

Effect of the type of reducing agents of copper ions in interpolyelectrolyte-metal complexes on the structure and properties of copper-containing nanocomposites

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The structural features, thermomechanical and electrical properties of copper-containing polymer nanocomposites formed by chemical reduction of copper ions in interpolyelectrolyte-metal complexes like pectin-Cu²⁺-polyethyleneimine with the use of various reducing agents (sodium borohydride, hydrazine, and ascorbic acid) are investigated. X-ray diffraction analysis reveals that the use of NaBH₄ and C₆H₈O₆ reducing agents results in formation of nanocomposites with Cu/Cu₂O "core-shell" nanoparticles, while when using N₂H₄ as a reductant, nanocomposites with only metallic copper nanoparticles are formed. Thermo-mechanical analysis shows that the reduction process becomes more efficient with increasing in the molar ratio of (NaBH₄ or C₆H₈O₆):Cu²⁺ from 2 to 6, whereas, in the case of N₂H₄, complete reduction occurs already at a molar ratio of N₂H₄:Cu²⁺ = 2. Copper-containing nanocomposites formed by NaBH₄ and N₂H₄ are established to exhibit semiconductor properties, whereas the initial interpolyelectrolyte complexes and nanocomposites prepared with C₆H₈O₆ are typical dielectrics.

Keywords: interpolyelectrolyte complexes, interpolyelectrolyte-metal complexes, copper-containing nanocomposite, structure, properties.

Исследованы особенности структуры, термомеханические и электрические свойства медьсодержащих полимерных нанокомпозитов, сформированных методом химического восстановления ионов меди в интерполиэлектролит-металлических комплексах пектин-Cu²⁺-полиэтиленимин с использованием различных восстановителей (боргидрида натрия, гидразина, аскорбиновой кислоты). Методом рентгеноструктурного анализа выявлено, что при использовании восстановителей NaBH₄ и C₆H₈O₆ формируются нанокомпозиты с наночастицами типа "ядро-оболочка" Cu/Cu₂O, тогда как при использовании восстановителя N₂H₄ формируются нанокомпозиты с наночастицами только металлической меди. Методом термомеханического анализа установлено, что восстановление происходит эффективнее при увеличении мольного соотношения (NaBH₄ или C₆H₈O₆):Cu²⁺ от 2 до 6 тогда как при применении N₂H₄ полное восстановление происходит уже при молярном соотношении (N₂H₄:Cu²⁺) = 2. Установлено, что медьсодержащие нанокомпозиты, сформированные с использованием NaBH₄ и N₂H₄, проявляют полупроводниковые свойства, тогда как выходной интерполиэлектролитный комплекс нанокомпозит, полученный с использованием восстановителя C₆H₈O₆, являются типичными диэлектриками.

Вплив типу відновлювача іонів міді в інтерполіелектроліт-металевих комплексах на структуру і властивості медьсодержащих наноконкомпозитів. В.Л.Демченко, С.Рябов, В.І.Штомпель, С.М.Кобилінський, Л.А.Гончаренко

Досліджено особливості структури, термомеханічні та електричні властивості мідьвмісних полімерних наноконкомпозитів, сформованих методом хімічного відновлення іонів міді в інтерполіелектроліт-металевих комплексах пектин- Cu^{2+} -поліетиленімін з використанням різних відновників (борогідриду натрію, гідразину, аскорбінової кислоти). Методом рентгеноструктурного аналізу виявлено, що при використанні відновників NaBH_4 і $\text{C}_6\text{H}_8\text{O}_6$ формуються наноконкомпозити з наночастинками типу "ядро-оболонка" $\text{Cu}/\text{Cu}_2\text{O}$, тоді як при використанні відновника N_2H_4 формуються наноконкомпозити з наночастинками тільки металеві міді. Методом термомеханічного аналізу встановлено, що відновлення відбувається ефективніше при збільшенні мольного співвідношення (NaBH_4 або $\text{C}_6\text{H}_8\text{O}_6$): Cu^{2+} від 2 до 6; тоді як при застосуванні N_2H_4 повне відновлення відбувається вже при молярному співвідношенні (N_2H_4 : Cu^{2+}) = 2. Встановлено, що мідьвмісні наноконкомпозити, сформовані з використанням NaBH_4 і N_2H_4 , проявляють напівпровідникові властивості, тоді як вихідний інтерполіелектролітний комплекс та наноконкомпозит, отриманий з використанням відновника $\text{C}_6\text{H}_8\text{O}_6$, є типовими діелектриками.

1. Introduction

In the last years, interest in the study of polymer nanocomposites containing nanoparticles of various metals or their oxides has been rapidly increasing, due to their unique physical-chemical, physical-mechanical and biological properties [1–3]. The formation of metal-containing nanocomposites using high-molecular compounds is an actual direction of scientific research, which is associated with the wide possibilities of their practical application. Copper nanoparticles have interesting optical properties, high catalytic, antibacterial and fungicidal activity, and this causes interest in the design and preparation of metal-polymer and hybrid composites having a controlled structure and nano-size particles [4]. In the last decade, researches of such hybrid materials have been intensively developed [4–8], including the synthesis of Cu nanoparticles directly in polymer films [9–11]. When filling polymer matrices with copper nanoparticles, they acquire new extremely valuable properties and can be used for the design of catalytic systems, in optoelectronics, nano-photonics, as well as effective antibacterial and antiviral drugs in medicine, pharmacology, biochemistry [1–3]; therefore, fundamental investigations of their structure and properties are required.

So, the aim of this work was to study the structural features, thermomechanical and electrical properties of polymer films based on interpolyelectrolyte complexes and copper nanoparticles obtained by chemical reduction of copper ions in interpolyelectrolyte-metal complexes using various reducing agents.

2. Experimental

To obtain the interpolyelectrolyte complexes (IPEC) the following reagents were used: anionic polyelectrolyte citrus pectin (Cargill Deutschland GmbH, Germany) with $M = 3 \cdot 10^4$, cationic polyelectrolyte anhydrous branched polyethyleneimine (PEI) (Aldrich) with $M_n = 1 \cdot 10^4$, $M_w = 2.5 \cdot 10^4$.

IPEC samples were formed by mixing of 5 % aqueous solutions of pectin and PEI taken at a molar ratio of 1:1, at $T = 20 \pm 2^\circ\text{C}$. IPEC as films were prepared by pouring onto PTFE plates and drying up to constant masses at the same temperature. The dry IPEC films were washed in distilled water until neutral and repeatedly dried at the same temperature to constant weight. The resulting films were 100 μm thick.

Samples of interpolyelectrolyte-metal complexes (IMC) were prepared by immersion of IPEC films into an aqueous solution of CuSO_4 with a concentration of 0.1 mol/L at $T = 20 \pm 2^\circ\text{C}$ for 24 h. The colorless IPEC films became dark blue.

The sorption capacities of films, A (mmol/g), were calculated through the formula:

$$A = (c_{in} - c_{eq})V/m, \quad (1)$$

where m is the mass of the sorbent, V is the solution volume, and c_{in} and c_{eq} are the initial and the equilibrium concentrations of copper ions. For the IMC films $A = 2.9$ mmol/g.

Chemical reduction of Cu^{2+} ions in the bulk of IMC occurred using the following reducing agents: sodium borohydride NaBH_4 , hydrazine N_2H_4 and ascorbic acid $\text{C}_6\text{H}_8\text{O}_6$ in an aqueous medium for 3 hours at $T = 60 \pm 2^\circ\text{C}$; the molar ratios of [reducing

agent]:[Cu²⁺] = 2 and 6 were used. The concentration of reducing agents in aqueous solutions was 0.1 mol/l. As a result of the copper reduction, the IPEC films with copper complexes changed color from blue to dark brown with a metallic sheen. All the samples after reduction were washed with alcohol and dried at room temperature to a constant weight.

The structural features of copper-containing nanocomposites were studied by wide-angle X-ray diffraction on a DRON-4-07 diffractometer using an X-ray optical scheme in the transmission mode. The X-ray diffraction measurements were performed at $T = 20 \pm 2^\circ\text{C}$ in a Ni-filtered CuK $_{\alpha}$ -radiation.

Thermomechanical studies of polymer systems were carried out using the penetration method in the mode of a uniaxial constant load ($\sigma = 0.5$ MPa) on a UIP-70M device. Linear heating of samples was performed at a rate of $2.5^\circ\text{C}/\text{min}$ in the temperature range from 20 to 350°C .

The frequency dependence of the real part of the complex ac conductivity of a polymer system, $\sigma_{ac}(f)$, was determined by the method of dielectric spectroscopy using an R5083 ac bridge [10]; $\sigma_{ac}(f)$ was estimated from the relationship $\sigma_{ac}(f) = 2\pi f \epsilon'(f) \text{tg} \delta \epsilon_0$, where f is the frequency, $\epsilon'(f) = C(f)/C_0$ is the frequency dependence of the polymer permittivity, C is the capacitance of the measuring capacitor with a sample, C_0 is capacitance of a capacitor filled with air, and $\epsilon_0 = 8.85 \cdot 10^{-12}$ F/m is the electric constant. Measurements were performed in the frequency range of 10^2 – 10^5 Hz and temperature range of 20– 100°C .

3. Results and discussion

Analysis of wide-angle X-ray diffraction patterns showed that the IPEC, which is formed by equimolar amounts of the anionic and cationic polyelectrolytes, is characterized by short-range ordering during translation of fragments of oppositely charged polyelectrolyte macromolecular chains in space. This fact is indicated by the appearance of one diffuse diffraction maximum at $2\theta_m \approx 20.8$ deg on the X-ray diffraction pattern of the IPEC sample (Fig. 1, curve 1). The average value of the period of the short-range ordering of fragments of complementary macromolecular chains of oppositely charged polyelectrolytes in the IPEC (the Bragg distance between the macromolecule chains of anionic and cationic polyelectro-

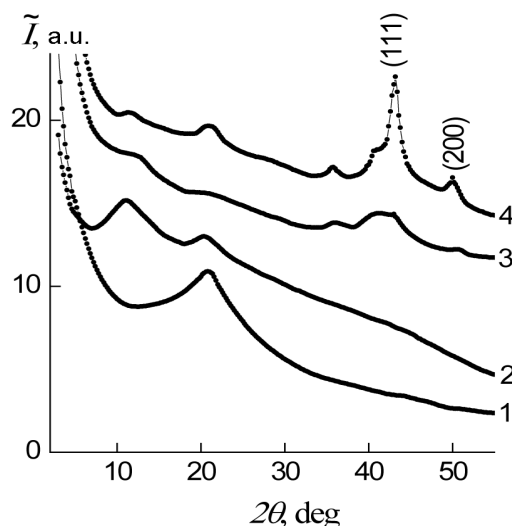


Fig. 1. Wide-angle X-ray diffraction patterns of IPEC (1); IMC (2) and copper-containing nanocomposites obtained by chemical reduction of copper ions using sodium borohydride at different molar ratios $[\text{BH}_4^-]:[\text{Cu}^{2+}] = 2$ (3) and 6 (4).

lytes in the IPEC) is 4.3 \AA according to the Bragg equation

$$d = \lambda(2\sin\theta_m)^{-1},$$

where λ is the wavelength of the characteristic X-ray radiation ($\lambda = 1.54 \text{ \AA}$ for CuK $_{\alpha}$ -radiation).

However, the sorption of CuSO $_4$ by the initial IPEC sample and formation of the IPEC-Cu $^{2+}$ IMC is accompanied by a change in the diffraction pattern: appearance of an intense diffuse diffraction maximum at $2\theta_m \approx 11.2$ deg (curve 2) in the presence of a low-intensity amorphous halo, which, unlike that for the initial IPEC, has an angular position at $2\theta_m \approx 20.4$ deg ($d \approx 4.4 \text{ \AA}$). This diffraction maximum characterizes the existence of metal complexes between the central ions (Cu $^{2+}$) and ligands, which are nitrogen atoms of the PEI amino groups and carbonyl oxygen atoms of pectin. In accordance with the angular position of this diffraction peak on the X-ray diffraction pattern of the IMC, the average Bragg distance d between the macromolecule chains of polyelectrolytes coordinated with Cu $^{2+}$ ions is 7.9 \AA .

After chemical reduction of Cu $^{2+}$ ions in the IMC bulk by sodium borohydride (molar ratio of $[\text{BH}_4^-]/[\text{Cu}^{2+}] = 2$) with formation of nanocomposite based on IPEC and Cu $_2\text{O}$, the intensity of the diffraction maximum

decreases (Fig. 1, curve 3) with its slight shift to the larger 2θ angles from 11.2 deg to 12.4 deg; this indicates the existence of interpolyelectrolyte-metal complexes and, accordingly, a decrease in the average value of the distance between the layers of macromolecules coordinated by Cu^{2+} ions, from 7.9 Å to 7.1 Å.

The appearance of four diffraction maxima at $2\theta_m \approx 30.0$ deg and 41.4 deg, according to [10], indicates the formation of Cu_2O nanoparticles in the IPEC bulk, and the maxima at $2\theta_m \approx 43.1$ deg and 50.8 deg characterize the metal phase Cu concentrated inside the Cu_2O nanoparticles. An increase in the amount of reducing agent (molar ratio $[\text{BH}_4^-]/[\text{Cu}^{2+}] = 6$) leads to a weakening of the intensity of the diffraction maximum at $2\theta_m \approx 11.5$ deg in X-ray diffraction patterns of nanocomposites based on IPEC and Cu_2O (curve 4); this indicates the existence of inter-polyelectrolyte-metal complexes in the IPEC volume. The intensity of two diffraction maxima at $2\theta_m \approx 43.1$ deg and 50.0 deg, which characterize the Cu structure, also increases. In our work [10], using X-ray diffraction analysis, we found that the structure of the Cu metal phase is completely manifested at the molar ratio of $\text{BH}_4^-/\text{Cu}^{2+} = 6$, which is optimal for the formation of copper-containing nanocomposites.

When ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) is used as the reducing agent, a slightly different diffraction pattern is observed (Fig. 2). At the molar ratio of $[\text{C}_6\text{H}_8\text{O}_6]/[\text{Cu}^{2+}] = 2$, the nanocomposite is formed on the basis of IPEC and Cu_2O . This is evidenced by two diffraction maxima at $2\theta_m \approx 29.4$ deg and 36.2 deg, which characterize the structure of Cu_2O , and two diffraction maxima at $2\theta_m \approx 43.2$ deg and 50.3 deg characteristic of the Cu structure (curve 3). The absence of the diffraction maximum at $2\theta_m \approx 11.2$ deg relevant to the structure of interpolyelectrolyte-metal complexes indicates the complete reduction of Cu^{2+} ions in the Cu/ Cu_2O nanoparticles. A shift in the halo of the amorphous IPEC structure from 20.8 to 22.6 deg is observed, and, accordingly, a decrease from 4.3 to 3.9 Å in the average Bragg distance between layers of macromolecules of oppositely charged PE. At the molar ratio of $[\text{C}_6\text{H}_8\text{O}_6]/[\text{Cu}^{2+}] = 6$, the intensity of the diffraction maxima of the Cu structure at 43.2 deg and 50.3 deg strongly increases, the maximum at $2\theta_m \approx 29.4$ deg is absent and the maximum of the Cu_2O structure at $2\theta_m \approx 36.2$ deg

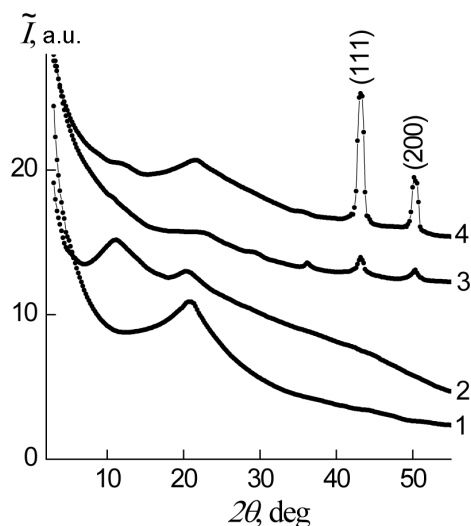


Fig. 2. Wide-angle X-ray diffraction patterns of IPEC (1); IMC (2) and copper-containing nanocomposites obtained by chemical reduction of copper ions with ascorbic acid at different molar ratios $[\text{C}_6\text{H}_8\text{O}_6]/[\text{Cu}^{2+}] = 2$ (3) and 6 (4).

weakens (curve 4). The angular position of the amorphous IPEC halo is $2\theta_m \approx 21.5$ deg (4.1 Å). That is, with an increase in the amount of reducing agent, the average Bragg distance between layers of oppositely charged PE macromolecules increases from 3.9 Å to 4.1 Å. The diffraction maximum at $2\theta_m \approx 12.2$ deg observed on the diffraction pattern of this nanocomposite is probably due to the formation of complexes between ascorbic acid and polyethyleneimine.

When hydrazine (N_2H_4) is used as a reducing agent of Cu^{2+} ions, copper-containing nanocomposites containing Cu nanoparticles are formed at molar ratios of $[\text{N}_2\text{H}_4]/[\text{Cu}^{2+}] = 2$ and 6 (Fig. 3). This is evidenced by the presence of two diffraction maxima at $2\theta_m \approx 43.1$ deg and 50.2 deg on the X-ray diffraction patterns; these characterize the structure of metallic copper (curves 3, 4). Similarly to the case of ascorbic acid, when hydrazine is used, the angular position $2\theta_m$ of the amorphous IPEC halo changes in the sequence: ≈ 20.8 deg (IPEC) $\rightarrow \approx 22.8$ deg (IPEC-Cu, molar ratio is 2) $\rightarrow \approx 20.8$ deg (IPEC-Cu, molar ratio is = 6). In this case, the average Bragg distance between the layers of macromolecules of oppositely charged PE varies in the sequence 4.3 Å \rightarrow 3.9 Å \rightarrow 4.3 Å, respectively. That is, when the amount of reducing agent increases, this distance also increases.

Along with the study of the structural organization of IPEC, IMC and copper-containing nanocomposites, studies of their thermomechanical behavior were carried out. Analysis of the thermomechanical curve of the initial IPEC (see Fig. 4a, curve 1) shows that glass transition and viscous-flow occur in the temperature ranges 25–145°C and 265–350°C, respectively. Furthermore, in the range of 150–245°C, there is a transition that is likely due to the melting of pectin crystallites in the IPEC [10]. During the melting of the crystalline phase of pectin in IPEC, a sharp change in deformation occurs. However, the introduction of CuSO_4 into the initial IPEC, which causes the IMC formation, is accompanied by the appearance of a transition at 205°C on the thermomechanical curve; the phenomenon is probably related to the melting of CuSO_4 in the IPEC. This leads to the transition of the polymer to the viscous-flow state (see Fig. 4a, curve 2). Therefore, the analysis of the thermomechanical curve of IMC indicates that in the temperature range from 170 to 205°C (see Fig. 4a, curve 2) the following sequential processes occur in the IMC sample: interpolyelectrolyte-metal complexes are destroyed, then the salt (CuSO_4) transfers from its ionic form to crystalline and then melts.

The analysis of thermomechanical curves of IPEC-Cu/ Cu_2O nanocomposites obtained by reduction of Cu^{2+} ions in IMC using NaBH_4 at different molar ratios of reducing agent : metal ion shows that at the molar ratio of $\text{BH}_4^-/\text{Cu}^{2+} = 2$, the reduction does not completely occur (Fig. 4b, curve 1). This is indicated by the corresponding temperature transitions in the temperature range 190–210°C, associated with the destruction of IMC, the transition of the salt from the ionic form to the crystalline form and its melting. The shape of the ther-

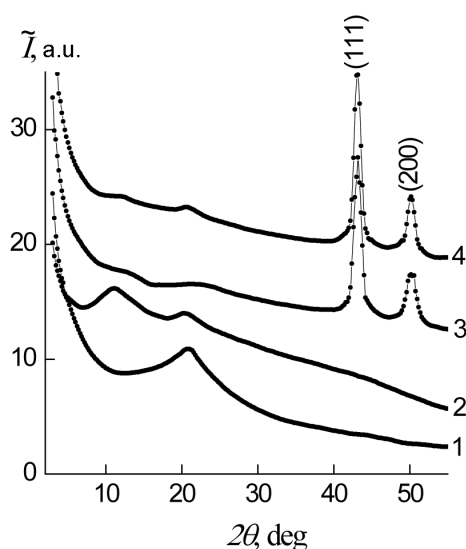


Fig. 3. Wide-angle X-ray diffraction patterns of IPEC (1); IMC (2) and copper-containing nanocomposites obtained by chemical reduction of copper ions with hydrazine at different molar ratios $[\text{N}_2\text{H}_4]:[\text{Cu}^{2+}] = 2$ (3) and 6 (4).

mechanical curve of the IPEC-Cu/ Cu_2O nanocomposite obtained at the molar ratio of $\text{BH}_4^-/\text{Cu}^{2+} = 6$ indicates a complete reduction of copper ions in IMC (curve 2) [1, 10].

When ascorbic acid is used as the reducing agent, and the molar ratio of $[\text{C}_6\text{H}_8\text{O}_6]/[\text{Cu}^{2+}]$ increases from 2 to 6, the reduction is more effective, but also not complete (Fig. 4c); this is confirmed by temperature transitions in the temperature range 155–210°C associated with crystallization and melting of the CuSO_4 salt.

From the analysis of thermomechanical curves of the copper-containing nanocomposites obtained during the reduction of copper ions in IMC by hydrazine, it is seen that the complete reduction occurs already at the MC molar ratio ($\text{N}_2\text{H}_4/\text{Cu}^{2+}$) = 2. This is evi-

Table 1. Temperature transitions of copper-containing nanocomposites

Sample	T_g , °C	T_f , °C
IPEC	53	319
IPEC- CuSO_4	57	205
IPEC-Cu/ Cu_2O (molar ratio $[\text{BH}_4^-]:[\text{Cu}^{2+}] = 2$)	58.5	224
IPEC-Cu/ Cu_2O (molar ratio $[\text{BH}_4^-]:[\text{Cu}^{2+}] = 6$)	54.8	287
IPEC-Cu/ Cu_2O (molar ratio $[\text{C}_6\text{H}_8\text{O}_6]:[\text{Cu}^{2+}] = 2$)	62.3	200
IPEC-Cu/ Cu_2O (molar ratio $[\text{C}_6\text{H}_8\text{O}_6]:[\text{Cu}^{2+}] = 6$)	52.4	239
IPEC-Cu (molar ratio $[\text{N}_2\text{H}_4]:[\text{Cu}^{2+}] = 2$)	55.9	290
IPEC-Cu (molar ratio $[\text{N}_2\text{H}_4]:[\text{Cu}^{2+}] = 6$)	58.9	319

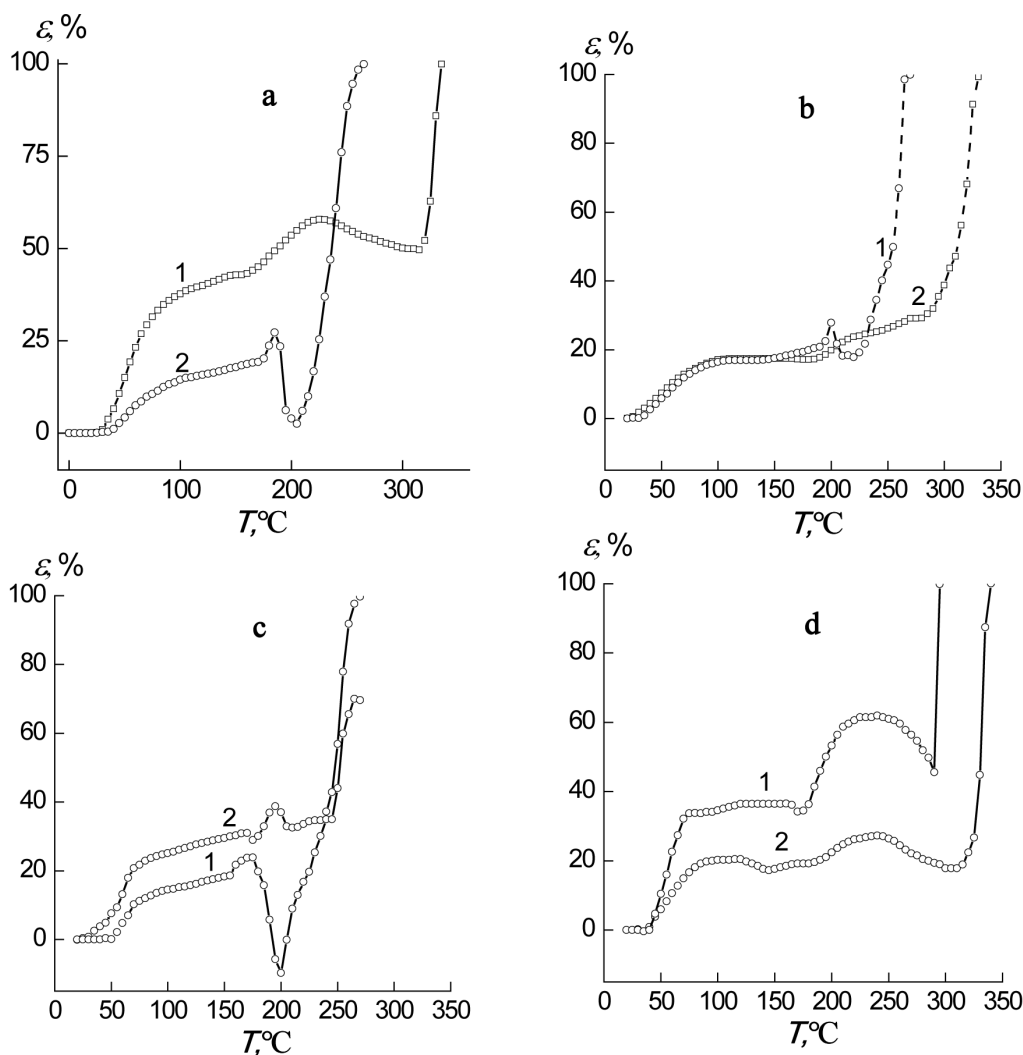


Fig. 4. Thermomechanical curves (a) of IPEC (1); IMC (2); and copper-containing nanocomposites prepared using different reducing agents at different molar ratios (b) $[\text{BH}_4^-]:[\text{Cu}^{2+}] = 2$ (1) and 6 (2); (c) $[\text{C}_6\text{H}_8\text{O}_6]:[\text{Cu}^{2+}] = 2$ (1) and 6 (2); (d) $[\text{N}_2\text{H}_4]:[\text{Cu}^{2+}] = 2$ (1) and 6 (2).

denced by the absence of temperature transitions associated with the crystallization and melting of copper sulfate (Fig. 4d). In addition, the curves of this type of nanocomposites show intense temperature transitions in the temperature range 120–260°C associated with the melting of pectin in the IPEC (curves 1, 2).

The analysis of thermomechanical curves of the obtained IPEC, IMC and nanocomposites IPEC-Cu/Cu₂O (or Cu) (Fig. 4) shows that the transition from IPEC to IMC and copper-containing nanocomposites leads to an increase in the glass transition temperature T_g (Table 1).

An increase in the amount of NaBH₄ or C₆H₈O₆ reducing agent decreases T_g of nanocomposites; this is explained by a decrease in the number of interpolyelectro-

lyte-metal complexes involving Cu²⁺ ions and functional groups of pectin and PEI as well as the formation of a larger number of nanoparticles. Conversely, an increase in the amount of N₂H₄ reducing agent leads to an increase in T_g of the nanocomposite due to the complete reduction of copper already at the molar ratio $[\text{C}_6\text{H}_8\text{O}_6]:[\text{Cu}^{2+}] = 2$. In addition, the temperature of transition to the viscous state T_f for all nanocomposites obtained with various reducing agents increases with increasing molar ratios [reducing agent] : $[\text{Cu}^{2+}]$ from 2 to 6.

The analysis of the frequency dependence of the real part of the complex conductivity $\sigma_{ac}(f)$ at alternating current for the studied samples shows that the IPEC and nanocomposites formed with ascorbic acid as the reductants of copper ions in IMC are dielectrics. The

Table 2. Conductivity of IPEC and copper-containing nanocomposite samples at different temperatures ($f = 1$ kHz)

Sample	σ_{ac} , S/cm					
	20°C	40°C	50°C	60°C	80°C	100°C
IPEC	$3.12 \cdot 10^{-10}$	$1.10 \cdot 10^{-9}$	$1.39 \cdot 10^{-8}$	$2.56 \cdot 10^{-8}$	$2.95 \cdot 10^{-7}$	$1.40 \cdot 10^{-6}$
IPEC-Cu (NaBH ₄)	$1.77 \cdot 10^{-8}$	$4.85 \cdot 10^{-8}$	$4.52 \cdot 10^{-8}$	$1.04 \cdot 10^{-7}$	$2.32 \cdot 10^{-7}$	$1.05 \cdot 10^{-6}$
IPEC-Cu (N ₂ H ₄)	$5.39 \cdot 10^{-9}$	$1.01 \cdot 10^{-7}$	$8.97 \cdot 10^{-8}$	$1.04 \cdot 10^{-7}$	$2.25 \cdot 10^{-7}$	$3.05 \cdot 10^{-7}$

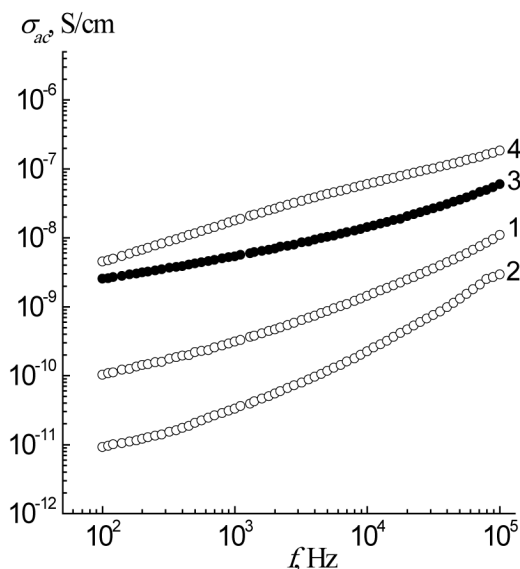


Fig. 5. Frequency dependences of the real part of complex conductivity $\sigma_{ac}(f)$ at $T = 20 \pm 2^\circ\text{C}$ for samples of IPEC (1); and nanocomposite obtained by the chemical reduction of Cu^{2+} ions in the IMC at molar ratios [reducing agent]/ $[\text{Cu}^{2+}] = 6$ using ascorbic acid (2), hydrazine (3) and sodium borohydride (4) as reductants.

copper-containing nanocomposites, in which the reductants of copper ions were sodium borohydride and hydrazine, exhibit semiconductor properties. It was found that for the initial IPEC, with an increase in temperature from 20°C to 100°C , the electrical conductivity increases by 4 orders of magnitude, whereas for all types of copper-containing nanocomposites in the same temperature range, the electrical conductivity increases within two orders of magnitude.

4. Conclusions

The influence of the type of a reducing agent for copper ions in interpolyelectrolyte-metal complexes on the structure and properties of the developed copper-contain-

ing nanocomposites was studied by wide-angle X-ray scattering, thermomechanical analysis and dielectric spectroscopy. It was shown that applying of hydrazine results in the complete reduction of copper ions with the formation of Cu nanoparticles in polymer films, but, at the same time, when using sodium borohydride or ascorbic acid, reduction process of Cu^{2+} is not completed, which leads to the formation of Cu/Cu₂O nanoparticles. It was established that the structure of the metal Cu phase manifests itself when the molar ratio (NaBH₄ or C₆H₈O₆) : Cu^{2+} increases from 2 to 6; whereas when using N₂H₄ as a reducing agent, the structural manifestation of Cu is observed already for the molar ratio 2. It was found that the copper-containing nanocomposites formed with borohydride and hydrazine exhibit semiconductor properties, while the nanocomposite obtained on the base of ascorbic acid is a typical dielectric.

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