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## PROPERTIES OF TRIPLE POLYELECTROLYTE-METAL SYSTEMS

*The authors have made investigations of the properties of triple polyelectrolyte-metal systems, including oxide nanoparticles Cuprum and Nickel. The regularities of thermomechanical features of experimental samples were determined. Also X-ray analysis as an example of polyelectrolyte system  $\text{Cu}^{2+}$  was made. Physical and chemical analysis of the systems by infrared spectroscopy (IR) was made. It is found, that versus PEC, PEMC– $\text{Me}^{2+}$  and nanocomposites are characterized by microheterogeneous structure, here with the transition from PEMC– $\text{Me}^{2+}$  to nanocomposites is followed, it is about nanoparticles  $\text{Cu}_2\text{O}$ , by decreasing of effective size  $l_p$  of the heterogeneity microfields from 11 to 6 nm, and when it is about nanoparticles  $\text{Ni}^0$  – from 37 to 35 nm. The change of the profile  $l_p$  by transition from PEMC to nanocomposites erodes completely with the decrease of  $T_g$ . It is known by data of thermomechanical analysis.*

**Keywords:** *nanocomposites polymer systems, properties of triple polyelectrolyte-metal systems, IR-spectral analysis.*

Recently scientists began to pay more and more attention to the polymer nanocomposites which fillers are nanoscale particles of different metals or their oxides. As rule, metal nanoparticles are ultrafine and they are in the polymeric matrix, that's why they have specific features (high level of hardness, semi- and full conductance, high chemical activity). They are effective catalysts in chemical and photochemical processes, that's why appear new opportunities for their practical use [1; 2]. Furthermore exists also possibility to use polymer nanocomposites for getting medical and biological remedies [3; 4].

General statements for the synthesis and research of nanocomposites involving nanoparticles of metals or their oxides, which are dispersed in a polymer matrix, are known and described in modern monographs [2; 3]. Especially, scientists

distinguish among the main methods of getting nanocomposites by graining techniques with further introduction of them into the polymer matrix and the recovery of metal ions in the polymer matrix. The last one was used by us in this work. It should be mentioned that nevertheless of the existence of a large number of published works on triple polymer-metallic systems, today almost no investigations of the processes of their structure formation.

Thereby the goal was the research of micro-heterogeneous structure and thermomechanical features of triple polyelectrolyte-metal complexes (PEMC), which are received by using contrarily charged polyelectrolytes (pectin and poly etylenimin) and ions of transitional metals  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$  and obtained on their base nanocomposites.

Researchers used weak polyelectrolytes (PE) for obtaining output weak polyelectrolytes' complexes (PEC):

5 anion PE – citrus' pectin produced by Cargill Deutschland GmbH (Germany),  $M_n = 3000$ – $300000$ .

6 cation PE – ramified (waterless) polyethyleneimine (PEI) produced by Aldrich,  $M_n = 10000$ ,  $M_w = 25000$ .

PEC formation in molar relation (MR) of anion and cation PE is 1:1, was made by mixing 5% aqueous solution of pectin and PEI by  $T = 22 \pm 2$  °C. Protonizing of PEI amides by pectin carboxyl groups ends with production intermolecular ions groups, and so PEC. These PEC liquids were poured out on polytetrafluor in ethylenic disk and were dried by  $T = 22 \pm 2$  °C to constant weight.

The films PEMC were obtained by sorption of PEC ions' films of transitional metals from aqueous solution of their salts. Experimentally it was made by placing the PEC films in aqueous salt' solution  $\text{CuSO}_4$  or  $\text{NiSO}_4$ , which concentration was  $6 \cdot 10^{-2}$  mole/l. Herewith PEMC films became coloured, what is the feature for conformable in complex bounded metals: for  $\text{Cu}^{2+}$ – dark blue, and for  $\text{Ni}^{2+}$ – bright violet, while output PEC films were uncoloured.

Chemical ions' recovery of transitional metals was made by adding  $\text{NaBH}_4$  with alkaline elements – in compound of solvents water- isopropanol during 40 minutes by  $T = 22 \pm 2$  °C. As result of recovery, PEC films, which contained cations  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$ , gained dark brown colour, which, in conformation with work [5], is result of creation of nanocomposites on base PEC and nanoparticles  $\text{Cu}_2\text{O}$  or  $\text{Ni}^0$  accordingly.

PEC and PEMC identification (type  $\text{PEC-Me}^{2+}$ ) and conformational nanocomposites were made by method IR-Fourier spectroscopy (FTIR) by using IR-spectrometer Tensor 37 Bruker.

Micro-heterogeneous structure was investigated by method acute angled dispersing of X-rays with using KPM-1, supported with slot collimator of the primary ray bundle, what is made by method Kratki. Geometric data of KPM-1 obeyed infinite height of primary ray bundle as researchable example [6]. Profiles of intensity were fixed on the dispersed volume magnitude and decrease factor of primary ray bundle by researchable polymer example.

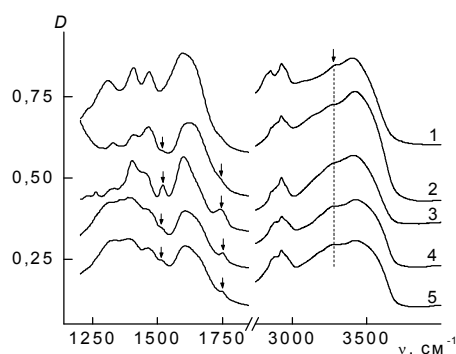
All X-rayed investigations were made by  $\text{CuK}_\alpha$ – radiation, monochromatised by Ni-filter and by  $T = 22 \pm 2$  °C.

Commensuration of nanoparticles and their apportionment in polymer matrix were researched by transmission electric microscope JEM-1230 (JEOL, Japan) with resolution 0,2 nm.

Thermomechanical investigations of polymer systems examples were made by method penetration in monoaxial constant loading mode  $\sigma = 0.5$  (TMAQ400 EMTA Instruments). Linear heating of examples was performed with velocity 5 grad/min. Investigations were fulfilled in temperature interval -100 to 200°C.

By comparison examples of IR-Fourier spectrum (fig. 1) as output PEC with equimolar correlation anion and cation polyelectrolytes, as so by PEMC type  $\text{PEC-Me}^{2+}$  and nanocomposites is determined, that in all spectra is absorption zone by  $\nu = 3280 \text{ cm}^{-1}$  (broken curve). This zone, according to works [7; 8], affirms existence electrostatic interaction between anions ( $-\text{COO}^-$ ) of intermolecular ions groups PEC and protons of amides, which are in macromolecular chains of cation PE. But insertion of cations  $\text{Cu}^{2+}$  to this output PEC with further formation  $\text{PEC-Cu}^{2+}$  causes appearance in IR-Fourier spectrum two weeny absorption zones by  $\nu = 1521$  and  $1742 \text{ cm}^{-1}$ .

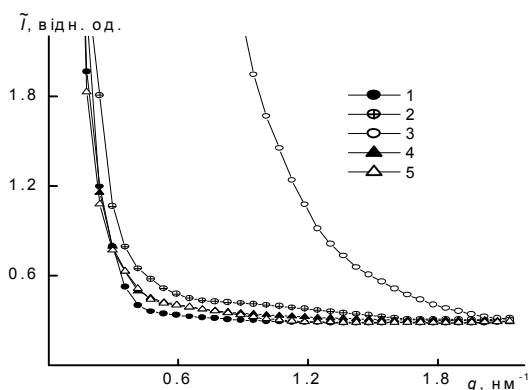
These etwozones become more intensively (in fig.1 they are indicated with cursors) after recovery copperions with formation in PEC volume nanoparticles  $\text{Cu}_2\text{O}$ , that, maybe, is caused by formation hydrogen connections between atoms of oxygen these nanoparticles and protons of amides cations PE. Accordingly, these two intensively zones identify transformations  $\text{PEC-Cu}^{2+}$  innanocomposite, what have nanoparticles  $\text{Cu}_2\text{O}$ .



**Fig. 1. IR-Fourier output PEC spectra (1), PEMC  $\text{PEC-Cu}^{2+}$  (2), nanocomposite  $\text{PEC-Cu}_2\text{O}$  (3), PEMC  $\text{PEC-Ni}^{2+}$  (4), nanocomposite  $\text{PEC-Ni}^0$  (5)**

That fact attracts attention, that insertion of cations  $\text{Ni}^{2+}$  in PEC volume and formation in sinter molecular space PEMC type PEC- $\text{Ni}^{2+}$  caused also appearance of two absorption zones by  $\nu = 1516$  и  $1750 \text{ cm}^{-1}$  (on the fig. 1 they are indicated with cursors), but after nickel ions recovery with formation, accordingly to work [5], metal  $\text{Ni}^0$  nanoparticles, intensity of these two zones decreases slightly. It is caused by the absence of interaction between nanoparticles of this type and polar groups in macrochains of the anion' and cation' polyelectrolytes, which form PEC.

Analyzing the x-rays acute angled dispersion profiles of the investigated polymer systems, which were displayed as subordination graphs  $\tilde{I}$  from  $q$  (fig. 2),  $\text{cos}^3 \tilde{I}$  from  $s^3$  (Ruland graphs) [9, 10], where  $\tilde{I}$  – dispersing intensity without adding collimational correction, and  $q = (4\pi/\lambda)\sin\theta = 2\pi s$ , was determined, that with the exception output PEC, all they are characterized by microheterogeneous structure, in other words contrast existence of electric density  $\Delta\rho$  ( $\Delta\rho = \rho - \langle\rho\rangle$ , where  $\rho$ ,  $\langle\rho\rangle$  – local and mean value of electric density).



**Fig. 2. Intensity profiles of x-rays acute angled dispersing PEC (1), PEMC PEC- $\text{Cu}^{2+}$  (2), nanocomposite PEC- $\text{Cu}_2\text{O}$  (3), PEMC PEC- $\text{Ni}^{2+}$  (4), nanocomposite PEC- $\text{Ni}^0$  (5)**

It means, that involume as PEMC type PEC- $\text{Me}^{2+}$  so nanocomposites based on PEC and  $\text{Cu}_2\text{O}$  or  $\text{Ni}^0$  are round two microfields types of heterogeneity with different value of local electric density  $\rho$ . Notable, that PEC- $\text{Cu}^{2+}$ , an especially nanocomposite PEC- $\text{Cu}_2\text{O}$  have more

higher dispersing intensity, and soelectric contrast of the density  $\Delta\rho$  (curves 2, 3), in comparison with polymer systems PEC- $\text{Ni}^{2+}$  and PEC- $\text{Ni}^0$  accordingly (curves 4, 5). It is caused higher PEC ability for sorbtion of the cations  $\text{Cu}^{2+}$ , and so for formation of their complexes, versus cations  $\text{Ni}^{2+}$  [5]. At once, absence of the appearance of the interferential max in all intensity profiles indicates on stochastic character of the location of the heterogeneity microfields of different types.

Assessment of effective size (value order) of the heterogeneity microfields, which are in volume PEMC type PEC- $\text{Me}^{2+}$  and received from them nanocomposites, was made by Ruland' and Perret' methods and by determination of such kind of structure profile as range of in homogeneity  $l_p$  that is directly bound with averaged diameter of microfields of inhomogeneity ( $\langle l_1 \rangle$ ,  $\langle l_2 \rangle$ ) in diphasic system:

$$l_p = \varphi_2 \langle l_1 \rangle = \varphi_1 \langle l_2 \rangle,$$

where  $\varphi_1$ ,  $\varphi_2$  – microfields volume fraction ( $\varphi_1 + \varphi_2 = 1$ ). As a result of calculation the parameter  $l_p$  is found that the polymer system PEC- $\text{Cu}^{2+}$  and PEC- $\text{Cu}_2\text{O}$  have much smaller effective size of the microfields of heterogeneity than the PEC- $\text{Ni}^{2+}$  and PEC- $\text{Ni}^0$ . At the same time, the transition from PEC- $\text{Cu}^{2+}$  to nanocomposites PEC- $\text{Cu}_2\text{O}$  is followed by decrease almost twice the effective size microfields heterogeneity, while the transition from PEC- $\text{Ni}^{2+}$  to nanocomposites PEC- $\text{Ni}^0$  only leads to a slight decrease in  $l_p$  (chart).

By comparison of the thermomechanical curves of the output PEC, PEMC type PEC- $\text{Cu}^{2+}$  and nanocomposite PEC- (fig. 3) is found, that by transition from PEC to PEC- $\text{Cu}^{2+}$  and to nanocomposite essentially decreases the temperature of the structural glassing  $T_g$  (chart). Also the decrease of the temperature is observed by transition to rubberlike condition ( $T_{h-el}$ ) in row PEC > PEC- $\text{Cu}^{2+}$  > PEC- $\text{Cu}_2\text{O}$ . At the same time the display of transition of the examples PEC and PEC- $\text{Cu}^{2+}$  in viscoflowed condition is happened by the same temperature ( $T_{v-f} \sim 190^\circ\text{C}$ ). But by transition to nanocomposite PEC- $\text{Cu}_2\text{O}$  is fixed decrease of temperature of displaying the process of the transition to viscoflowed condition ( $T_{v-f} = 180^\circ\text{C}$ ).

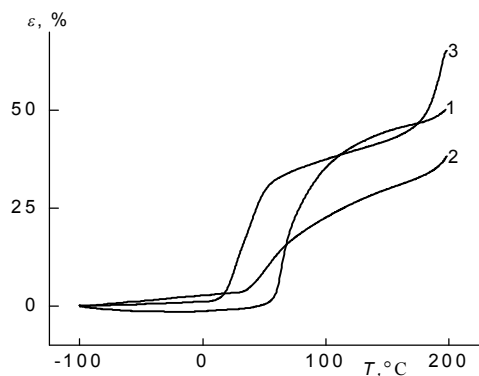


Fig. 3. Thermomechanical PEC curves (1), PEMC PEC-Cu<sup>2+</sup> (2) and nanocomposite PEC-Cu<sub>2</sub>O (3)

In return, transition from PEC to PEC-Ni<sup>2+</sup> and nanocomposite PEC-Ni<sup>0</sup> is followed also by decrease of  $T_g$ , but more less than by transition to polymer systems PEC-Cu<sup>2+</sup> and PEC-Cu<sub>2</sub>O. At the same time, herewith increase  $T_{h-el}$  from 86°C (PEC) to 87°C (PEC-Ni<sup>2+</sup>) and 95°C (PEC-Ni<sup>0</sup>) (tbl 1). At the same time, absence on the thermomechanical curves the transition in viscoflowed condition of the examples PEMC and PEC-Ni<sup>2+</sup> and also nanocomposite PEC-Ni<sup>0</sup> affirms higher heat-resistance of these polymer systems in comparison to their analogs (PEC-Cu<sup>2+</sup> and PEC-Cu<sub>2</sub>O).

Table 1

Some structural profiles  
of investigated polymer systems

Example	$l_p$ , nm	$T_g$ , °C	$T_{h-el}$ , °C
PEC	–	57	86
PEC-Cu <sup>2+</sup>	11	37	74
PEC-Cu <sub>2</sub> O	6	17	53
PEC-Ni <sup>2+</sup>	37	43	87
PEC-Ni <sup>0</sup>	35	39	95

Researches affirm that the transition from PEC to PEMC-Me<sup>2+</sup> is followed by appearance in IR-spectra two absorption zones: on the interval 1516-1521 cm<sup>-1</sup> and 1742-1750 cm<sup>-1</sup>, moreover the transition from PEMC-Cu<sup>2+</sup> to nanocomposite PEC-Cu<sub>2</sub>O causes considerable increase of their intensity, and to nanocomposite PEC-Ni<sup>0</sup>—only inconsiderable decrease.

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