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The Modification of Polyamide Tapes by the Conducting Copper Sulfide–Copper Selenide Layers

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The selenopentathionate anions are sorbed−diffused into a polyamide tapes if they are treated with the not acidified (or acidified) with hydrochloric acid solutions ($0.025 - 0.2$ mol·dm^{-3}, $30 - 50$ °C) of potassium selenopentathionate, $K_2SeS_4O_6$. The sorption–diffusion from the acidified solutions proceeds more intensive: the concentrations of diffused from the acidified solution selenium and sulfur are about 5 times higher compared with those reached using the non acidified solution of the same concentration and at the same temperature. The concentration of sorbed selenopentathionate ions increases with the increase of temperature and concentration of a $K_2SeS_4O_6$ solution, and the duration of treatment. The $SeS_4O_6^{2-}$ anions diffused into polyamide gradually decompose and the decomposition products – sulfate ions and SO_2 – are washed out from a polymer but elemental selenium remains in it. Therefore, the colour of polyamide tapes depending on a degree of $SeS_4O_6^{2-}$ ions decomposition changes from colourless to yellow, brown or red. The copper sulfide and copper selenide layers are formed in the surface of polyamide tape if the chalcogenized polymer is treated with the water solution of copper(II/I) salt: the anionic particles containing sulfur and selenium atoms of low oxidation state react with the copper ions. The conditions of a polymer initial chalcogenation (the concentration and temperature of $K_2SeS_4O_6$ solution) determine the amount of copper and the composition of chalcogenide layer: the amount of copper in the polyamide tape increases with the increase of concentration and temperature, and varies from $0.2 \cdot 10^{-2}$ to $33.5 \cdot 10^{-2}$ mg/cm^2. The results of X−ray structural analysis confirmed the formation of mixed copper sulfide−copper selenide layers in the surface of polyamide. The phase composition of layer changes depending on the duration of initial treatment in a $K_2SeS_4O_6$ solution: Cu_xS-Cu_ySe layers are composed of little conductive *chalcocite*, Cu_2S, electrically conductive *digenite*, $Cu_{1.8}S$, *djurleite*, $Cu_{1.9375}S$, *anilite*, $Cu_{1.75}S$, and of copper selenides – *bellidoite*, Cu_2Se, *umangite*, Cu_3Se_2, *klockmannite*, CuSe, *krutaite*, $CuSe_2$ and Cu_2Se_x. Therefore the phase composition determines the electrical characteristics of the layers: the sheet resistance may vary from 12.2 Ω/□ to 4.8 MΩ/□. The determination of layers composition (in depth to 1 nm) studied by the method of X–ray photoelectron spectroscopy confirmed the formation of copper sulfides and selenides of various phases. The regularities determined enable formation by sorption–diffusion method of mixed copper sulfide and copper selenide layers of desirable composition and electrical conductance using the selenopentathionate as a polyamide chalcogenation agent.

Keywords: selenopentathionate, polyamide, sorption–diffusion, copper sulfide layers, copper selenide layers.

INTRODUCTION

The polymeric materials are distinquished by a variety of properties, for example, they are elastic, light, environmentally resistant etc. The modification of polymers by formation in their surface of thin layers of compounds with important physical properties leads to obtaining of composites with different properties. The interest in Cu_xS and Cu_ySe thin films was previously focused mostly on their possible use in solar cells [1 – 5]. Chemically deposited CuS thin films have been found to posses near – ideal solar control characteristics: transmittance in the visible region of 20 – 50 %, low transmittance, 10 – 20 %, in the infrared region, low reflectance, < 10 %, in the visible region so as to avoid glare, and relatively higher reflectance, > 15 %, in the near–infrared region [6]. $Cu_{2-x}Se$ films are typically p-type, highly conducting semitransparent, semiconductors with band gap varying between 1.1 and 1.4 eV, suitable for solar energy conversion and as semitransparent layer in high speed detectors working in visible range [7, 8].

More recently their applications in solar control coatings for architectural and automobile glazings [9 – 11], in transparent and conductive coatings on glass, polymers, and as elastic thin film Cu sensor electrodes [12 – 14], in the production of electronic and optical devices, thermoelectric converters [15 – 17] were reported.

Various methods were used for the formation of copper sulfide and copper selenide layers on various dielectrics, and on the polymers too: vacuum evaporation [8, 18], activated reactive evaporation [19], spray pyrolysis [20], electroless deposition [21, 22], successive ionic layer adsorption and reaction (SILAR) [23, 24], chemical bath deposition [25 – 32]. Methods of copper sulfide coatings were reviewed in the works of [25 – 27, 29, 30, 32].

The sorption–diffusion methods for the formation of thin semiconductive and electrically conductive layers of copper sulfide and copper selenide in the surface of polyamide (PA), on the basis of gained during earlier decades experience in the chemistry of polythionates and selenopolythionates [33 – 35], during last years at the department of Inorganic chemistry of KTU were studied. Using these methods, a PA tape is first treated with the solution of polythionic acids, $H_2S_nO_6$ (n – an average number of sulfur atoms in the molecule), containing chains of divalent sulfur atoms in low oxidation state in the molecule $^{-}O_3S\text{–}S\text{–}S\text{–}......\text{–}S\text{–}S\text{–}SO_3^{-}$ [36] when looking for the formation of sulfide layers [37, 38]. When the goal is the formation of copper selenide layers in the surface of

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PA [39 – 41], the latter is treated with the solution of potassium selenotritionate, $K_2SeS_2O_6$, containing one divalent selenium atom of low oxidation state $^-O_3S–Se–SO_3^-$ [42] in the first stage of the process. But the formation of mixed copper sulfide–copper selenide layers in the surface of PA at the beginning of our studies in this direction [43] was not studied despite the similarity of sulfur and selenium atoms and their ability to replace each other in various molecules was obvious and could be illiustrated by the egzistence of relatively stable cycloocta $Se_{8–x}S_x$ molecules [44].

A mixed chain of three divalent chalcogen atoms $^-O_3S–S–Se–S–SO_3^-$ of low oxidation state is present in the anion of salts of monoselenopentathionic acid, $H_2SeS_4O_6$, [36, 45]. Thus it was reasonable to apply these compounds for the formation of mixed copper sulfide–copper selenide layers in the surface of PA tapes.

The aim of present work was to put in the whole and to discuss the results received by us during studies of selenopentathionate ions sorption–diffusion into PA process, also processess of mixed copper sulfide–copper selenide layers in the surface of PA tapes formation and the characterization of the copper chalcogenide layers obtained, since only separate fragments of these studies in our previous publications were described [46 – 49]. The chemical and phase composition of the $Cu_xS–Cu_ySe$ layers, their electrical conductance were studied by the methods of atomic absorption spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy (XPS), electron microscopy and by the measurements of electrical resistance.

EXPERIMENTAL

The layers of copper sulfide–copper selenide were deposited on a PA PK–4 (specification TY 6-05-1775-76) tape of 70 μm thickness. The samples 15 × 70 mm in size were used. Before the sulfuration, they were boiled in distilled water for 2 h to remove the remainder of the monomer. Then they were dried using filter paper and then over $CaCl_2$ for 24 h. Distilled water, reagents of the grades "especially pure", "chemically pure" and "analytically pure" were used in the experiments.

The salt of potassium selenopentathionate, $K_2SeS_4O_6 \cdot 1.5\,H_2O$, was prepared and chemically analyzed according to published procedures [50].

The samples of PA tape were chalcogenized in the 0.025, 0.05, 0.1 and 0.2 mol·dm^{-3} solutions of $K_2SeS_4O_6$ acidified with the addition of HCl (0.1 mol·dm^{-3} HCl, pH ~ 1,5) and without acid addition at the temperatures of 30, 40 and 50 °C. The total duration of experiments was 4.5 h.

For the formation of $Cu_xS–Cu_ySe$ layers the samples of chalcogenized PA were treated with a Cu(II/I) salt solution at the temperature of 78 °C. A Cu(II/I) salt solution was made from crystalline $CuSO_4 \cdot 5H_2O$ and a reducing agent hydroquinone [25]. It is a mixture of univalent and divalent copper salts, in which independent of temperature there is 0.34 mol/dm^3 Cu(II) salt and 0.06 mol/dm^3 Cu(I) salt [51]. After having been kept in $K_2SeS_4O_6$ solution, the sample was treated with a Cu(II/I) solution, then rinsed with distilled water, dried over $CaCl_2$ and used in consequent experiments.

The amount of selenium and copper in a PA sample was determined using an atomic absorption spectrometer "Perkin–Elmer 503" [52]. A PA sample first treated in the solution of selenopentathionate and then with a solution of Cu(II/I) salt, was dissolved in concentrated nitric acid and selenium and copper, present in the resulting solution, was determined by the atomic absorption spectrometer. The concentration of sulfur in PA was determined nephelometrically as described in [53].

The resistances to constant current of $Cu_xS_y–Cu_xSe_y$ layers with different composition were measured on an E7–8 numerical measuring device with special electrodes.

The phase composition of the copper sulfide–copper selenide layer was investigated by means of X-ray diffraction using a DRON-6 diffractometer (radiation Cu–K_α). X-ray diffractograms of PA samples with layers of Cu_xS were treated using the programs "Search Match", "ConvX", "Xfit", "Dplot95" and "Photo Styler" to eliminate the maxima of PA.

Microscopic studies of the $Cu_xS–Cu_ySe$ layers were performed using scaning electronic microscope JEOL SM–IC25S.

XPS spectra of $Cu_xS–Cu_ySe$ layers were recorded by a spectrometer „ESCALAB MKII" (VG Scientific, radiation Mg K_α – 1253.6 eV, output 300 W). Vacuum in the analysing chamber was kept at level of $1.33 \cdot 10^{-8}$ Pa, the distribution of elements in the depth was determined by sputtering with an Ar^+ gun with the ion energy of about 1.0 keV. The samples were etched in a preparation chamber with the vacuum $9.3 \cdot 10^{-3}$ Pa and current 20 μA; duration of etching was 10 s. Maximum accuracy of the method is ± 0.1 at. %.

To investigate the layers obtained by the XPS method the photoelectron spectra of Cu $2p_{3/2}$, Se $3d_{5/2}$ and S 2p were recorded. Empirical sensitivity factors for these elements were taken from the literature [54] and the spectra obtained were compared with the standart ones [55].

Three reactions were studied during investigation of $SeS_4O_6^{2-}$ ions interaction with Ag^+, Cu^+ ions and with a mixture of Cu^{2+}/Cu^+ ions. The $K_2SeS_4O_6 \cdot 1.5H_2O$ 0.1 mol·dm^{-3} solution (5 mmol) was treated with: 1) 0.4 mol·dm^{-3} (20 mmol) and 0.6 mol·dm^{-3} (30 mmol) solutions of $AgNO_3$; 2) 0.6 mol·dm^{-3} (30 mmol) and 0.8 mol·dm^{-3} (40 mmol) Cu^+ salt solution; 3) 0.6 mol·dm^{-3} (30 mmol) and 0.8 mol·dm^{-3} (40 mmol) solution of Cu^{2+}/Cu^+ salts [51]. The solutions with the precipitates to reach the completeness of the reactions were kept 24 h. Precipitates filtered were dried at the temperature of 60 °C untill their weight became constant, and the phase composition was determined by X-ray diffraction method.

ANALYSIS AND RESULTS

The modification of PA tape by the formation in its surface of mixed copper sulfide–copper selenide layers was performed in our studies in two stages. In the first stage, the PA tape was treated in a solution of potassium selenopentathionate and sulfur and selenium containing anions sorb–diffuse into the PA surface matrica layer. In the second stage, the chalcogenized PA tape was treated with the water solution of Cu(II/I) salt: the interaction of copper ions with the sulfur and selenium atoms of low oxidation state present in the sorbed selenopentathionate ions leads to the formation of mixed copper sulfide–copper selenide layers of various chemical, phase composition and electrical conductance in the surface of the polymer. The visual examination of the PA samples colour gave the first indications that the selenopentathionate ions are sorbed–diffused into the tapes: colourless PA tapes depending on the concentration of sorbed–diffused $SeS_4O_6^{2-}$ ions gradually acquires yellow, brown or red (liberation of red amorphous selenium) colour.

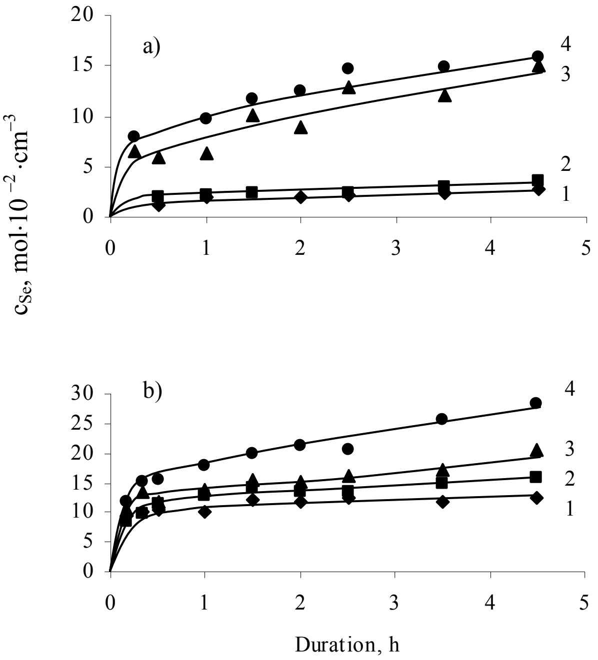

Fig. 1. Changes of selenium concentration in PA with time during its treatment with the not acidified (a) and acidified (b) $K_2SeS_4O_6$ solution of different concentration at 50 °C. Concentration of $K_2SeS_4O_6$ solution, mol·dm^{-3}: 1 – 0.025; 2 – 0.05; 3 – 0.1; 4 – 0.2

The sorption–diffusion of selenopentathionate ions from not acidified solutions of $K_2SeS_4O_6$ was studied first. The 0.025 – 0.2 mol·dm^{-3} solutions of $K_2SeS_4O_6$ at the temperature of 50 °C during study of solution concentration influence were used. The choice of such interval of concentration was dictated by the stability of $K_2SeS_4O_6$ solution. By preliminary experiments it was determined that the sorption–diffusion using solutions of lower concentration was to slow and insufficient but at higher concentrations (> 0.2 mol·dm^{-3}) of solution its stability decreases. The mass of PA tapes increases during treatment in the solution of $K_2SeS_4O_6$: the change of weight (Δm) increases with the increase of $K_2SeS_4O_6$ solution concentration. The concentration of selenium in PA increases with increasing of chalcogenation solution concentration (Fig. 1a), but the saturation of PA tape was not reached even during 4 – 5 h from the beginning of the experiment when the solutions of higher concentration (0.1 and 0.2 mol·dm^{-3}) were used. The constant sulfur concentration in PA at the temperature of 50 °C was reached already after ~1 h (Fig. 2a). That may be explained by the change (reduction) of S/Se molar ratio with time as a result of the gradual decomposition of sorbed–diffused $SeS_4O_6^{2-}$ ions. At the beginning of the experiment (up to about 1 h), the ratio S:Se is close to 4, i.e. to stoichiometrical ratio in the $K_2SeS_4O_6$ molecule. With the prolongation of the experiment and more noticeable – after 1.5 – 2 h this ratio reduces and more significantly when the concentration of initial $K_2SeS_4O_6$ soltion is higher. That indicates that the decomposition of diffused into PA $SeS_4O_6^{2-}$ ions starts about 1 h after the beginning of the experiment [56]

$$SeS_4O_6^{2-} \rightarrow S_4O_6^{2-} + Se\downarrow, \qquad (1)$$

$$S_4O_6^{2-} \rightarrow SO_4^{2-} + SO_2 + 2\,S\downarrow, \qquad (2)$$

the colour of PA tapes changes from colourless to yellow and gradually acquire red colour (amorphous selenium).

The products of the decomposition (SO_4^{2-} ions and SO_2) are washed out from the polymer. The value of S/Se molar ratio at least during first 1 h remains rather close to the initial one in the undecomposed selenopentathionate ion: the sulfur concentration in PA untill 1 h was increasing.

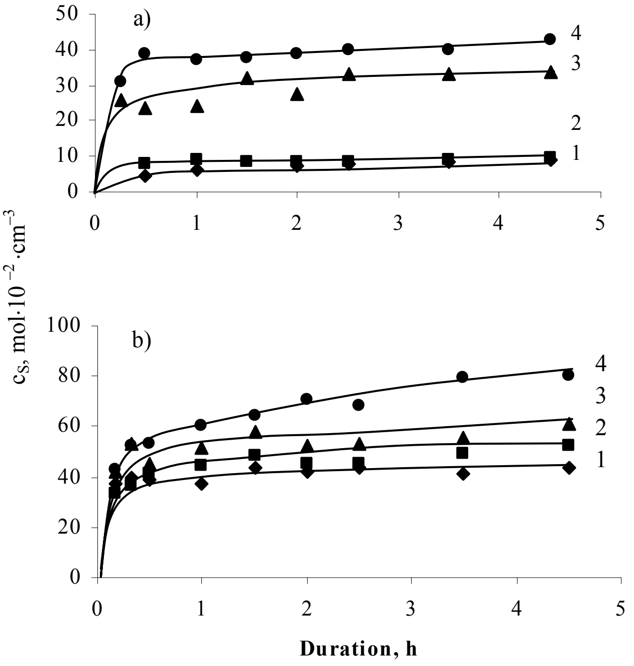

Fig. 2. Changes of sulfur concentration in PA with time during its treatment with the not acidified (a) and acidified (b) $K_2SeS_4O_6$ solution of different concentration at 50 °C. Concentration of $K_2SeS_4O_6$ solution, mol·dm^{-3}: 1 – 0.025; 2 – 0.05; 3 – 0.1; 4 – 0.2

Our studies showed that the stability of $K_2SeS_4O_6$ solution decreases with the increase of its concentration: solution gradually acquires yellow colour and later – after the beginning of elemental selenium liberation – became red coloured. 0.025 mol·dm^{-3} $K_2SeS_4O_6$ solution at the temperature of 50 °C remains clear during all experiment (4.5 h), the decomposition of 0.05 mol·dm^{-3} solution starts after ~2 h, of 0.1 mol·dm^{-3} solution – after 1 h, and of 0.2 mol·dm^{-3} solution – already after 20 min. Therefore in other experiments during study of temperature influence on the sorption–diffusion of selenopentathionate ions into PA, we have used more stable 0.05 mol·dm^{-3} solutions of $K_2SeS_4O_6$ at the temperatures 30 – 50 °C. Such interval of temperatures was chosen because the sorption–diffusion at lower temperature was too slow and the stability of solution at higher temperature was low.

The data presented in Fig. 3a show that the saturation of PA tape with selenium during 4.5 h was reached only at the temperature of 30 °C, and the maximum value of c_{Se} was ~1.1 mg·cm^{-3}.

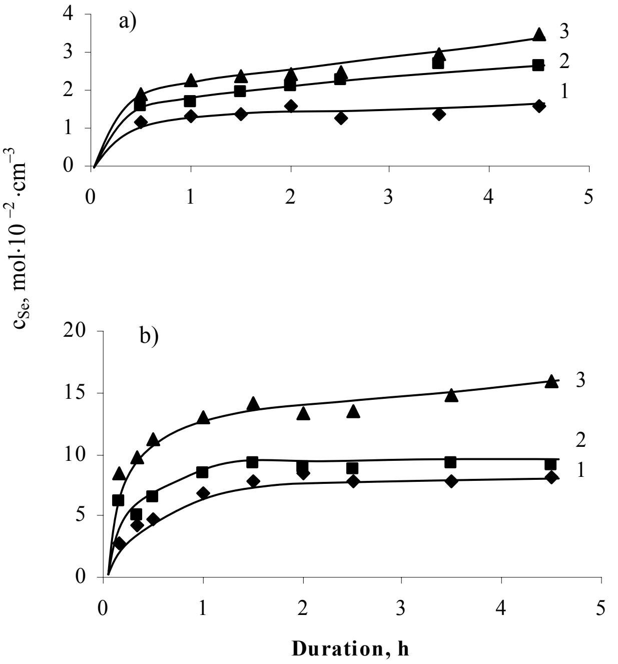

Fig. 3. Changes of selenium concentration in PA with time during its treatment with the not acidified (a) and acidified (b) 0.05 mol·dm^{-3} solution of $K_2SeS_4O_6$ at different temperatures. Temperature, °C: 1 – 30; 2 – 40; 3 – 50

Increase of the chalcogenation solution temperature, as it was expected, leads to the increase of selenium concentration in PA. For example, the concentration of Se after 3.5 h chalcogenation at the temperature of 50 °C was twice higher compared with that reached at 30 °C (Fig. 3a, curves 1, 3). But the saturation of polymer with selenium at 40 and 50 °C in the conditions of the experiment was not reached (Fig. 3a, curves 2, 3).

That was confirmed by analytically determined values of molar ratio S/Se: after 1.5 h at 30 °C S/Se = 3.93, at 40 °C – 3.89 and at 50 °C – 3.74; at the end of experiment (4.5 h) the values of S/Se were respectively 3.21, 3.09 and 2.51. That means that diffused $SeS_4O_6^{2-}$ ions at higher temperature decompose according to the equation (1) faster and the values of S/Se, after products of decomposition SO_2 and SO_4^{2-} became gradually washed out, are lower.

The sulfur concentration diffused into PA increases with increase of the chalcogenation solution temperature too (Fig. 4a). In the interval of temperature studied, PA tape was saturated with sulfur after 2 h. That may be explained (like was mentioned before) by the change of values of molar ratio S/Se in the polymer with time which is caused by the gradual decomposition of diffused $SeS_4O_6^{2-}$ ions. The solution of $K_2SeS_4O_6$ at 30 °C remains clear during all experiment (4.5 h), its decomposition at 40 °C begins after 3 h and at 50 °C – after 2 h. It was determined earlier [57] that PA tapes under the action of hydrochloric acid undergo amorphization and swelling. The degree of swelling increases with the increase of tempeature, and the protonization of nitrogen atoms of amide groups during which the amorphization takes place begins. That does not cause the destruction of a polymer.

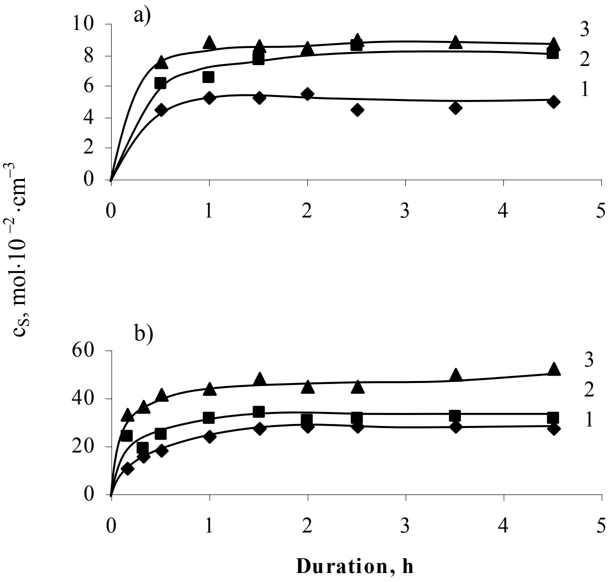

Fig. 4. Changes of sulfur concentration in PA with time during its treatment with the not acidified (a) and acidified (b) 0.05 mol·dm^{-3} solution of $K_2SeS_4O_6$ at different temperatures. Temperature, °C: 1 – 30; 2 – 40; 3 – 50

Analogical action of selenopolythionates on the structure of PA, increases with decrease of solution pH value (increase of acidity), but the influence of the solution concentration is not significant [57]. Therefore it was reasonable to expect more easy sorption–diffusion of the selenopentathionate ions into PA from the acidified solutions because of the polymer structure changes compared with the effectiveness of the process using not acidified solution of $K_2SeS_4O_6$. In the works of O. Foss [50, 58] it was shown that hydrogen ions do stabilize the anion of selenopentathionate. It was determined also [56] that the decomposition of selenopentathionate at the values of solution pH < 5 is very slow and its degree at the lower values of solution pH is even smaller. Thus use of the acidified solutions of $K_2SeS_4O_6$ could result in the more intensive sorption–diffusion of selenopentathionate ions into PA.

The increase of PA samples mass with the increase of $K_2SeS_4O_6$ solution concentration and temperature was determined during study of the selenopentathionate ions sorption–diffusion from the acidified solutions. The influence of temperature is more expressed at the beginning of the experiment (up to 1.5 h). The increase of mass while increasing temperature from 30 to 50 °C after

0.5 h from the beginning of the experiment is ~ 4.5 times higher. This difference on prolongation of the experiment diminishes and on the end do disappear. Most reasonable explanation for that is more fast saturation of PA with the $SeS_4O_6^{2-}$ ions reached at the higher temperature.

It is seen (Fig. 1b) that the changes of selenium concentration in PA kept in a $K_2SeS_4O_6$ solution of different concentration are of the analogical character. Most fast increase of selenium concentration in PA takes place during first 30 min but the saturation in conditions of our experiments during all time (4.5 h) was not reached.

The increase of $K_2SeS_4O_6$ solution temperature accelerates the sorption–diffusion of selenopentathionate ions too. The concentration of Se at the beginning of the experiment (up to 1 h) increases twice and at the end (after ~4 h) – ~1.4 times (Fig. 3b) with the increase of temperature by 20 °C. The change of sulfur concentration in this case is even more pronounced: ~3.3 and ~5 times respectively (Fig. 4b, curves 1 and 3). Different changes of Se and of S concentrations may be explained by the faster decomposition of $SeS_4O_6^{2-}$ ions at the higher temperature.

The acidified $K_2SeS_4O_6$ solution, as expected, was found being more stable: 0.025 ir 0.05 mol·dm^{-3} solutions did not decompose during all experiment, the gradual liberation of red amorphous selenium from 0.1 mol·dm^{-3} solution started after 2 h and from 0.2 mol·dm^{-3} solution – after 1 h. The changes of diffused into PA sulfur and selenium molar ratios S/Se confirmed results of visual observations. The value of this ratio slightly decreases with the increase of temperature and duration, but even after 4.5 h this ratio was ~3.3 when the 0.05 mol·dm^{-3} $K_2SeS_4O_6$ solution at 50 °C was used. The value of S/Se ratio when the $K_2SeS_4O_6$ solution of higher concentration was used, reduces faster: in cases of 0.1 mol·dm^{-3} and 0.2 mol·dm^{-3} solutions after 4.5 h of experiment its values were 2.97 and 2.81 respectively.

If compared the kinetic curves of changes of selenium and sulfur concentrations in PA, received using not acidified and acidified $K_2SeS_4O_6$ solutions of analogous concentration and temperature (Fig. 1 – 4), it was obvious that in case of acidified solutions ~5 times higher sorbed–diffused concentrations of selenium and sulfur, and thus – of selenopentathionate ions were reached. That may be, as it was mentioned above, explained by the PA amorfization and swelling under the action of hydrochloric acid what do enable the more easy penetration of selenopentathionate ions into the polymer.

An apparent sorption–diffusion coefficient (D) and apparent activation energy (E) for the characterization of the selenopentathionate ions sorption–diffusion into PA tape were calculated [59]. The calculated (using data of Fig. 5) thermal effect ($\Delta H_{Se} = -40.66$ kJ·mol^{-1}) and activation energy ($E_{Se} = 20.8$ kJ·mol^{-1}) of selenium sorption–diffusion into PA are few times higher compared with those calculated during study of selenotrithionate ions ($SeS_2O_6^{2-}$) sorption–diffusion into PA: E_{Se} = 2.1 kJ·mol^{-1}, $\Delta H_{Se} = -5.36$ kJ·mol^{-1} [39]. That is reasonable taking into account the bigger size of selenopentathionate ions.

The apparent diffusion coefficient increases with the increase of $K_2SeS_4O_6$ solution concentration (in case of not acidified solution $D = 1.6\cdot10^{-8} - 2.8\cdot10^{-8}$ cm^2·s^{-1}, in case of acidified solution $D = 3.7\cdot10^{-8} - 5.3\cdot10^{-8}$ cm^2·s^{-1}) and temperature (in case of not acidified solution $D = 1.2\cdot10^{-8} - 2.0\cdot10^{-8}$ cm^2·s^{-1}, in case of acidified solution $D = 2.4\cdot10^{-8} - 4.1\cdot10^{-8}$ cm^2·s^{-1}), but its values are significantly lower than those calculated in cases of smaller selenotrithionate ions sorption–diffusion into PA [39]. A value of solution pH significantly influence the value of $SeS_4O_6^{2-}$ ions diffusion coefficient: it increases few time when the value of solution pH is reduced from 5 to 1.5. For example, the value of $D = 2.0\cdot10^{-8}$ cm^2·s^{-1} in case of PA modification by the not acidified 0.05 mol·dm^{-3} $K_2SeS_4O_6$ solution at 50 °C and $D = 4.1\cdot10^{-8}$ cm^2·s^{-1} when the acidified solution of selenopentathionate of the same concentration and temperature was used.

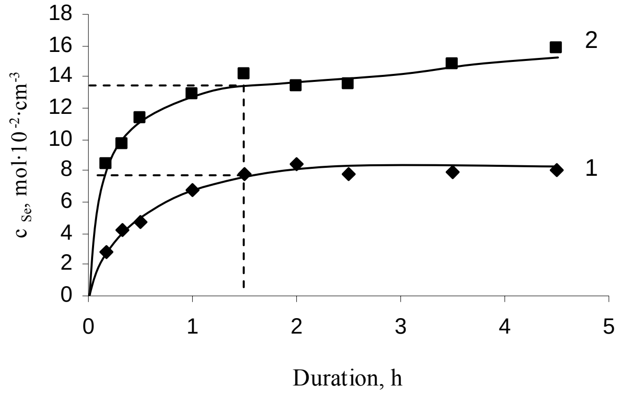

Fig. 5. Changes of selenium concentration in PA with time during its treatment with the acidified $K_2SeS_4O_6$ solution of different temperature. Temperature of the $K_2SeS_4O_6$ solution, °C: 1 – 30; 2 – 50

Summarizing results of the first stage of PA tape modification – chalcogenation – we may conclude that the water solution of potassium selenopentathionate is suitable agent for the inclusion in the PA surface matrica layer divalent atoms of sulfur and selenium of low oxidation state: the $SeS_4O_6^{2-}$ ions sorb – diffuse into PA tape treated with the not acidified (or acidified) solution of potassium selenopentathionate of various concentration and temperature.

The obtained concentrations of selenopentathionate ions in the PA enabled us to modify the surface of this polymer with thin electrically conductive layers of mixed copper sulfide – copper selenide. As it was mentioned above, the second stage of PA tape modification is the treatment of chalcogenized tape with the water solution of copper(II/I) salt resulting in the formation of $Cu_xS - Cu_ySe$ layer on its surface.

The conditions of chalcogenized PA samples treatment with the solution of Cu(II/I) salt which enable the formation in the polymer surface of copper chalcogenide coatings having the lower electrical resistance were determined in our previous works [39 – 41]. In these studies the solutions of the first member of selenopolythionates homologues series $SeS_nO_6^{2-}$ (n = 2, 3, 4) – of selenotrithionate, $SeS_2O_6^{2-}$, – were used. Since the selenopentathionate belong to this series of homologues (n = 4), the chalcogenized in $K_2SeS_4O_6$ solution PA samples were treated with the solution of Cu(II/I) salt at the same like in previous works [39 – 41] experimental conditions, i.e. during 10 min at the temperature of 78 °C.

Cu_xS–Cu_ySe layer on the PA tape is formed during the interaction of chalgenized polymer with the copper ions. The anionic particles containing selenium and sulfur atoms of low oxidation state react with the copper ions resulting in the formation of copper sulfides and copper selenides of various composition. During study of influence of the chalcogenation agent concentration and temperature on the properties of Cu_xS−Cu_ySe layers, the experiments with the PA samples initially treated with the not acidified (and acidified) solutions of $K_2SeS_4O_6$ were performed.

It was determined that the amount of chalcogenide copper in the PA tape samples initially treated with the acidified solution of $K_2SeS_4O_6$ is higher compared with those samples initially treated with the not acidified selenopentathionate solution. For example, m_{Cu} is ~14 times higher in PA initially treated with the 0.05 mol·dm^{-3} acidified $K_2SeS_4O_6$ solution at 50 °C compared with the amount of copper in PA treated with the not acidified solution at the same experimental conditions (Fig. 6, curve 3; Fig. 7, curve 3). The reason is the higher sorbed by PA $SeS_4O_6^{2-}$ ions concentration from the acidified $K_2SeS_4O_6$ solution.

Increase of the temperature increases the m_{Cu} only in PA samples treated with the not acidified solution of $K_2SeS_4O_6$ (Fig. 6).

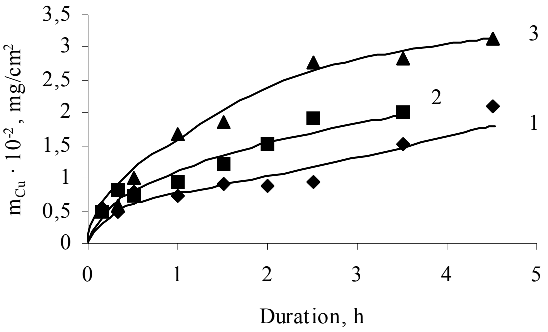

Fig. 6. Changes of copper amount in PA with time. PA was initially treated with the not acidified 0.05 mol·dm^{-3} solutions of $K_2SeS_4O_6$ at different temperatures and later with the solution of Cu(II/I) salt. Temperature, °C: 1 – 30; 2 – 40; 3 – 50

The amount of copper in PA samples treated with the acidified chalcogenation solution increases continuously only in case of the experiment carried out at the temperature of 30 °C (Fig. 7, curve 1). At higher temperature the increase of m_{Cu} is observed only in PA tapes sulfured up to 1 h duration (Fig. 7, curves 2 and 3). In the PA tapes chalcogenized at the temperature of 40 °C, the copper amount reaches the maximum value in tapes sulfured about 1 h and later remains almost constant, and in the tapes chalcogenized at the temperature of 50 °C the copper amount gradually reduces. That may be explained by the known reducing $SeS_4O_6^{2-}$ ions stability with the increase of the solution temperature: these ions gradually decompose (equations 1 and 2) and selenium at the beginning is liberated in the more reactive red amorphous form. Later under action of temperature it is transformed into nonreactive black trigonal modification, which does not interact with the Cu(I/II) salts.

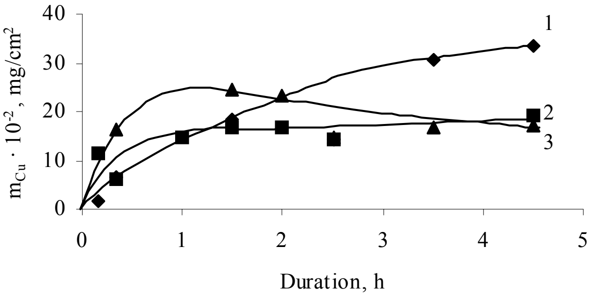

Fig. 7. Changes of copper amount in PA with time. PA was initially treated with the acidified 0.05 mol·dm^{-3} solutions of $K_2SeS_4O_6$ at different temperatures and later with the solution of Cu(II/I) salt. Temperature, °C: 1 – 30; 2 – 40; 3 – 50

The decomposition of $SeS_4O_6^{2-}$ ions in the acidified $K_2SeS_4O_6$ solutions of higher concentration is faster too. But the values of m_{Cu} in PA tapes chalcogenized up to 2 h (untill the beginning of Se liberation) are bigger. The reason is an increasing influence of H^+ and selenpolythionate ions on the structure of PA [57] (amorphization of the structure) with increase of these ions concentration. Exception is the acidified 0.05 mol·dm^{-3} $K_2SeS_4O_6$ solution since the value of m_{Cu} in PA initially treated with this solution (up to 2 h duration) is higher compared with the case when the 0.2 mol·dm^{-3} $K_2SeS_4O_6$ solution was used (Fig. 8).

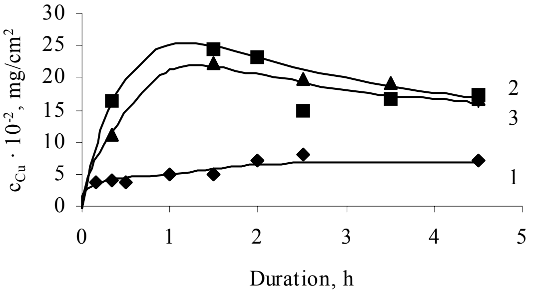

Fig. 8. Changes of copper amount in PA with time. PA was initially treated with the acidified solution of $K_2SeS_4O_6$ of different concentration at 50 °C and later with the solution of Cu(II/I) salt. Concentration, mol·dm^{-3}: 1 – 0.025; 2 – 0.05; 3 – 0.2

Probably, in the solution of this concentration and acidity $SeS_4O_6^{2-}$ ions are most stable and bigger amount of copper chalcogenides are formed on the surface of the polymer after the interaction with the copper(II/I) salt solution.

Changes of a PA tape appearance after its treatment with the Cu(II/I) salt solution indicate also the formation of copper chalcogenide layers on the surface of a polymer. Colour of tapes from colourless transforms into yellow, then − into brown, it acquires a metallic lustre. Electrical measurements finally indicate that layers from the dielectric become semiconductors, and conductors.

Summarizing the results of the PA tape modification at the second stage study, we may conclude that the amount of copper is dependent on the conditions of initial PA chalcogenation − on the acidity, concentration and temperature of a $K_2SeS_4O_6$ solution, and the duration of treatment with it.

The microscopic analysis of the chalcogenides PA tapes surface modified with copper, showed that the formation of Cu_xS–Cu_ySe layers takes place not regularly but they formed as islands. As a result the layer is not even. These unevenness increase the probability of the layer interactions with the impurities and cause some difficulties to the measurements of the surface electrical resistance. A detailed study of the modified with the Cu_xS–Cu_ySe layers PA conductivity properties was complicated, therefore we were satisfied by the measurements of the electrical resistance of the chalcogenide surface outer layer only.

The electrical resistance of copper chalcogenide layers in PA initially chalcogenized with the not acidified $K_2SeS_4O_6$ solutions and later treated with a Cu(I/II) salt solution were from 4.8 MΩ/□ to 4.4 kΩ/□. Rather low values of electrical resistance were measured on the chalcogenide layers obtained by the use of acidified $K_2SeS_4O_6$ solutions (Table 1): they vary from 12 to few hundred Ω/□.

Neglecting the data on layers formed in PA initially chalcogenized shortly, the tendency of electrical resistance decrease with the increase of initial chalcogenation solution concentration is observed: the increase $K_2SeS_4O_6$ solution concentration from 0.025 to 0.2 mol·dm^{-3} reduces a value of the chalcogenide layer electrical resistance depending on the duration of chalcogenation from three to five time. Direct dependence of the chalcogenide layer resistance on the amount of copper in the layer is observed not in all cases, since the copper sulfides and selenides of various stoichiometry and electrical conductivity, and in different amounts may be formed in the surface of PA. It is known [32] that the electrical resistance of Cu_xS reduces by one million times while a value of x is reduced from 2 to 1.

The results presented show that after the chalcogenized in the $K_2SeS_4O_6$ solution PA treatment with the Cu(II/I) salt solution it is possible to form the layers of copper sulfides and selenides having electrical resistance varying from less than 1 kΩ/□ to even few tenth of Ω/□.

Looking for the information about the Cu_xS–Cu_ySe layers phase composition, first we tried to simulate the process of these layers formation. We have undertaken the preparative study of the interaction of $K_2SeS_4O_6$ solution with the Ag^+ and Cu^+ ions, and with the Cu(II/I) salt solution previously used for the formation of chalcogenide layers in the surface of PA. A reason why the reaction with Ag^+ ions was studied too is that this reaction is one of the most characteristic rections of polythionates and selenopolythionates [33, 35]: the interaction of any polythionic compound with the Ag^+ ions leads to the fast precipitation of silver chalcogenides. The solid state products of interactions were studied by means of X-ray diffraction.

Rather early by Riezerfeld and Feld it was determined [60] that the interaction of trithionate and Cu^{2+} ions leads to the formation of one mole of Cu(II) sulfide:

$$S_3O_6^{2-} + Cu^{2+} + 2H_2O \rightarrow CuS\downarrow + 2SO_4^{2-} + 4H^+. \quad (3)$$

According the data of Heuer [61], the potassium selenotrithionate, $K_2SeS_2O_6$, treated with the ammonia solution of $AgNO_3$ decomposes into silver(I) selenide and sulfate:

$$K_2SeS_2O_6 + Ag_2O{\cdot}2NH_3 + H_2 \rightarrow K_2SO_4 + Ag_2Se + (NH_4)_2SO_4\,. \quad (4)$$

Higher selenopolythionates (analogically like the sulfur polythionates) react with the Ag^+ ions too with the liberation of black Ag_2Se precipitate. Authors of the work [62] stated the the selenopolythionates of the type $Se_nS_2O_6^{2-}$ react with the Ag^+ ions quantitatively according the equation

Table 1. Dependence of chalcogenized (in acidified $K_2SeS_4O_6$ solution at 50 °C) and then treated with the Cu(I/II) salt solution on a PA surface formed chalcogenide layer electrical resistance value (Ω/□) on the concentration of chalcogenation solution and duration of treatment with it

Duration of chalcogenation, h	Resistance of the chalcogenide layer formed using a chalcogenation solution of different concentration (mol·dm^{-3}) at 50 °C					
	0.025	0.05	0.05*	0.05**	0.1	0.2
0.17	122.5	167.5	220.0	465.80	104.0	119.0
0.33	60.5	93.37	212.3	382.7	68.0	130.0
0.5	178.0	88.0	145.8	176.2	48.6	60.0
1.0	99.7	70.39	84.5	148.1	71.0	32.7
1.5	72.0	63.83	54.3	121.4	48.0	19.8
2.0	68.7	61.75	44.2	115.7	52.5	14.4
2.5	61.54	51.78	47.9	148.7	47.0	13.6
3.5	53.6	42.93	42.8	122.6	32.5	12.3
4.5	18.8	60.53	42.7	115.2	20.8	13.0

* – the temperature of chalcogenation solution 30 °C

** – the temperature of chalcogenation solution 40 °C

$Se_nS_2O_6^{2-} + 2nAg^+ + 2H_2O \rightarrow nAg_2Se + 2H_2SO_4$, (5)

i.e. all selenium precipitates as black silver selenide and only sulfuric acid remains in the solution. But the charge balance of this equation may be reached in case of n equal to 1 [35]:

$SeS_2O_6^{2-} + 2Ag^+ + 2H_2O \rightarrow Ag_2Se + 2H_2SO_4$. (6)

Therefore, the opinion of author of the work [35] was that black precipitate formed in this reaction in cases of higher selenopolythionates may be a mixture of Ag_2Se and Se or a polyselenide of silver, i.e. the reaction may proceed according to the following overall equation:

$Se_nS_2O_6^{2-} + 2Ag^+ + 2H_2O \rightarrow Ag_2Se_n + 2H_2O$, (7)
or $Ag_2Se + (n-1)Se$.

The analogous reaction of the selenopolythionates of the type $Se_nS_3O_6^{2-}$ was studied in the work [63]. According authors of this work, reaction proceeds in accordance with the equation:

$Se_nS_3O_6^{2-} + (2n+2)Ag^+ + 2H_2O \rightarrow nAg_2Se + Ag_2S\downarrow + 2H_2SO_4$. (8)

But in this case, like in the case of the selenopolythionates of $Se_nS_2O_6^{2-}$ type to reach the charge balance of the equation is impossible. Therefore, the opinion of author of the work [35] was that black precipitate fromed in the interaction of selenotetrathionate, $SeS_3O_6^{2-}$, and silver ions may be:

a) a mixture of Ag_2Se and elemental sulfur, S;
b) a mixture of Ag_2S and elemental selenium, Se;
c) a mixed silver(I) dichalcogenide, Ag_2SeS; therefore the reaction may proceed according the equations [35]:

$SeS_3O_6^{2-} + 2Ag^+ + 2H_2O \rightarrow Ag_2SeS + 2H_2SO_4$, (9)
or $Ag_2Se + S$,
or $Ag_2S + Se$.

The diffractograms of precipitates formed after the interaction of selenopentathionate with Ag^+ ions taken in the molar ratios 1:4 and 1:6 showed that they are composed of Ag_2Se, Ag_2S and elemental sulfur. The part of silver sulfide in the second case, i.e. when the larger excess of Ag^+ ions was used, was found bigger. The solid phase product obtained during the interaction of $SeS_4O_6^{2-}$ and Cu^+ ions taken in the molar ratio 1 : 6 was composed of Cu_2S, CuSe, Cu_2Se, elemental selenium and sulfur. When the molar ratio was changed into 1 : 8, i.e. in case when the larger excess of Cu^+ ions was used, the phases of $Cu_{1.96}S$, CuSe and elemental sulfur, S_8 were found, but not phase of elemental selenium. We must point out some doubt about the presence of elemental sulfur, since S_8 reacts with the Cu(I) ions [51]. During the experiment small yellow crystals (possibly of sulfur) were detected visually in the precipitate filtered but the peaks of sulfur in the diffractograms did coincide with the peaks of other phases in many cases. Elemental selenium according to our experience does not react with the Cu(I) ions and its peaks in diffractograms coincide with the peaks of copper chalcogenide phases too. The analogous experiments carried out using the solution of Cu^{2+}/Cu^+ salts showed that in the case of reagents molar ratio 1 : 6, the solid product consists of copper sulfides Cu_2S, $Cu_{1.75}S$, copper selenides Cu_2Se, CuSe and of elemental sulfur. When the molar ratio was changed into 1 : 8, the phases of $Cu_{1.75}S$, $Cu_{1.8}S$, CuSe and elemental S_8 were found in the precipitate. Thus, the data received by the preparative method indicates that the solid phase product formed during interaction of $SeS_4O_6^{2-}$ and Ag^+ ions consists of Ag(I) sulfide and Ag(I) selenide (the oxidation state +1 for silver is very pronounced in the compounds), and of some amount of elemental S_8. While changed the Ag^+ ions by Cu^+ ions (the oxidation states of +1 and +2 are common for a copper atom in the compounds), not only both Cu(I) chalcogenides, i.e. Cu_2S and Cu_2Se, but also Cu(II) selenide, CuSe, and some amount of elemental sulfur and selenium were found in the solid state products of the reaction. That proves that part of Cu^+ ions did participate in the redox reaction resulting in the formation of Cu(II) selenide. The activity of Cu(I) atoms towards elemental sulfur is studied [51], therefore probably the redox interaction between the Cu^+ ions and selenium atom of low oxidation state which is present in the selenopentathionate ion, is possible too. This interpretation is confirmed by the X-ray diffraction analysis of precipitate received during the interaction of $SeS_4O_6^{2-}$ ions with the bigger amount of Cu^+ ions ($SeS_4O_6^{2-} : Cu^+ = 1 : 8$) when all selenium in the Cu(II) selenide, CuSe, was found. Thus it is reasonable that the interaction of $SeS_4O_6^{2-}$ ions with the mixture of Cu^+/Cu^{2+} ions (Cu^{2+} ions takes a major part in this mixture) resulted in the formation of both Cu(I) and Cu(II) sulfides and selenides.

The phase composition of Cu_xS–Cu_ySe may be qualitatively and approximately quantitatively characterized by the X-ray diffraction but the study of Cu_xS–Cu_ySe layers in the polymer surface faces some difficulties because of the pecularities of these composite materials. Firstly, the sulfide–selenide layers are polycrystalline; secondly, usually number of Cu_xS–Cu_ySe phases with the different composition and structure are present in the layer. Despite of these difficulties, the phase composition of formed in PA surface mixed Cu_xS–Cu_ySe layers was studied by the method of X-ray diffraction since this method was successfully used to characterize the phase composition of only copper sulfide or copper selenide layers in the surface of this polymer earlier [38, 39, 41].

X-ray diffraction analysis of the PA tapes first treated with the solutions of potassium selenopentathionate different period of time at the different temperature and later – with the solution of Cu(II/I) salt – confirmed the presumption of formation of mixed Cu_xS–Cu_ySe layers in the surface of the polymer. The phases of monoclinic *djurleite*, $Cu_{1.9375}S$, (JCPDS 83–1463; $2\theta = 30.6$; 34.2; 38.08), cubic *digenite*, $Cu_{1.8}S$, (JCPDS 4–861; $2\theta = 37.5$; 46.2), orthorhombic *chalcocite*, Cu_2S, (JCPDS 2–1272; $2\theta = 32.8$; 45.5; 58.03) and tetragonal *belidoite*, Cu_2Se, (JCPDS 29–575; $2\theta = 38.681$; 43.3; 44.9) were determined in the copper chalcogenide layer on the surface of PA initially treated at the lower (30 °C) temperature. The concentration of electrically low conductive *chalcocite* phase decreases and of the more conductive $Cu_{1.9375}S$, $Cu_{1.8}S$ and Cu_2Se increases when the duration of the initial PA chalcogenation is prolonged. In accordance with that, the measured values of the chalcogenide layers in the surface of the modified PA tapes electrical conductivity increases with an increaes of the initial PA chalcogenation time. If the temperature of the initial PA chalcogenation is increased (50 °C), besides the phases mentioned above the phases of orthorhombic *anilite*, $Cu_{1.75}S$, (JCPDS 33–489; $2\theta = 32.1$; 41.6; 43.9), tetragonal *umangite*, Cu_3Se_2, (JCPDS 19–402; $2\theta = 35.04$; 42.2; 51.3) orthorhombic *klokmannite*, CuSe, (JCPDS 27–184; $2\theta = 31.1$; 45.9; 49.9) were detected. If the duration of PA chalcogenation is increased to 4.5 h (but the concentration of $K_2SeS_4O_6$ solution and temperature are unchanged), the phase composition of Cu_xS–Cu_ySe layer remains unchanged too. But, the concentration of low conductive *chalcocite* diminishes and the concentration of electrically conductive copper sulfides and selenides in the polymer chalcogenide layer increases.

When the PA samples initially were treated with the $K_2SeS_4O_6$ solution of higher concentration (0.2 mol·dm^{-3}), the concentration of copper selenides in the chalcogenide layer formed increases with the increase of the chalcogenation duration: appears the phases of orthorhombic $CuSe_2$ (JCPDS 74–280; $2\theta = 32.5$; 45.71; 56.88) and orthorhombic Cu_2Se_x, (JCPDS 47–1448; $2\theta = 43.99$; 38.7), and the low conductive *chalcocite* phase transforms into copper sulfide phases of higher conductivity. In these conditions, the highest concentration of electrically conductive copper selenides are formed and the stoichiometrical composition of copper sulfides, Cu_xS, changes in the direction of x decrease resulting in the formation of copper chalcogenide layers in the surface of PA the electrical resistance of which reaches the very low values, even values of 167 – 12 Ω/□ (Table 1).

The changes of mixed copper sulfide and copper selenide layers composition determines the electrical conductivity of the layers. The chalcogenide layer of low conductivity (high resistance) is formed on the surface of initially shortly chalcogenized PA. The reason for that probably is the formation of low conductive *chalcocite* and of other copper sulfides the stoichiometry of which is close to Cu_2S at the beginning of the process. When the duration of PA initial chalcogenation is prolonged and the concentration of chalcogenation solution is increased, the formation of higher conductive copper selenides is observed and not conductive copper sulfide phases transforms into the phases of higher conductivity. The PA tapes modified with the such chalcogenide layers are characterized by the rather low values of electrical resistance.

The determined regularities of the Cu_xS–Cu_ySe layers formation enable to select conditions under which the semiconductive and electrically conductive mixed Cu_xS–Cu_ySe layers of desirable chemical and phase composition and of predicted electrical resistance may be formed on the surface of polyamide.

The phase composition of Cu_xS–Cu_ySe layers studied by the method of X-ray photoelectron spectroscopy (XPS) was restricted by the study of chemical and phase composition of very thin Cu_xS–Cu_ySe surface layer (up to 1 nm in depth) as compared with the thickness of the all chalcogenide layer (about few tenths of μm).

It was determined that when the treated in the chalcogenation solution different period of time PA tape samples are affected with the solution of Cu(II/I) salt, the formation of layer composed of different copper, sulfur and selenium compounds take place in the surface of the polymer. The following compounds were identified: Cu_2S, CuS, Cu_2O, CuO, CuSe, Cu_2Se and Se.

As it was mentioned above, the values of x and y in the Cu_xS–Cu_ySe layers change from 1 to 2, i.e. the nonstoichiometric copper sulfides and selenides are formed. It is impossible from the data of XPS analysis to determine accurately the values of x and y compared with the data received by the method of X-ray diffraction which enable the direct identification of various intermediate copper sulfides and selenides.

The study of the elements Cu, S, Se and O distribution in the Cu_xS–Cu_ySe layer showed (Table 2) that the oxygen takes a largest part (49 – 61 at.%) on the surface of all PA tape samples. All processes of the copper chalcogenide layer formation proceeds in the natural environment. Therefore it is impossible to prevent the influence of the environment on the chemical composition of the layers. That is a reason of the oxygen presence in the surface of chalcogenide layer. The presence of water connected by the physical and chemical adsorption is possible too. The oxygen in deeper layer is undoubtly bound into the oxides Cu_2O and CuO. Therefore, the chalcogenide layers in the surface of the polymer are formed in the form of islands which enable the easy contacts of the atmospheric oxygen with the ions of copper and chalcogens. The amount of oxygen significantly reduces (1 – 9 at.%) when the surface of the sulfide layer was etched by the Ar^+ ions. That prooves that the oxygen is present on the surface of the chalcogenide layer only. The amount of O in the deeper layers is very small and its presence should not have influence on the chemical composition of the layer and its properties. The data of the XPS analysis shows that the composition of Cu_xS–Cu_ySe layers formed in different experimental conditions is rather similar (Table 2). For example, the oxygen takes 56.89 at.% on the surface of the chalcogenide layer when the PA was initially chalcogenized in 0.05 mol·dm^{-3} $K_2SeS_4O_6$ solution during 10 min and at the temperature of 50 °C. The bond energy values of $E_b = 530.1$ and 531.5 eV in the spectra of O 1s show that a part of oxygen should be joined into the Cu(I) oxide, Cu_2O, and the bond energy $E_b = 533.5$ eV indicated the presence of HO^- groups. These groups may be in the composition of $Cu(OH)_2$, which may be formed during washing of the chalcogenide layer with water. The bond energy of 161.3 eV in the spectra of S 2p shows the presence in the surface of Cu(I) and Cu(II) sulfides. The values of $E_b = 53.8$, 54.2, 55.3, eV in the spectra of Se $3d_{5/2}$ indicates the presence of elemental selenium. The spectra of Cu $2p_{3/2}$ confirmed the presence of the copper sulfides mentioned and of Cu(I) oxide, Cu_2O ($E_b = 932.1$ eV), and of Cu(II) oxide, CuO ($E_b = 933.9$ eV). Changes of the chemical composition and of the elements amounts occur when the chalcogenide layer was etched with the Ar^+ ions.

The amount of oxygen reduces by 6 times (to 9.38 at.%) but the amounts of Cu, S and Se increase significantly. S 2p spectra indicates the formation of copper sulfides in the layer: the bond energy $E_b = 161.5$ eV shows a Cu_2S, and E_b = 162.5 eV – CuS. The bond energy E_r = 932.2 eV in the spectra of Cu $2p_{3/2}$ confirms the presence of copper sulfides and of Cu(I) oxide, Cu_2O, in the chalcogenide layer.

The studies of $Cu_xS–Cu_ySe$ layers on the surface of PA initially chalcogenized during 1 – 4.5 h showed that the chemical composition is similar to the composition of layers formed when a polymers chalgenation stage was shorter. Again, the large amount of oxygen was found on the surface of copper chalcogenide layer. This amount reduces to a minimum after the surface etching with the Ar^+ ions. The traces of elemental selenium were found in the all samples studied since the chalcogenation solution gradually decomposes with time.

These results confirms the results received by the X-ray diffraction analysis of the layers: the composition of the layer on prolongation of the polymer initial chalcogenation stage in the solution of the same concentration and temperature untill 4.5 h, remains almost the same.

Summarizing the results of our studies we may state that the solution of potassium selenopentathionate is a suitable agent of the polyamide chalcogenation for the formation on its surface of electrically conductive $Cu_xS–Cu_ySe$ layers. This agent of chalcogenation because of a unique structure of the anion $^{-}O_3S–S–Se–S–SO_3^{-}$

Table 2. The data of XPS analysis of $Cu_xS–Cu_ySe$ layers formed in the surface of PA

The duration of PA chalcogenation in a $K_2SeS_4O_6$ solution, min	Etching conditions	Element	Content, at %	Binding energy, eV	Composition of the layer
10	Before etching	Cu	11.96	932.1; 933.9	Cu_2S, Cu_2O,CuO
		S	22.67	161.3; 162.3; 168.5	Cu_2Se, CuS
		Se	8.47	54.2; 55.3; 58.5	Se
		O	56.89	530.1; 531.5; 533,5	$Cu(OH)_2$; $CuSO_4$
	After etching	Cu	36.45	932.2	Cu_2S, CuS, Cu_2O
		S	39.33	161.5; 162.5	Cu_2Se, CuS, CuO
		Se	14.82	54.2; 55.4; 56.6	Se
		O	9.38	532.1; 533.8	
60	Before etching	Cu	17.37	932.1; 933.9	Cu_2S, CuS, Cu_2O
		S	24.65	161.3; 162.3, 168.5	Cu_2Se, CuSe
		Se	8.68	55.4; 55.6; 58.2	Se
		O	49.30	529.8; 531.1	$CuSO_4$
	After etching	Cu	50.89	932.2	Cu_2S, Cu_2O, CuS
		S	34.72	161.5; 162.5	Cu_2Se, CuSe
		Se	13.14	54.2; 55.6; 56.9	Se
		O	1.23	531.6	
150	Before etching	Cu	15.57	932.3; 934.0	Cu_2S, Cu_2O,
		S	18.19	161.3; 162.3; 68.7	CuSe, Cu_2Se, CuS
		Se	4.50	53.9; 55.3; 58.5	Se
		O	61.72	529.8; 531.2	$CuSO_4$, CuO
	After etching	Cu	46.96	932.3	Cu_2S, Cu_2O, CuS
		S	32.03	161.5; 162.5	Cu_2Se, CuSe
		Se	13.67	54.2; 56.6	Se
		O	7.33	531.1	
270	Before etching	Cu	15.29	932.1; 933.8	Cu_2S, Cu_2O, CuS
		S	22.85	161.3; 162.5; 167.8	Cu_2Se, CuSe
		Se	7.57	54; 55.4; 58.6	Se
		O	54.28	531; 532.6; 533.8	$CuSO_4$, CuO
	After etching	Cu	52.39	932.2	CuS, Cu_2O, Cu_2Se
		S	33.61	161.5; 162.4	Cu_2S, CuSe
		Se	11.82	54.2; 55.4; 56.6	Se
		O	2.17	531.8	

comprising sulfur and selenium atoms of low oxidation state enable the insertion into the PA surface matrica layer of the anionic particles of S and Se. The treatment of a modified in such a way polymer with the solution of Cu(II/I) salt results in the formation of mixed copper sulfide–copper selenide layer of desirable chemical composition and electrical resistance, and very high adhesion with the polymer. This chalcogenation agent enabled to form mixed chalcogenide layers for the first time. These coatings may have both to copper sulfides and copper selenides peculiar properties.

CONCLUSIONS

1. The selenopentathionate anions containing a mixed chain of divalent sulfur and selenium atoms of the low oxidation state $^{-}O_3S–S–Se–S–SO_3^{-}$ are sorbed–diffused into a polyamide tapes if they are treated with the neutral or acidified with hydrochloric acid solutions (0.025 – 0.2 mol·dm^{-3}, 30 – 50 °C) of potassium selenopentathionate, $K_2SeS_4O_6$. Exactly these central Se and S atoms are potential chalcogen atoms for the formation of mixed copper sulfide–copper selenide layers in the surface of the semihydrophilic polyamide tapes.

2. The sorption–diffusion of selenopentathionate ions from the acidified solutions proceeds more intensive because of the polymer structure amorphization under the action of H^+ and selenopentathionate ions: the concentrations of diffused from the acidified solution selenium and sulfur are about 5 times higher compared with those reached using the non acidified solution of the same concentration and at the same temperature. The concentration of sorbed selenopentathionate ions increases with the increase of temeperature and concentration of a $K_2SeS_4O_6$ solution, and the duration of treatment.

3. The diffused into polyamide $SeS_4O_6^{2-}$ anions gradually decompose and the decomposition products – sulfate ions and SO_2 – are washed out from a polymer but elemental selenium remains in it. Therefore, the colour of polyamide tapes depending on a degree of $SeS_4O_6^{2-}$ ions decomposition changes from colourless to yellow, brown or red.

4. The copper sulfide and copper selenide layers of various composition are formed on the surface of polyamide tape if the chalcogenized polymer is treated with the water solution of Cu(II/I) salt: the anionic particles containing sulfur and selenium atoms of low oxidation state react with the copper ions. The colour of the modified with copper chalcogenide layer polyamide tape is in direct dependence on the conditions of initial polymer treatment with the solution of chalcogenation agent: tapes with the low concentration of sorbed–diffused selenium (colourless) after the interaction with the Cu(II/I) salt solution acquire a light yellow colour and tapes with the bigger concentration of selenium – dark brown colour and the metallic lustre.

5. The conditions of a polymer initial chalcogenation (the concentration and temperature of $K_2SeS_4O_6$ solution) determines the amount of copper and the composition of chalcogenide layer: the amount of copper in the polyamide tape increases with the increase of concentration and temperature, and varies from 0.2·10^{-2} to 33.5·10^{-2} mg/cm^2. The amount of copper in the copper chalcogenide layer increases with the increase of concentration and temperature of the selenopentathionate solution used for the initial chalcogenation of the polymer. The amount of joined into chalcogenide copper in the PA tape samples initially treated with the acidified solution of $K_2SeS_4O_6$ is significantly higher compared with those samples initially treated with the not acidified selenopentathionate solution.

6. The results of X-ray diffraction analysis confirmed the formation of mixed copper sulfide–copper selenide layers in the surface of polyamide. The phase composition of layer changes depending on the duration of initial treatment in a $K_2SeS_4O_6$ solution: $Cu_xS–Cu_ySe$ layers are composed of little conductive *chalcocite*, Cu_2S, electrically conductive *digenite*, $Cu_{1.8}S$, *djurleite,*, $Cu_{1.9375}S$, *anilite*, $Cu_{1.75}S$,and of copper selenides – *bellidoite*, Cu_2Se, *umangite*, Cu_3Se_2, *klockmannite*, CuSe, *krutaite*, $CuSe_2$ and Cu_2Se_x. The phase composition determines the electrical characteristics of the layers.

7. The use of selenopentathionate solutios enables the formation on the surface of a polymer of electrically conductive layer of copper sulfides–selenides the electrical resistance of which varies from 12.2 Ω/□ to 4.8 MΩ/□. The values of electrical resistance of the copper chalcogenide layer formed initially using the acidified solution of chalcogenation (R = 465.8 Ω/□ – 12.3 Ω/□) are few thousand times lower as compared with the electrical resistance values of layers formed using the not acidified chalcogenation solution (R = 4.8 MΩ/□ – 4.4 kΩ/□).

8. The determination of $Cu_xS–Cu_ySe$ layers chemical composition in depth up to 1 nm studied by the method of X-ray photoelectron spectroscopy confirmed the formation of copper sulfides and selenides of various phases in the surface of a polyamide.

9. The regularities determined enable formation by sorption–diffusion method of mixed copper sulfide and copper selenide layers of desirable composition and electrical conductivity using the selenopentathionate as a polyamide chalcogenation agent.

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