magnetite modified with copper iodide that are shown on figure 2. For resultant magnetite Fe$_3$O$_4$ (figure 2a), the average value of diameter is equal to 9 nm. On electronic images (figure 2 б), nanoparticles of magnetite coated with copper iodide are present as separate nanoparticles and nanoparticles aggregated in larger structures. The average size of nanoparticles CuI/Fe$_3$O$_4$ is equal to 12 ± 3 nm.

Figure 3 shows results of thermogravimetric analysis of synthesized samples of magnetite (curve 1), dispersed copper iodide (curve 4) and nanocomposites: 0.27CuI/Fe$_3$O$_4$ (curve 2) and 0.58CuI/Fe$_3$O$_4$ (curve 3). The magnetite is characterized by mass loss of 7% within temperature range from 373 K to 1273 K. Mass loss of almost 3% up to 423 K is caused by removal of physically absorbed water. This nature of changes is demonstrated by curves TG for samples of magnetite modified with copper iodide. Abrupt changes in mass loss curves for Fe$_3$O were not observed within temperature range from 423K to 1023 K. Further increase of the temperature up to 1237 K causes the change of crystal structure of ferrous oxides due to oxidation of magnetite with oxygen [29]. Mass loss for synthesized copper iodide upon treatment up to 623 K is equal to 3% (curve 4) due to water removal absorbed on sample surface. When the temperature exceeds 723 K, copper iodide melting process starts. Temperature of transformation of phases from γ-CuI to β-CuI (645 К) and also transformation to α- CuI (713 K) do not change significantly. The shift in temperature of melting process of copper iodide for samples 2 and 3 is associated with creation of particles of different size and different thickness of CuI on the surface of magnetite. This process causes the increase of thermal resistance of magnetite particles coated with copper iodide.
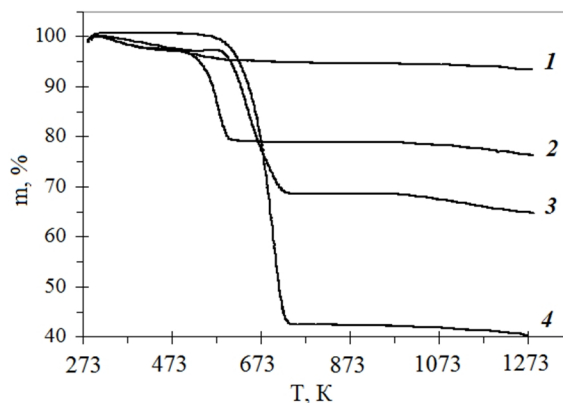
Figure 4 shows hysteresis loops of nanoparticles



**Fig. 3.** Curve of weight loss of synthesized nanocomposites: *1* – Fe$_3$O$_4$, *2* – 0.27CuI/Fe$_3$O$_4$, *3* – 0.58CuI/Fe$_3$O$_4$, *4* – CuI.

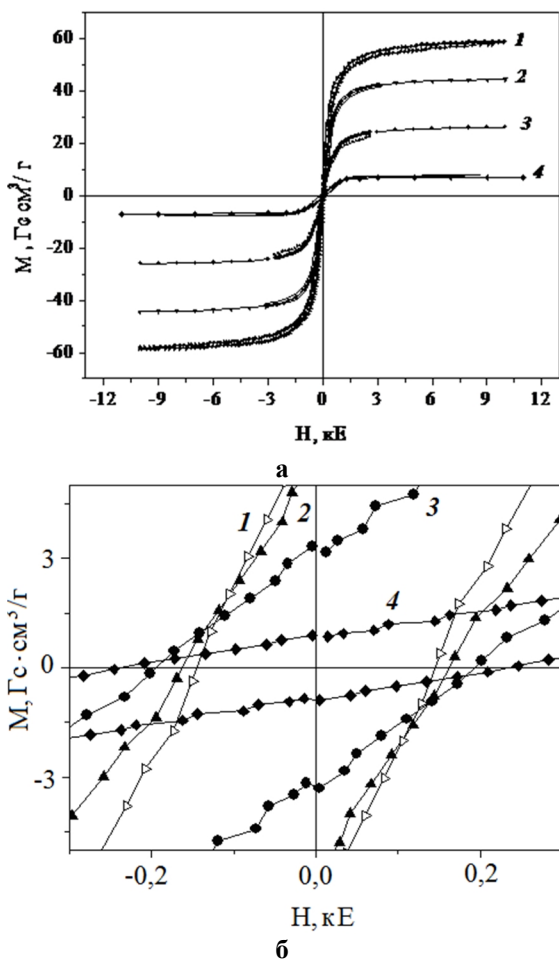R.V. Mazurenko, M.V. Abramov, S.M. Makhno, G.M. Gunya, P.P. Gorbik

**Fig. 4.** Hysteresis loop (*a*) of samples CuI/Fe$_3$O$_4$ and primary area of hysteresis loop (*b*) at volume content of copper iodide: *1* – 0; *2* – 0,27; *3* – 0,4; *4* – 0,58.



**Fig. 5.** The coercive force of nanocomposites CuI/Fe$_3$O$_4$ at volume content (φ) of copper iodide.



**Fig. 6.** The concentration dependence (*a*) and temperature dependence (*b*) of the logarithm of the electrical conductivity of nanocomposites CuI/Fe$_3$O$_4$. The volume fraction of CuI: *1*– 0,27; *2* – 0,4; *3* – 0,58.

initial magnetite and magnetite modified with copper iodine. It was disclosed that ferromagnetic properties are peculiar to nanoparticles of magnetite and CuI/Fe$_3$O$_4$ nanocomposites. Since specific density of components are almost similar ($r_{CuI} = 5.62\,\text{g/cm}^3$; $r_{Fe_3O_4} = 5.24\,\text{g/cm}^3$), specific intensity of magnetization of CuI/Fe$_3$O$_4$ samples changes in proportion to the content of nanoparticles of magnetite. The absolute value of coercive effect (figure 5) increases with the increase of the content of copper iodide in CuI/Fe$_3$O$_4$ composites. It is known [32], that magnetic anisotropy of nanoparticles consists of crystallographic magnetic anisotropy, shape anisotropy, surface anisotropy etc. Size distribution and shape of magnetite particles were unchanged and the dipole-dipole interaction between them was absent. Therefore the shell of copper iodine on the surface of magnetic iron probably has the effect on the value of its effective surface magnetic anisotropy, which explains nonmonotonic dependency of coercive force from the size of nanoparticles [33]. It should be mentioned the surface anisotropy plays a special role for nanoparticles. Unlike other types of anisotropy, surface anisotropy is proportional to the area of particle surface but not is
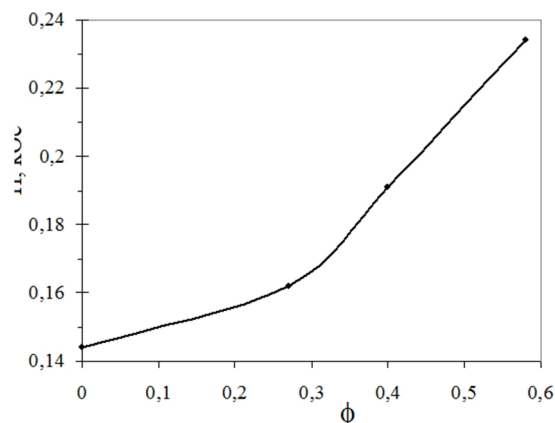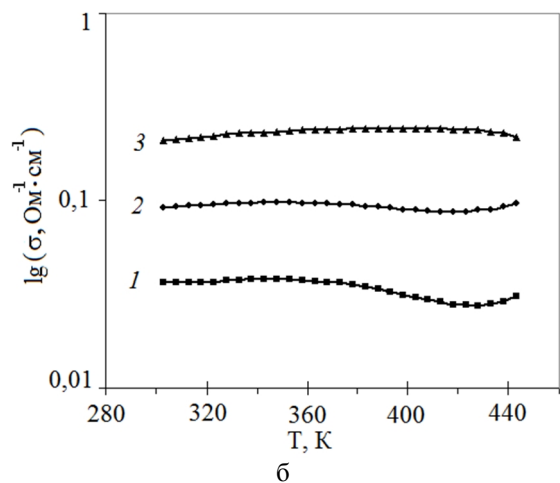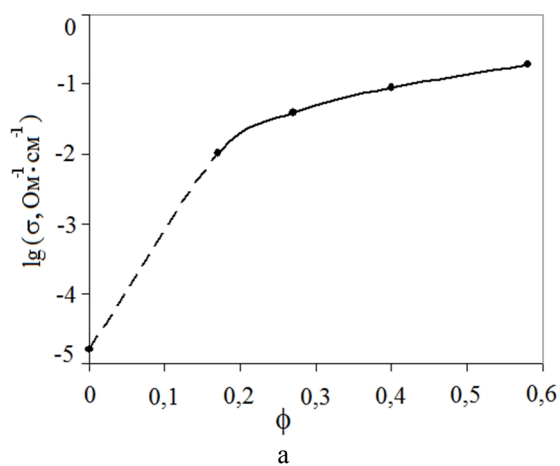
volume [33].

Figure 6a shows the dependency of electrical conductivity of nanocoposites CuI/Fe$_3$O$_4$ from volumetric content of copper iodide. You can see that CuI makes the major contribution to electrical conductivity of composites. The increase in σ values of samples from the content of copper iodide is not monotonous. These suggest the threshold nature of conductivity. Namely, two areas are clearly visible:
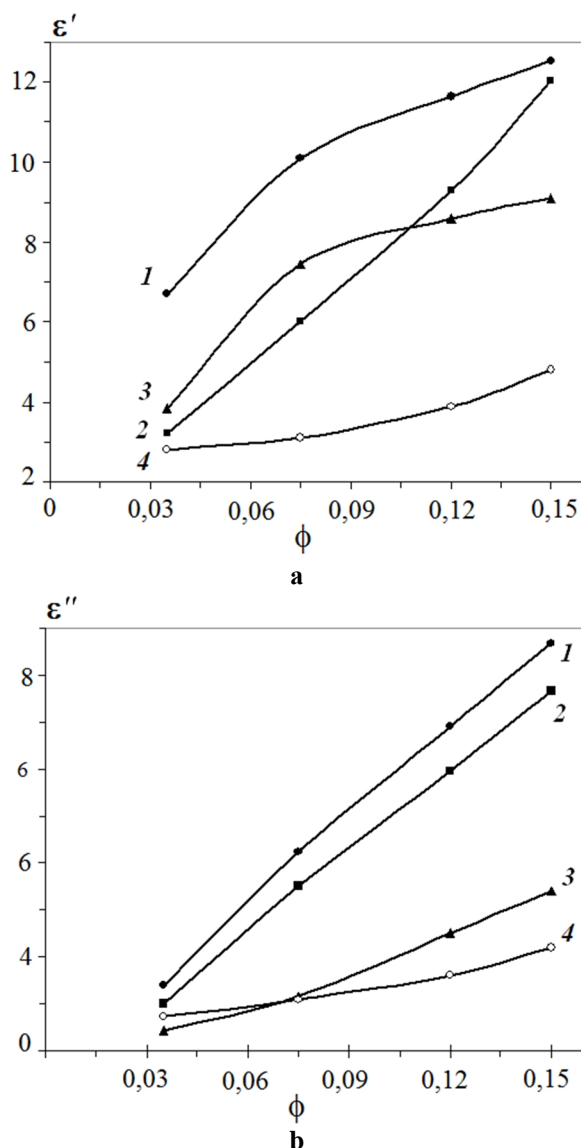
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**Fig. 7.** Dependence of $\varepsilon'$ (*a*) and $\varepsilon''$ (*b*) at a frequency of 9 GHz polymer nanocomposites by volume content ($\phi$) of copper iodide in systems: *1* – 0,27CuI/Fe$_3$O$_4$–PCTFE; *2* – 0,4CuI/Fe$_3$O$_4$–PCTFE; *3* – 0,58CuI/Fe$_3$O$_4$–PCTFE; *4* – CuI–PCTFE.

abrupt increase of $\sigma$ values with the increase of volumetric content CuI ($\phi < 0.17$) up to the percolation threshold and more monotonous increase of conductivity at the area of increase of copper iodide concentration ($\phi > 0.17$) above of percolation threshold. The study of temperature dependencies of electrical conductivity of CuI/Fe$_3$O$_4$ composites at different content of copper iodide (figure 6 *б*) show that the increase in CuI content ($\phi$) results in the increase the conductivity that reaches maximum values at $\phi = 0.58$. It should be mentioned that electrical conductivity changes insignificantly with the increase of temperature however the samples (curve 1 and 2) show insignificant changes of electrical conductivity, which is provably explained by the change in electronic state of conductive phase on the surface of magnetite under these technological conditions of CuI/Fe$_3$O$_4$ synthesis. This is expressed by the availability of metallic type of surface electrical conductivity, which

is caused by the defects of crystal structure on the surface of CuI nanoparticles. Due to metallic type of conductivity in adjacent layers, the optimal concentration of CuI on Fe$_3$O$_4$ surface may be the value that is a bit higher than percolation threshold. The size of crystals of copper iodide increases insignificantly when the value of effective surface interaction increases.

The results of electrophysical studies have determined optimal concentrations of copper iodide in CuI/Fe$_3$O$_4$ system ($0.2 < \phi < 0.58$), at which maximum values of component of complex permittivity and electrical conductivity were observed. The modification of the surface of magnetite with copper iodide results in the increase of $\varepsilon'$ and $\varepsilon''$ in high frequency range of polymer composites (CuI/Fe$_3$O$_4$–PCTFE) against the system that doesn't contain modified components (CuI–PCTFE) (figure 7). This effect is conditioned by the specifics of the structuration of CuI/Fe$_3$O$_4$ particles in polymer matrix and the effect of adjacent polymer layers on electrophysical properties of obtained composites. Abrupt change of $\varepsilon'$ and $\varepsilon''$ values in concentration dependencies is observed at lower content of CuI ($> 0.4$) in three-component systems (figure 7) since Fe$_3$O$_4$ particles coated with clusters of copper iodide creates separated clusters in polymer at lower concentration. This probability will reduce the quantity of conductive components in polymer composites by more than two times while saving the same electrophysical indexes due to optimal distribution of electrical conductive component in composites. As to the systems above the increase of electrical conductivity at low frequencies (figure 8) is observed. The adding of CuI/Fe$_3$O$_4$ to polychlorotrifluoroethylene results in the increase of the values of electrical conductivity almost by two times. Percolation threshold decrease was also observed in low concentration area when the concentration of copper iodide was up to 0.4. Insignificant reduction $\sigma$ values upon the increase of CuI content up to 0.58 on Fe$_3$O$_4$ surface. These concentration dependencies are associated with the change in size of cooper iodine particles or
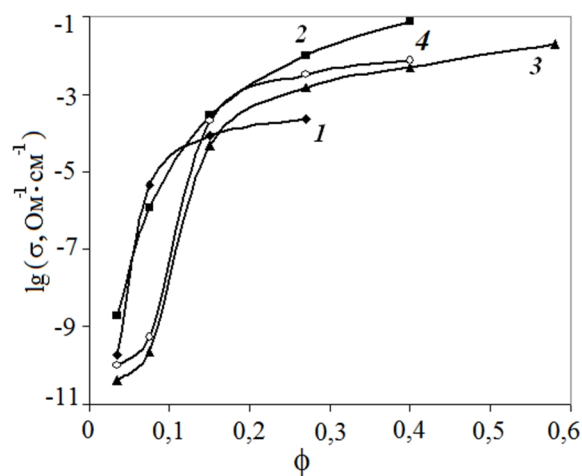


**Fig. 8.** Dependence of the logarithm of conductivity ($\sigma$) at a frequency of 100 Hz by volume content of copper iodide of systems CuI/Fe$_3$O$_4$– PCTFE with a volume content of copper iodide: *1* – 0.27; *2* – 0.4; *3* – 0.58; та *4* – CuI– PCTFE.

structure of their clusters on the surface of magnetite.

## Conclusions

We have synthesized nanocoposites based on nanosized magnetite with copper iodide settled on its surface and determined optimal content of CuI (~ 0.4), at which ε', ε" and σ have maximum values due to optimal distribution of CuI particles on $Fe_3O_4$ surface and creation of maximum surface of interface interaction. Results of electronic microscopic study have disclosed that modified nanoparticles $CuI/Fe_3O_4$ have spherical shape and its size is equal to approximately 12 nm. We have determined the effect of the shell of copper iodide located on the surface of magnetite on effective magnetic surface anisotropy magnetite that manifest itself in the increase of coercive force with the increase of copper iodine in $CuI/Fe_3O_4$ composites.

It was shown that the most efficient interaction of electromagnetic irradiation within ultra-high frequency range take place with components of the system $0.4CuI/Fe_3O_4$–PCTFE in comparison with the system that does not contain modified components.

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# Синтез, електричні та магнітні властивості композитів йодид міді/магнетит–поліхлортрифторетилен

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Досліджено структурні, магнітні, електрофізичні властивості композитів на основі нанорозмірного магнетиту хімічно модифікованого йодидом міді та поліхлортрифторетилена в інтервалі температур 298 - 450 К і концентрацій CuI від 0 до 0,58 об'ємних часток. Встановлено оптимальний об'ємний вміст йодиду міді (~ 0,4) в композитах $CuI/Fe_3O_4$, при якому максимально проявляється міжфазна взаємодія та електрофізичні, магнітні параметри набувають максимальних значень. Значення коерцитивної сили нанокомпозитів $CuI/Fe_3O_4$ збільшуються із зростанням вмісту йодиду міді. Показано, що полімерні композити, до складу яких входить $CuI/Fe_3O_4$, мають вищі значення дійсної та уявної складових комплексної діелектричної проникності та електропровідності в порівнянні з системою, яка містить тільки йодид міді.

**Ключові слова**: магнетит, йодид міді, нанокомпозити, питома намагніченість, міжфазна взаємодія.