

Modification of Polyamide (PA) Films by Layers of Mixed Copper Sulfides–Copper Tellurides

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A polyamide film if treated with the sodium telluropentathionate, $\text{Na}_2\text{TeS}_4\text{O}_6$, solution in hydrochloric acid, absorbs tellurium and sulfur in the form of telluropentathionate anion. The concentration of tellurium in PA film is higher, when polymer is treated with chalcogenation solution of higher concentration. Further interaction of chalcogenized PA films with Cu(I–II) salts solution leads to the formation of mixed copper chalcogenide layers on the polymer surface. Number of phases of copper chalcogenides were identified in the layers formed depending on the conditions of polyamide chalcogenation: *orthorhombic anilite*, Cu_7S_4 (72–617), *hexagonal copper(I) telluride*, Cu_2Te (40–1325), *monoclinic djurleite*, $\text{Cu}_{1.9375}\text{S}$ (71–1383), *orthorhombic copper sulfide*, $\text{Cu}_{1.8}\text{S}$ (75–2241), *hexagonal copper(I) telluride*, Cu_2Te (40–1325), *orthorhombic copper(II) telluride*, CuTe (13–258), and two *tetragonal copper tellurides*, $\text{Cu}_{3.18}\text{Te}_2$ (43–1402) and $\text{Cu}_{2.72}\text{Te}_2$ (43–1401). The sheet resistance of the layers formed depends on their chemical and phase composition, and varies from $4.39 \cdot 10^{-3}$ to $3.31 \text{ k}\Omega/\square$.

Keywords: telluropentathionate, polyamide, sorption-diffusion, copper sulfide layers, copper telluride layers.

INTRODUCTION

New composites materials with different combinations of properties are rapidly gaining importance in emerging fields of nanotechnology. Polymers modified by thin films of binary copper chalcogenides on their surface represent those new materials with important electroconductive or semiconductive properties [1] and continue to report fascinating application in established areas such as solar radiation control [6], photovoltaic devices [5], sensitive elements for gas sensors [4], IR polaroids [3]; absorption of radio waves [2].

Polyamide (PA) as semi hydrophilic polymer is capable of adsorbing ions of various electrolytes from aqueous solutions [7]. This fact enabled us to introduce the anions of simplest polythionates, $\text{S}_n\text{O}_6^{2-}$ ($n = 3 - 5$), [8, 9], and ions of selenotrithionate, $\text{SeS}_2\text{O}_6^{2-}$, [10] from aqueous solutions into PA surface matrix. After treating such polythionic ions containing polymer films with Cu(I–II) salts water solutions Cu_xS_y and Cu_xSe_y , layers of various electrical conductivity and composition can be obtained on their surface depending on experimental conditions [11, 12]. The aqueous solutions of potassium selenopentathionate, $\text{K}_2\text{SeS}_4\text{O}_6$, were applied to obtain mixed copper sulfides–copper selenides layers on the PA surface by using sorption-diffusion method [13]. However, the formation of layers of copper tellurides or mixed layers of copper sulfides–copper tellurides on the polymers surface weren't reported.

The purpose of the present work was to obtain the thin layers of copper tellurides or mixed – copper sulfides–copper tellurides on the surface of PA employing the acidified solutions of sodium telluropentathionate by sorption–diffusion method and to investigate their phase composition and electrical properties.

EXPERIMENTAL

A PA film PK–4 of 70 μm thickness was used. Prior to the experiments pieces of the film of 15 – 70 mm in size were boiled in distilled water for two hours to remove the remainder of the monomer. Then they were dried with filter paper and left in desiccator over CaCl_2 for 24 h.

The salt of sodium telluropentathionate, $\text{Na}_2\text{TeS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, was prepared according to the published procedures [14].

The samples of PA were added to a solution of sodium telluropentathionate of different concentration in the 25 cm^3 test tube. At certain time intervals, samples were removed, rinsed carefully with distilled water. After the chalcogenised samples of PA were dried for 24 hours in the dessicator over CaCl_2 they were stored in it for the subsequent experiments.

The kinetics of the $\text{TeS}_4\text{O}_6^{2-}$ ions sorption-diffusion into PA was studied by the changes of sorbed Te concentration in the polymer. The concentration of sulfur in PA was determined nephelometrically as described in [15]. The amount of tellurium and copper in a PA sample was determined using an atomic absorption spectrometer “Perkin–Elmer 503” [16].

The kinetics of telluropentathionate ions sorption-diffusion into PA studied at the temperatures of -1 and 20°C from the $0.01 - 0.1 \text{ mol}\cdot\text{dm}^{-3}$ solutions of $\text{Na}_2\text{TeS}_4\text{O}_6$ in hydrochloric acid ($0.2 \text{ mol}\cdot\text{dm}^{-3}$). Chalcogenized samples of PA later have been treated for 10 min at 80°C in $0.4 \text{ mol}\cdot\text{dm}^{-3}$ solution of copper sulfate with an addition of 1% of hydroquinone as a reducing agent. The composition of this solution irrespective on the temperature is $0.34 \text{ mol}\cdot\text{dm}^{-3}$ of Cu(II) and $0.06 \text{ mol}\cdot\text{dm}^{-3}$ of Cu(I) ions [17].

The resistance to constant current of Cu_xS_y – Cu_xTe_y layers with different composition was measured on an E7-8 numerical measuring device with special electrodes.

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The phase composition of the layers was investigated by means of X-ray diffraction using a DRON-6 diffractometer (radiation Cu- K_{α}).

ANALYSIS AND RESULTS

It is known [18, 19] that the concentration of sorbed-diffused into PA polythionic compounds anions increases with the increase of polythionic compound solution concentration, temperature and with decrease of pH value. But the significant increase of the polythionic compound solution concentration and temperature causes the faster decomposition of the polythionate ions. At the same time, the increase in H^+ ions concentration causes the amorphization of the PA structure [20] and enables more easy diffusion of polythionate ions into it. The low value of solution pH may cause the destruction of PA sample. Therefore we were looking for the optimal conditions when the maximum concentration of sorbed-diffused into PA $TeS_4O_6^{2-}$ ions and relative stability of these ions in solution is achieved.

First we selected the concentration of HCl for dissolution of $Na_2TeS_4O_6$ salt. The samples of PA were 3 h treated in the $0.1 \text{ mol}\cdot\text{dm}^{-3}$ $Na_2TeS_4O_6$ solution in 0.1 and $0.2 \text{ mol}\cdot\text{dm}^{-3}$ HCl at 20°C . It was determined that the influence of the acidity of $Na_2TeS_4O_6$ solution on the PA chalcogenation is noticeable at the beginning of the experiment and later the concentrations of diffused into PA tellurium became similar. For example, the sorbed-diffused Te concentrations in PA samples kept 0.5 h in $Na_2TeS_4O_6$ solutions in 0.1 and $0.2 \text{ mol}\cdot\text{dm}^{-3}$ HCl were 1.67 and $2.51 \text{ mg}\cdot\text{g}^{-1}$ respectively, and on the end of experiment (after 3 h) – 6.08 and $6.10 \text{ mg}\cdot\text{g}^{-1}$ respectively. It is known [21], that the concentration of H^+ ions increases the stability of $TeS_4O_6^{2-}$ ions, and, by the way, the solution of $0.2 \text{ mol}\cdot\text{dm}^{-3}$ HCl are used for the synthesis of $Na_2TeS_4O_6$. Therefore in further experiments the $Na_2TeS_4O_6$ solutions in $0.2 \text{ mol}\cdot\text{dm}^{-3}$ HCl were used for the PA chalcogenation.

We have determined that the decomposition of $Na_2TeS_4O_6$ $0.1 \text{ mol}\cdot\text{dm}^{-3}$ solution at 30°C begins during 15 min (its colour changes from light yellow to light green and after the beginning of elemental tellurium liberation appears the colour of moss). Therefore, to exclude the decomposition of $TeS_4O_6^{2-}$ ions, the influence of the temperature of the $Na_2TeS_4O_6$ solution of this concentration was studied at the temperatures of -1 and 20°C . From the data presented in the Figure 1 follow, that the higher concentration of tellurium is found in PA kept in the solution of $Na_2TeS_4O_6$ at higher temperature (curve 1), but the difference in Te concentration diminishes with time. For example, in the PA samples 1 h chalcogenized at different temperatures, the concentrations of sorbed-diffused tellurium approximately are 0.64 and $2.1 \text{ mg}\cdot\text{g}^{-1}$, i. e. the concentration of Te in PA chalcogenized at 20°C is ~ 3.3 times higher than in the solution of lower temperature. This difference after the 3 h chalcogenation reduces to 2.6 times and the concentrations of Te are 2.34 and $6.2 \text{ mg}\cdot\text{g}^{-1}$ respectively. In addition, the decomposition of $Na_2TeS_4O_6$ solution at 20°C begins after 1 h, but at -1°C temperature solution remains unchanged during all experiment.

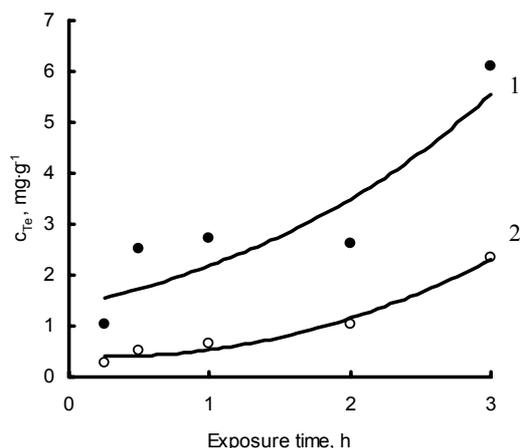


Fig. 1. Changes of tellurium concentration in PA with time during its treatment with the acidified ($HCl, c = 0.2 \text{ mol}\cdot\text{dm}^{-3}$) $0.1 \text{ mol}\cdot\text{dm}^{-3}$ solution of $Na_2TeS_4O_6$ at different temperatures. Temperature, $^\circ\text{C}$: 1 – 20 (\bullet), 2 – -1 (\circ)

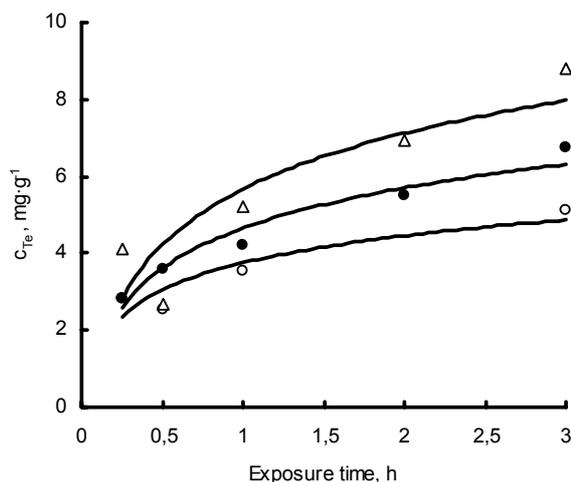


Fig. 2. Changes of tellurium concentration in PA with time during its treatment with the acidified ($HCl, c = 0.2 \text{ mol}\cdot\text{dm}^{-3}$) $Na_2TeS_4O_6$ solution of different concentration at 20°C . Concentration of $Na_2TeS_4O_6$ solution, $\text{mol}\cdot\text{dm}^{-3}$: 1 – 0.01 (\circ), 2 – 0.025 (\bullet), 3 – 0.05 (Δ)

In further experiments, looking for the higher concentrations of sorbed-diffused $TeS_4O_6^{2-}$ ions and, as sequence – more thick layers of copper chalcogenides, our choice was the temperature of 20°C at which the solution of $Na_2TeS_4O_6$ is less stable but the degree of PA chalcogenation reached is higher.

It is known [22], that the stability of sodium selenopentathionate, $Na_2SeS_4O_6$, solution increases with diminishing of its concentration. Since the structure and origin of the $TeS_4O_6^{2-}$ and of $SeS_4O_6^{2-}$ ions are similar, it was likely that the reduction of $Na_2TeS_4O_6$ solution concentration will result in the increase of its stability. As expected, the decomposition of $0.1 \text{ mol}\cdot\text{dm}^{-3}$ $Na_2TeS_4O_6$ solution after reduction of its concentration to $0.05 \text{ mol}\cdot\text{dm}^{-3}$ started only after 2.5 h, and after reduction

by 4 and 10 times (until 0.025 and 0.01 mol·dm⁻³ respectively) the solutions remains transparent during all experiments. Therefore, the experiments of Na₂TeS₄O₆ solution concentration influence on the PA chalcogenation effectiveness were done with 0.05, 0.025 and 0.01 mol·dm⁻³ solutions. It was determined that the concentration of Te in PA samples increases with the increase of chalcogenation solution concentration and the duration of treatment (Fig. 2, curves 1 – 3).

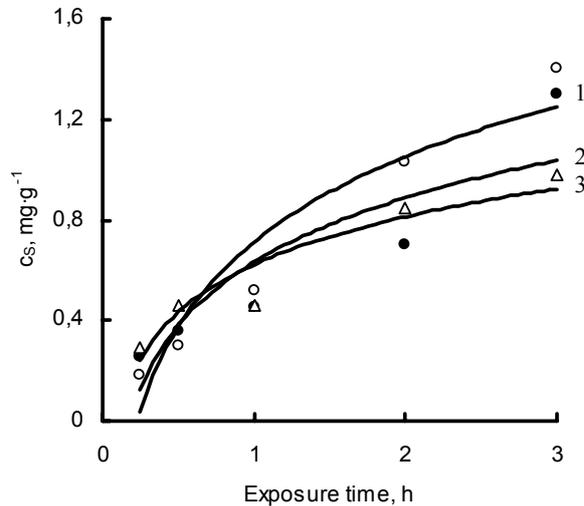


Fig. 3. Changes of sulfur concentration in PA with time during its treatment with the acidified (HCl, $c = 0.2 \text{ mol}\cdot\text{dm}^{-3}$) Na₂TeS₄O₆ solution of different concentrations at 20 °C. Concentration of Na₂TeS₄O₆ solution, mol·dm⁻³: 1 – 0.01 (○), 2 – 0.025 (●), 3 – 0.05 (Δ)

The concentration of sulfur in PA (in controversy to concentration of Te) increases with the reduction of telluropentathionate solution concentration (Fig. 3, curves 1 – 3). This phenomenon is related to the stability of TeS₄O₆²⁻ ions. With its decrease, more ions of TeS₄O₆²⁻ decomposes according to the equation



SO₂ formed is washed out from the polymer and the concentration of sulfur decreases. Decomposition of sorbed-diffused into PA TeS₄O₆²⁻ ions reflects the values of molar ratios Te:S determined in it. For example, the value of Te:S in PA after it was kept 15 min in 0.01 mol·dm⁻³ Na₂TeS₄O₆ solution is ~1 : 4.0, and after the exposure time of 30 min – ~1 : 2.6, and on the end of the experiment – 1 : 1.6.

Table 1. Dependence of electrical resistance of copper sulfide–copper telluride layers on PA on initial concentration of Na₂TeS₄O₆ solution and exposure time of chalcogenation

Exposure time of chalcogenization, h	The initial concentration of Na ₂ TeS ₄ O ₆ , mol·dm ⁻³ (Sheet resistance, kΩ/□)		
	0.01	0.025	0.05
0.15	3.36·10 ³	4.39·10 ³	2.31·10 ³
0.30	2.53·10 ³	3.43·10 ³	3.14·10 ³
1.00	2.25·10 ³	–	–
2.00	55.92	85.30	17.37
3.00	39.29	13.04	3.31

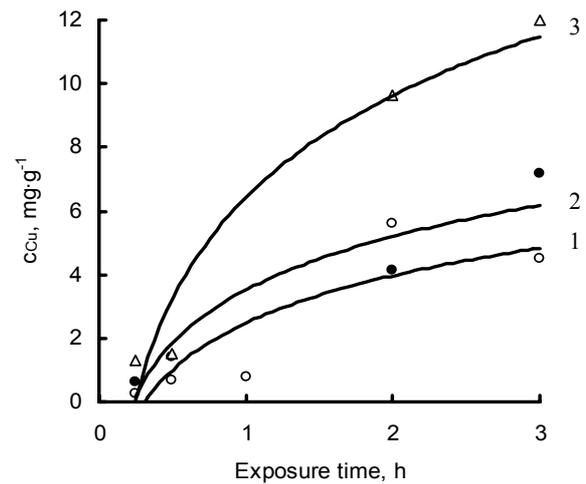


Fig. 4. Changes of copper concentration in PA with time after its treatment with the acidified (HCl, $c = 0.2 \text{ mol}\cdot\text{dm}^{-3}$) Na₂TeS₄O₆ solution of different concentration at 20 °C. Concentration of Na₂TeS₄O₆ solution, mol·dm⁻³: 1 – 0.01 (○), 2 – 0.025 (●), 3 – 0.05 (Δ)

Layers of copper sulfides-copper tellurides are formed on the surface of PA samples when the chalcogenized polymer is treated by the solution of Cu(I-II) salt. These layers are electrically conductive, the appearance of PA surface becomes significantly changed too. The chalcogenized PA samples initially yellow or slightly green become dark brown and acquire metallic reflectance. The concentration of copper in the copper sulfides-copper tellurides layers on PA increases with increase of the used for the chalcogenation Na₂TeS₄O₆ solution concentration and polymer treatment with this solution duration (Fig. 4, curves 1 – 3). The sheet resistance of copper chalcogenide layers decreases with the increase of copper concentration in the layer: its value changes from 4.39·10⁻³ to 3.31 kΩ/□ (Table 1.).

After the X-ray examination of formed on the surface of PA copper sulfide-copper telluride layers it was determined, that their composition becomes more complicated when the concentration of chalcogenation solution is increased. For example, in the layers formed after the 3 h exposition in 0.01 mol·dm⁻³ solution of Na₂TeS₄O₆ at 20 °C only two phases – *orthorhombic anilite*, Cu₇S₄ (72–617), (maxima at 2θ = 40.92 and 62.8°) and *hexagonal copper(I) telluride*, Cu₂Te (40–1325), (maxima at 2θ = 42.87°) (Fig. 5, curve 1) were identified.

On the PA sample chalcogenized at the same conditions in $0.025 \text{ mol}\cdot\text{dm}^{-3}$ $\text{Na}_2\text{TeS}_4\text{O}_6$ solution, mixed copper sulfide-copper telluride layer in addition two phases of *orthorhombic anilite*, Cu_7S_4 (72–617), (maxima at $2\theta = 40.92, 55.94$ and 62.8°) and of *hexagonal copper(I) telluride*, Cu_2Te (40–1325), (maxima at $2\theta = 63.5$ and 66.4°), contains two new phases: *monoclinic djurleite*, $\text{Cu}_{1.9375}\text{S}$ (71–1383), (maxima at $2\theta = 38.3^\circ$) and *tetragonal copper telluride*, $\text{Cu}_{2.72}\text{Te}_2$ (43–1401), (maxima at $2\theta = 37.2^\circ$) (Fig. 5, curve 2). After the twofold increase in concentration of $\text{Na}_2\text{TeS}_4\text{O}_6$ solution (until $0.05 \text{ mol}\cdot\text{dm}^{-3}$), six phases of copper chalcogenides on the surface of PA were detected: *orthorhombic anilite*, Cu_7S_4 (72–617), (maxima at $2\theta = 40.92^\circ$), *monoclinic djurleite*, $\text{Cu}_{1.9375}\text{S}$ (71–1383), (maxima at $2\theta = 38.3^\circ$), *orthorhombic copper sulfide*, $\text{Cu}_{1.8}\text{S}$ (75–2241), (maxima at $2\theta = 59.85^\circ$), *hexagonal copper(I) telluride*, Cu_2Te (40–1325), (maxima at $2\theta = 66.4^\circ$), *tetragonal copper telluride*, $\text{Cu}_{3.18}\text{Te}_2$ (43–1402), (maxima at $2\theta = 47.6^\circ$) and *orthorhombic copper(II) telluride*, CuTe (13–258), (maxima at $2\theta = 41.5$ and 58.3°) (Fig. 5, curve 3).

The increased number of phases and the intensity of its maxima reflects the increased concentration of copper sulfides and copper tellurides on the surface of PA. The decrease of electrical resistance of these layers may be explained not only by the increase of copper chalcogenide phases concentration, but by the qualitative its changes.

It is known that the resistance of Cu_xS after diminishing of the value x from 2 to 1, reduces by 1 billion times [23]. For example, the electrical resistance of mixed

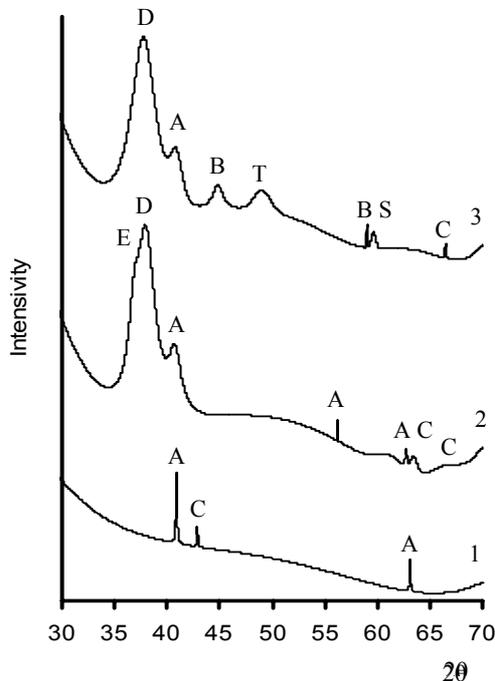


Fig. 5. X-ray diffraction patterns (A – Cu_7S_4 , D – $\text{Cu}_{1.9375}\text{S}$, S – $\text{Cu}_{1.8}\text{S}$, C – Cu_2Te , T – $\text{Cu}_{3.18}\text{Te}_2$, B – CuTe) of the PA tapes initially treated 3 h with the $\text{Na}_2\text{TeS}_4\text{O}_6$ solution of different concentration at 20°C and then with Cu(I–II) salt solution. The concentration of $\text{Na}_2\text{TeS}_4\text{O}_6$ solution, $\text{mol}\cdot\text{dm}^{-3}$: 1 – 0.01, 2 – 0.025, 3 – 0.05

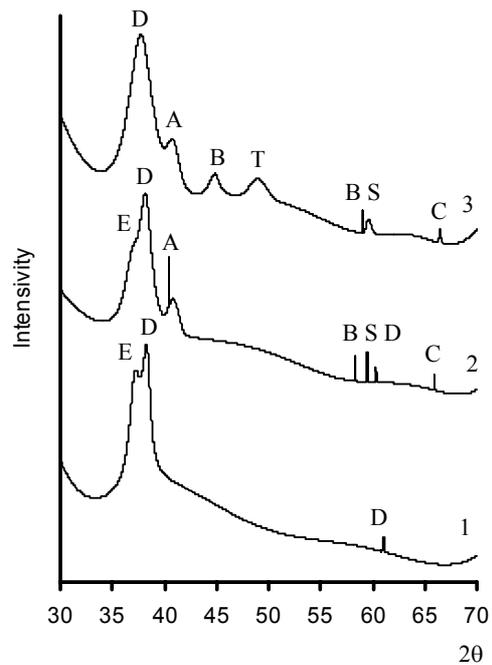


Fig. 6. X-ray diffraction patterns (A – Cu_7S_4 , D – $\text{Cu}_{1.9375}\text{S}$, S – $\text{Cu}_{1.8}\text{S}$, C – Cu_2Te , T – $\text{Cu}_{3.18}\text{Te}_2$, B – CuTe , E – $\text{Cu}_{2.72}\text{Te}_2$) of the PA tapes initially treated different time with the $0.05 \text{ mol}\cdot\text{dm}^{-3}$ solution of $\text{Na}_2\text{TeS}_4\text{O}_6$ at 20°C and then with Cu(I–II) salt solution. The exposure time, h: 1 – 0.5, 2 – 2, 3 – 3

copper chalcogenide layer composed of *orthorhombic anilite*, Cu_7S_4 (72–617), and *hexagonal copper(I) telluride*, Cu_2Te (40–1325), is about $40 \text{ k}\Omega/\square$, and of layers which contains copper tellurides – *tetragonal* $\text{Cu}_{2.72}\text{Te}_2$ (43–1401) or *orthorhombic* CuTe (13–258) and *tetragonal* $\text{Cu}_{3.18}\text{Te}_2$ (43–1402), – i.e. when the values of x are equal to one or approaches to 1 are smaller, about 13.0 and $3.3 \text{ k}\Omega/\square$ respectively.

Analogous changes of copper sulfide-copper telluride layers on PA phase composition and of electrical resistance are observed when the duration of the polymer treatment in the $0.05 \text{ mol}\cdot\text{dm}^{-3}$ solution of $\text{Na}_2\text{TeS}_4\text{O}_6$ is increased. For example, on the surface of PA 30 min treated in the solution of Cu(I–II) salt only two phases of copper chalcogenides were identified: *monoclinic djurleite*, $\text{Cu}_{1.9375}\text{S}$ (71–1383), (maxima at $2\theta = 38.3$ and 61.1°) and *tetragonal copper telluride*, $\text{Cu}_{2.72}\text{Te}_2$ (43–1401), (maxima at $2\theta = 37.2^\circ$) (Fig. 6, curve 1), and the sheet resistance – about $2.3 \cdot 10^{-3} \text{ k}\Omega/\square$. If the polymer in the solution of chalcogenation is treated 2 h, the mixed layer of copper chalcogenides is composed of six phases. Four more phases in addition to previously mentioned appears: of *orthorhombic anilite*, Cu_7S_4 (72–617), (maxima at $2\theta = 40.92^\circ$), *orthorhombic copper sulfide*, $\text{Cu}_{1.8}\text{S}$ (75–2241), (maxima at $2\theta = 59.85^\circ$), of *hexagonal copper(I) telluride*, Cu_2Te (40–1325), (maxima at $2\theta = 66.4^\circ$) and of *orthorhombic copper(II) telluride*, CuTe (13–258), (maxima at $2\theta = 58.3^\circ$) (Fig. 6, curve 2), and the value of sheet resistance of the layer reduces to $17.4 \text{ k}\Omega/\square$. Seven phases of copper chalcogenides on the surface of PA tapes

chalcogenized during 3 h were identified (Fig. 6, curve 3), the sheet resistance of the layer – 3.3 kΩ/□.

The results presented above shows that by the modification of PA with layers of mixed copper sulfides-copper tellurides when in the first stage the solutions of sodium telluropentathionate of different concentration are used, it is possible to form on the surface of the polymer electrically conductive layers of controlled chemical and phase composition.

CONCLUSIONS

1. Study of the kinetics of telluropentathionate ions sorption-diffusion into PA tapes showed, that if these tapes are treated in 0.01 – 0.1 mol·dm⁻³ acidified (HCl, $c = 0.1 \text{ mol}\cdot\text{dm}^{-3}$) solutions of Na₂TeS₄O₆ up to 3 h, the diffusion of telluropentathionate ions into PA is observed. The concentration of sorbed-diffused TeS₄O₆²⁻ ions in PA increases with the increase of Na₂TeS₄O₆ solution concentration, temperature and the duration.
2. When chalcogenized in telluropentathionate solution PA film is affected by the Cu(I–II) salt solution, mixed copper chalcogenide, Cu_xTe_y–Cu_xS_y, layers are formed on its surface.
3. The chemical and phase composition, and electrical conductivity of formed on PA copper chalcogenide layers may be very different and they depend on the concentration of Na₂TeS₄O₆ solution used for the PA chalcogenation and duration of chalcogenation. If the treatment in the Na₂TeS₄O₆ solution duration is short (~30 min) the copper chalcogenide layer is composed of *monoclinic djurleite*, Cu_{1.9375}S, and *tetragonal copper telluride*, Cu_{2.72}Te₂; when the relatively long chalcogenation period is used (~2 h) these layers in addition to mentioned four copper chalcogenide phases contains also *orthorhombic anilite*, Cu₇S₄, *orthorhombic copper sulfide*, Cu_{1.8}S, *hexagonal Cu₂Te* and *orthorhombic CuTe*.
4. By varying the conditions of an initial PA treatment in the solution of Na₂TeS₄O₆, mixed copper chalcogenide layers of different sheet resistance (4.39·10⁻³ – 3.31 kΩ/□) on the surface may be obtained. Conductivity of the layers depends both on the copper concentration in PA and on the phase composition of the chalcogenide layer formed.

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