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Formation and Characterization of Mixed Copper Sulfide – Copper Telluride Layers on the Polyamide 6 Film Surface

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By a study of IR and UV absorption spectra it is shown that the telluropentathionate anions are sorbed-diffused into the polyamide 6 films if they are treated with the water solutions (0.01 mol·dm^{-3} – 0.1 mol·dm^{-3}, 20 °C) of sodium telluropentathionate, $Na_2TeS_4O_6$, or telluropentathionic acid, $H_2TeS_4O_6$. The concentration of sorbed telluropentathionate ions increases with the increase in duration of treatment and temperature of a $TeS_4O_6^{2-}$ containing solution. The mixed copper sulfide – copper telluride, $Cu_xS – Cu_yTe$, layers are formed in the surface of polyamide 6 film if the chalcogenized polymer is treated with Cu(II/I) salt solution (10 min, 78 °C): the anionic particles $TeS_4O_6^{2-}$ containing tellurium and sulfur atoms of low oxidation state react with the copper(II/I) ions. The conditions of a polymer initial chalcogenation determine the amount of copper and the composition of chalcogenide layer: the amount of copper in the chalcogenide layer increases with the increase of initial chalcogenation duration and the concentration of solution. The results of UV-VIS absorption spectra and X-ray structural analysis confirmed the formation of mixed copper sulfide – copper telluride layers in the surface of polyamide 6. The phase composition of layer changes depending on the conditions of the polymer initial treatment in a $TeS_4O_6^{2-}$ solution. Three copper sulfide phases, Cu_7S_4, $Cu_{1.9375}S$, $Cu_{1.8}S$, and four copper telluride phases, Cu_2Te, Cu_3Te_2, CuTe, $Cu_{2.72}Te_2$, were identified in the composition of the layers by X-ray diffraction. The regularities determined enable formation by sorption-diffusion method of electrically conductive (6.0·10^3 kΩ/□ – 1.0 kΩ/□) copper sulfide – copper telluride layers of desirable composition and conductivity using the solutions of telluropentathionates as a polyamide 6 chalcogenation agents.

Keywords: telluropentathionate, polyamide, sorption – diffusion, copper chalcogenide layers.

INTRODUCTION

Metal chalcogenide thin layers have a number of applications in various fields of modern technologies, including coatings, interference filters, polarizers, narrow band filters, solar cells, photoconductors, IR detectors, waveguide coatings, magnetic and superconducting films, microelectronic devices and etc. [1]. Many metal sulfide compounds have excellent optical properties in the visible and IR region of the spectrum [2]. Copper chalcogenide thin films have number of applications in various devices such as solar cells, super ionic conductors, photodetectors, photothermal conversion, electroconductive electrodes, microwave shielding coating, etc. [3 – 5]. The layers of copper chalcogenides are produced by the various methods [6]. But their formation is more convenient by the use of sorption methods.

Sorption-diffusion is a simple and promising method for obtaining binary chalcogenide layers. Hydrophilic and semi-hydrophilic polymers are capable of absorbing ions of various electrolytes from aqueous solutions [7]. It was shown that during treatment the anions of polythionates, ($^-O_3S–S_x–SO_3^-$), or selenopentathionate, $^-O_3S–S–Se–S–SO_3^-$, containing chains of divalent chalcogen atoms of low oxidation state [8], are sorbed by a polymer.

Over the last decade, a sorption method for the formation of copper sulfide, Cu_xS, and mixed copper sulfide – copper selenide, $Cu_xS – Cu_ySe$, layers on the surface of PA based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_nO_6^{2-}$, and selenopentathionate, $SeS_4O_6^{2-}$, has been under extensive investigation [9 – 13].

Electrically conductive mixed copper selenide – copper sulfide layers were formed on the surface of a polyamide film (PA) as a result of the reaction between selenopentathionate ions and $Cu^+ – Cu^{2+}$ ions present in a solution of copper(II/I) salt [9]. X-ray diffraction has been shown [10] to be suitable for the determination of phase composition of mixed $Cu_xS – Cu_ySe$ layers on the surface of PA formed.

The aim of the present study was to obtain layers of mixed copper telluride – copper sulfide on the surface of PA using solutions of telluropentathionic acid, $H_2TeS_4O_6$, and its sodium salt, $Na_2TeS_4O_6$, as precursors of sulfur and tellurium, and to determine their composition by chemical, optical (FT-IR, UV-VIS) and X-ray diffraction methods.

EXPERIMENTAL

A PA 6 film (specification TY 6-05-1775-76, grade PK–4, 70 μm thick) produced in Russia was used. This film is close to a nonporous material, because the pores of PA are much less than 1.5 nm. The porosity was measured by a β method using a Quantasorb (Japan). Prior to the experiments, pieces of PA of 15 mm × 70 mm in size were boiled in distilled water for two hours to remove the remainder of the monomer. After that, they have been dried by filter paper and then in the dessicator over $CaCl_2$ for 24 h.

The salt of sodium telluropentathionate, $Na_2TeS_4O_6·2\,H_2O$, was prepared and chemically analyzed according to published procedures [11]. The samples of PA were chalcogenized in 0.01, 0.025, 0.05, 0.1 mol·dm^{-3}

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solutions of $Na_2TeS_4O_6$ in 0.1 mol·dm^{-3} – 0.2 mol·dm^{-3} HCl (pH ~ 1.5) at the temperature of 20 °C.

Telluropentathionic acid was isolated from its barium salt, $BaTeS_4O_6·2\,H_2O$, in the reaction of precipitation of $BaSO_4$ with the solution of H_2SO_4 [12]. PA strips were treated 1 h – 121 h in 0.01, 0.025, 0.05 and 0.1 mol·dm^{-3} aqueous solutions of isolated telluropen-tathionic acid, $H_2TeS_4O_6$, at the temperature of 20 °C.

For the formation of mixed $Cu_xS – Cu_yTe$ thin films the samples of chalcogenized PA were treated with Cu(II/I) salt solution at 78 °C. Cu(II/I) salt solution was made from crystalline $CuSO_4·5\,H_2O$ and a reducing agent hydroquinone [13]. It is a mixture of univalent and divalent copper salts, in which there is 0.34 mol·dm^{-3} Cu(II) salt and 0.06 mol·dm^{-3} Cu(I) salt [13]. After having been kept in $Na_2TeS_4O_6$ or $H_2TeS_4O_6$ solution, the PA 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 tellurium and copper in PA sample was determined using an atomic absorption spectrometer “Perkin-Elmer 503“ [14]. Before the analysis, samples of PA with tellurium and sulfur containing thin films have been mineralized. Samples were treated with concentrated HNO_3 to destroy PA and to oxidize tellurium and sulfur compounds to tellurites and sulfates. Heating with concentrated hydrochloric acid removed the excess of nitric acid. For the conditions described above, the sensitivity of AAS method is 1 μg·ml^{-1} tellurium for the 1 % absorption [14].

The concentration of sulfur in PA in the form of sulfates was determined turbidimetrically [15]. Sulfate ion in the range of concentration of 1 mg·dm^{-3} – 15 mg·dm^{-3} may be readily determined by utilizing the reaction with barium chloride in slightly acidified with hydrochloric acid solution to give barium sulfate. The measurement of the intensity of the transmitted light as a function of the concentration of the dispersed phase of $BaSO_4$ was carried out photometrically by the photoelectric colorimeter KFK-4 (Russia) at $\lambda = 400.0$ nm. The standard deviation in the range of concentrations 5 mg·dm^{-3} – 10 mg·dm^{-3} is 8 %.

UV spectra were recorded on a Spectronic^{R} Genesis 8 UV/Visible spectrophotometer with compensation of the absorption of PA. IR spectra were recorded on a spectrophotometer Perkin Elmer FTIR Spectrum GX by averaging 64 scans with 0.3 cm^{-1} resolution at room temperature for every sample.

The phase composition of copper chalcogenides’ layers on the surface of PA was investigated by means of X-ray diffraction with a DRON-6 diffractometer provided with a special device for beam limitation at low and medium diffraction angles using graphite – monochromatized Cu–K_α radiation source (λ = 1.54178 Å) under a voltage of 30 kV and current of 30 mA. The XRD patterns were recorded with a step of 0.05° from $2\theta = 30°$ to 70°. X-ray diffractograms of PA samples with layers of copper chalcogenides were treated using the programs “Search Match”, “ConvX”, “Xfit”, “Dplot95” and “Photo Styler” to eliminate the maxima of PA.

The resistance to constant current of $Cu_xS – Cu_yTe$ layers with different composition was measured on an E 7 – 8 numerical measuring device with special electrodes.

RESULTS AND DISCUSSION

The nature of sulfur-containing particles sorbed by a PA film was studied by means of IR and UV absorption spectra of the polymer films treated in the solutions of telluropentathionates.

It was found that the peaks of most intensive bands in the IR spectra of chalcogenized PA samples recorded by the compensation method (PA absorption eliminated) were in the intervals 432 – 485, 523, 584 – 731, 835 – 1046, 1094 – 1264 cm^{-1} (Fig. 1). According to the literature data [16 – 19] the peaks in the first interval were assigned to the valence vibrations in the S–S bond ($\nu_{S–S}$), at 523 cm^{-1} – to the asymmetric deformation O–S–O vibrations, δ_{as}(O–S––O), in the third interval to the symmetric deformation O–S–O vibrations, δ_s(O–S–O), in the fourth interval – to the symmetric valence S–O vibrations, ν_s(S–O), and in the fifth interval – to the asymmetric valence S–O vibrations, ν_{as}(S–O). The similarity of the IR spectra of chalcogenized PA samples and of the polythionates – selenopolythionates indicates that the sorption of telluropentathionate ions by a PA occurs during the polymer treatment with the solutions of telluropentathionates.

The UV-VIS absorption spectra of PA, of PA treated in a solution of $H_2TeS_4O_6$ and of chalcogenized and treated with Cu(II/I) solution PA are shown in Figure 2. Four absorption maxima are observed in the spectra of chalcogenized PA: at ~228 nm, ~256 nm and ~284 nm – as the peaks, and at ~354 nm and ~428 nm – as the shoulders. According to the data of the study of the UV absorption spectra of polythionates and selenopolythionates [20 – 23], the absorption maxima of polythionate and selenopolythionate ions as shoulders and peaks are at ~215, ~250, ~290 and ~340 nm. Thus, the similarity of the UV spectra of chalcogenized PA samples and of the polythionates-selenopolythionates indicates again that the sorption of telluropentathionate ions by a PA occurs during the polymer treatment with the solutions of telluropentathionates.

In this work the kinetics of sorption-diffusion of tellurium and sulfur from the solutions of telluropentathionates into PA film was investigated (Figs 3, 4). It was found that the concentration of tellurium and sulfur in the samples (C_{Te}, C_s, μmol·cm^{-3}) during exposure in the solution of $H_2TeS_4O_6$ at 20 °C increases continuously with a time. Tellurium and sulfur concentrations in the ranges ~13 μmol·cm^{-3} – ~104 μmol·cm^{-3} and ~4.5 μmol·cm^{-3} – ~48 μmol·cm^{-3} respectively might be obtained by varying the conditions (duration of PA chalcogenation, the concentration and temperature of the solution of $H_2TeS_4O_6$) of PA chalcogenation.

In order to form copper chalcogenide layers on the surface of PA films, the chalcogenized PA samples were treated for 10 min with the Cu(II/I) salt solution at 78 °C. It was found that the amount of copper in the chalcogenide layer increased with the time of PA chalcogenation in the solutions of telluropentathionates (Fig. 5).

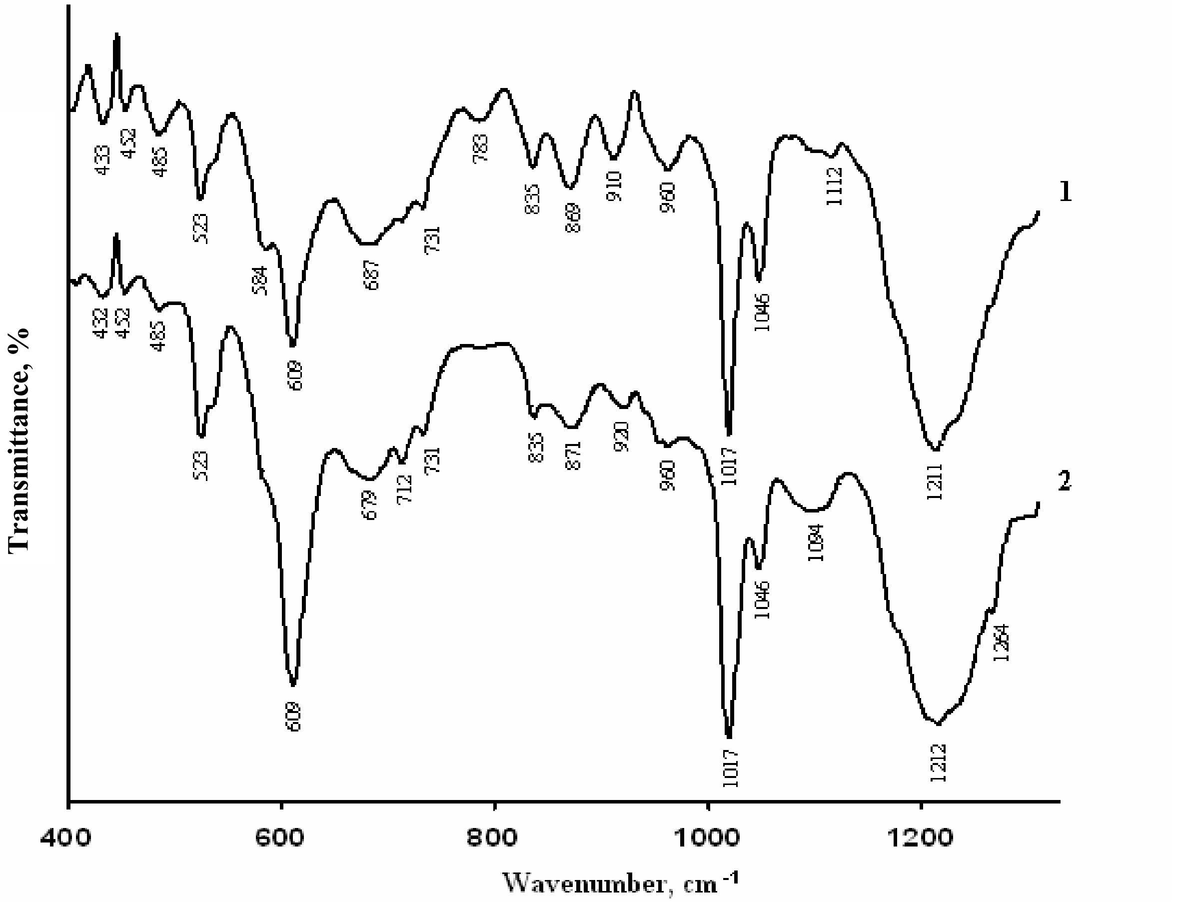

Fig. 1. IR absorption spectra of a PA films treated with a solution of $H_2TeS_4O_6$ of different concentration at 20 °C during 121 h. The concentration of $H_2TeS_4O_6$ solution, mol·dm^{-3}: 1 – 0.01, 2 – 0.05

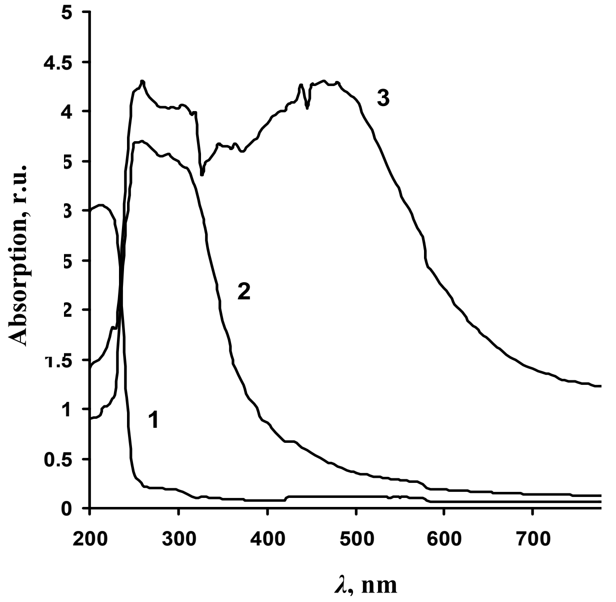

Fig. 2. UV absorption spectra: 1 – of PA film, 2 – of PA surface after 24 h exposure in 0.1 mol·dm^{-3} solution of $H_2TeS_4O_6$ at 20 °C, 3 – of copper chalcogenides on PA after interaction with Cu(II/I) salt solution

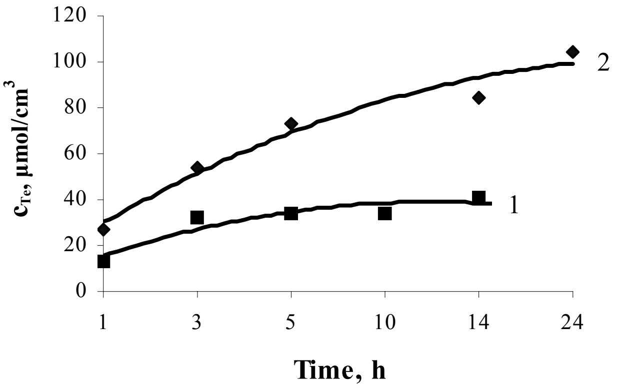

Fig. 3. Change of tellurium concentration in PA with time during its treatment with a $H_2TeS_4O_6$ solution at 20 °C. The concentration of $H_2TeS_4O_6$ solution, mol·dm^{-3}: 1 – 0.01, 2 – 0.05

The amount of copper in the layer increases with an increase in the chalcogen concentration. That is completely understandable since with a higher concentration of sulfur and tellurium sorbed-diffused into the PA a larger amount of Cu^+ and Cu^{2+} ions may be involved in a reaction with the sulfur–tellurium species.

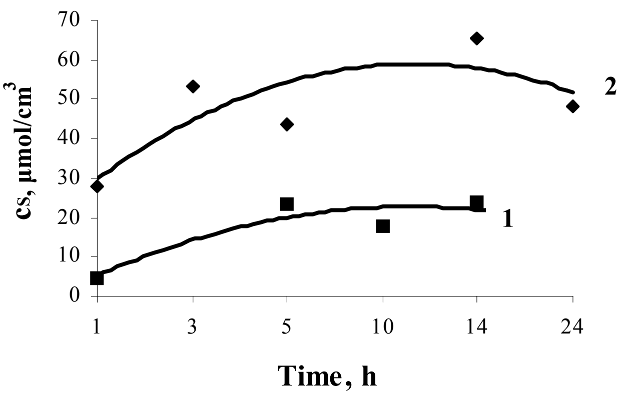

Fig. 4. Change of sulfur concentration in PA with time during its treatment with a $H_2TeS_4O_6$ solution at 20 °C. The concentration of $H_2TeS_4O_6$ solution, mol·dm^{-3}: 1 – 0.01, 2 – 0.05

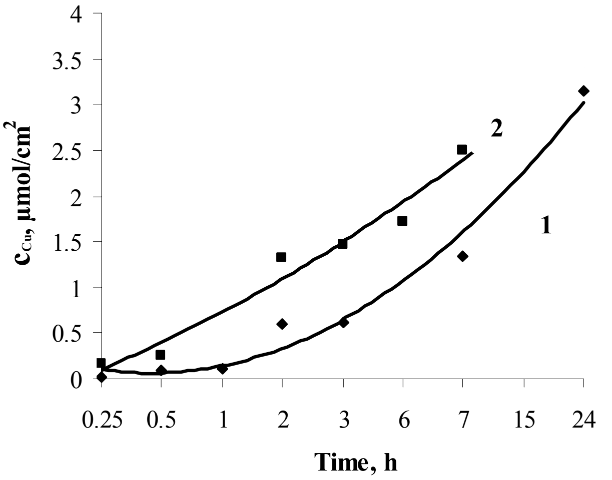

Fig. 5. Dependence of the amount of copper in chalcogenide layer on PA films on chalcogenation duration when treating it with $Na_2TeS_4O_6$ solutions in 0.2 mol·dm^{-3} HCl at 20 °C. The concentration of $Na_2TeS_4O_6$ solution, mol·dm^{-3}: 1 – 0.01, 2 – 0.05

Figure 2 shows spectrum of PA alone (absorption maximum at ~212 nm) as well as the spectra of PA chalcogenized in 0.1 mol·dm^{-3} solution of $H_2TeS_4O_6$ and of PA after treatment in Cu^+/Cu^{2+} salt solution. After interaction of copper ions with polyamide in the presence of telluropentathionate, a number of new peaks appear in the interval of 260 nm – 465 nm and change tendency was observed in comparison with that before the interaction with copper ions.

Some typical absorption peaks – a broad absorption peaks at ~465 nm and ~350 nm, respectively (Fig. 2, curve 3) in the spectra of PA chalcogenized in the solution of telluropentathionic acid and treated with a solution of Cu(II/I) salt appeared. All these peaks are higher than relevant peaks of PA before the interaction with copper indicating they belong to the absorption of copper chalcogenides species. These data in Fig. 2 are consistent with the number and intensity of copper chalcogenides phases detected according to our XRD measurements. It is suggested these new peaks show that copper sulfides – tellurides are produced after interaction with copper ions. In order to clarify the structural attribution of the new UV-VIS absorption bands, some experiments have to be carried out. The interpretation of the data on the surface of PA is complicated. Our future experiments will be focussed on the mechanism in the water solutions and further interpretation of the reactions on PA surface.

X-ray diffraction analysis enables the identification of copper chalcogenides formed on the surface of PA since the chemical composition and crystal structure of many minerals of Cu_xS and Cu_yTe has been investigated [24 – 27]. Results of this analysis are presented in Figure 6.

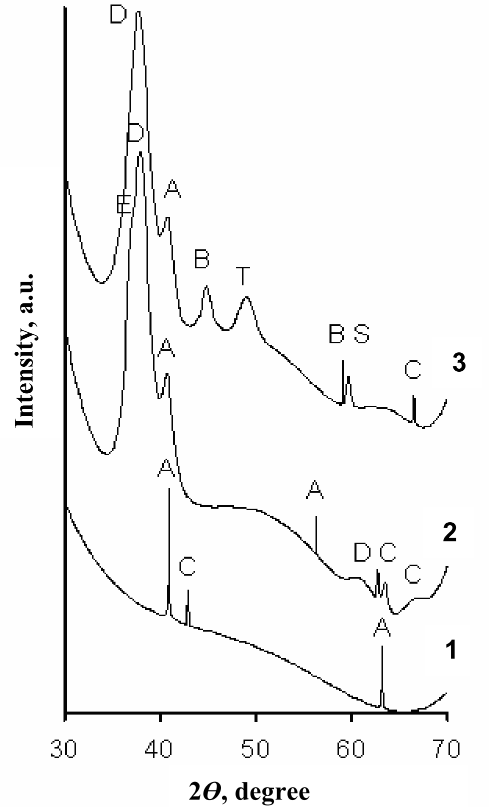

Fig. 6. X-ray diffraction patterns (A – Cu_7S_4, D – $Cu_{1.9375}S$, S – $Cu_{1.8}S$, C – Cu_2Te, T – $Cu_{3.18}Te_2$, B – CuTe, E – $Cu_{2.72}Te_2$) of copper chalcogenides layers on PA treated 3 h with $Na_2TeS_4O_6$ solution of different concentration in 0.2 mol·dm^{-3} HCl at 20 °C and with Cu(II/I) salt solution. The concentration of $Na_2TeS_4O_6$ solution, mol·dm^{-3}: 1 – 0.01, 2 – 0.025, 3 – 0.05

According to X-ray diffraction all the samples of copper chalcogenide layers on PA are polycrystalline and many of them have some binary phases such as Cu_2Te, $Cu_{3\pm\delta}Te_2$ and $Cu_{2-\delta}S$. The four phases of copper tellurides, *tetragonal* $Cu_{3.18}Te_2$ (maxima at $2\theta = 47.6°$), $Cu_{2.72}Te_2$ (maxima at $2\theta = 37.2°$), *hexagonal* Cu_2Te (maxima at $2\theta = 42.9°$, 63.5° and 66.4°) and *orthorhombic* vulcanite, CuTe (maxima at $2\theta = 41.5°$ and 58.3°), were found in the films on the PA surface, among them the three phases of copper sulfides such as *orthorhombic* anilite, Cu_7S_4 (maxima at $2\theta = 40.92°$, 55.94° and 62.8°), *monoclinic* djurleite, $Cu_{1.9375}S$ (maxima at $2\theta = 38.3°$ and 61.1°), and *orthorhombic* copper sulfide, $Cu_{1.8}S$ (maxima at $2\theta = 59.85°$).

The electrical resistances of the layers of copper chalcogenides with various composition formed over a wide concentration range 0.01 mol·dm^{-3} – 0.1 mol·dm^{-3} of precursors solution were measured at room temperature.

The electrical properties of investigated films are very dependent on the variations in the chemical and phase composition of the films, i. e. on the concentration of Te, S and amount of Cu in chalcogenide layer on PA surface (Table). The use of telluropentathionic acid enables the formation on the surface of PA electrically conductive layer of copper sulfides–tellurides with electrical resistance in the range of $6.0 \cdot 10^3$ kΩ/□ to 1.0 kΩ/□ (Table) in dependence on the concentration of initial precursor' solution. This value exhibits a minimum at the exposure time 121 h for copper sulfides–tellurides containing layers (Table 1).

Table 1. The resistance (kΩ/□) of Cu–Te–S films on PA for different concentration of initial solution of $H_2TeS_4O_6$ at 20 °C

Exposure time, h	Concentration of $H_2TeS_4O_6$ solution, mol·dm^{-3}		
	0.01	0.05	0.1
1	–	650	$1.45 \cdot 10^3$
2	–	–	$5.35 \cdot 10^3$
3	$2.0 \cdot 10^3$	2.70	568
5	$6.0 \cdot 10^3$	415	–
10	$1.6 \cdot 10^3$	14.2	–
14	$4.0 \cdot 10^3$	4.5	–
17	–	–	1.24
24	$2.7 \cdot 10^3$	2.8	1.31
65	–	–	–
121	$1.5 \cdot 10^3$	1.74	0.91

Variation in the conductivity of layers of Cu–Te–S on the surface of PA shows evident increase with increasing of the mass fraction of sorbed tellurium. The resistance value can be controlled by choosing the concentration of the original precursor solution and the exposure time.

CONCLUSIONS

1. The sorption-diffusion of telluropentathionate ions, $TeS_4O_6^{2-}$, from 0.01 mol·dm^{-3} – 0.1 mol·dm^{-3} water solution of telluropentathionic acid, $H_2TeS_4O_6$, by polyamide 6 films has been studied by IR (400 cm^{-1} – 1300 cm^{-1}), UV (200 nm – 400 nm) absorption spectra and chemical methods.
2. The peaks in the IR spectra of the telluropentathionate anions sorbed into a polyamide were found in the intervals 432 – 485, 523 – 524, 584 – 731, 835 – 1046, 1094 – 1264 cm^{-1}and assigned to the $\nu_{S–S}$, δ_{as}(O–S–O), δ_s(O–S–O), ν_s(S–O) and ν_{as}(S–O), respectively. Four absorption maxima were observed in the UV absorption spectra: at ~228 nm, ~256 and ~284 nm – as peaks, and at ~354 nm and ~428 nm – as shoulders. The spectral data indicates that the sorption of telluropentathionate ions by PA occurs during the polymer treatment with the solutions of telluropentathionates.
3. The concentration of tellurium and sulfur sorbed by a polymer increases with increasing the duration of polymer treatment in $H_2TeS_4O_6$ solution and the concentration of this solution. The layers of copper sulfide–copper telluride were formed in the surface of polyamide 6 film when the chalcogenized polymer later treated with an solution of Cu(II/I) sulfate.
4. The amount of copper in the chalcogenide layers increases with the increase of concentration of sulfur and tellurium in polyamide. The chemical and phase composition of copper chalcogenide layers depends on the conditions of the chalcogenation process. The four phases of copper tellurides, *tetragonal* $Cu_{3.18}Te_2$, $Cu_{2.72}Te_2$, *hexagonal* Cu_2Te, *orthorhombic* vulcanite, CuTe, and of the three phases of copper sulfides such as *orthorhombic* anilite, Cu_7S_4, *monoclinic* djurleite, $Cu_{1.9375}S$, and *orthorhombic* copper sulfide, $Cu_{1.8}S$, have been identified in the layers by X-ray diffraction.
5. The use of telluropentathionic acid as precursor enables the formation on the surface of PA electrically conductive layer of copper sulfides – tellurides with electrical resistance in the range of $6.0 \cdot 10^3$ kΩ/□ to ~1.0 kΩ/□ in dependence on the concentration of initial precursor solution. The resistance value can be controlled by choosing the concentration of the original precursor solution and the exposure time.

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