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Studies on Application as Precursor of Selenotrithionate and the Mechanism of Seleniumization Polyamide 6 Films

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Using of UV, VIS and IR absorption spectra it is shown that the selenotrihionate anions ($Se(SO_3)_2^{2-}$) are sorbed-diffused into a polyamide 6 films if they are treated with the solution (0.05 mol·dm^{-3}) potassium selenotrithionate $K_2Se(SO_3)_2$ in 0.1 mol·dm^{-3} HCl at 60 °C up to 4.0 h. The study of UV, VIS and IR absorption spectra and the chemical analyzes of polyamide 6 films treated with solution of potassium selenotrithionate have proved that sorbed $Se(SO_3)_2^{2-}$ anions decompose in polymer with time. It is also determined selenium containing anions remained in polyamide 6 but sulphur contained anions were washed out. The concentration of sorbed-diffused selenotrithionate ions increases with the increase in duration of treatment up to 1.5 h when the decomposition of sorbed-diffused anions begun. The atomic force microscopy (AFM) images of polyamide 6 film show that the surface of polymer is covered with the separate island of selenium when selenization time of polyamide 6 is 1.5 h. With the longer selenization time the island of selenium spread denser on surface of polyamide 6. The copper selenide, Cu_xSe, layers are formed in the surface of polyamide 6 film if the selenized polymer is treated with Cu(I–II) salt solution (10 min, 80 °C): the anionic particles $Se(SO_3)_2^{2-}$ and its decomposition products containing selenium atoms of low oxidation state react with the copper(I–II) ions. The X-ray diffraction analysis confirmed the formation of copper selenide layers in the surface of polyamide 6. Three phases – $CuSe_2$, $Cu_{2-x}Se$ and Cu_2Se were identified in the copper selenide layers by XRD analysis. The modified polymer from dielectric become electroconductive (56.8 Ω/□ – 135.0 Ω/□).

Keywords: selenotrithionate, polyamide 6, sorption-diffusion, IR and UV spectroscopy, copper selenide layers.

INTRODUCTION

Modification of polymeric materials broaden the fields of their application. Polymers are often modified by thin electrycally conductive or semi-conductive films of binary inorganic compounds, particulary of metal chalcogenides [1–4]. Copper chalcogenides are interesting semiconductor compounds with various applications. $Cu_{2-x}Se$ films are typically *p*-type, highly conductive, semitransparent, semiconductors with band gap varying between 1.1 eV and 1.4 eV, suitable for solar energy conversion and as semitransparent layer in high speed detectors working in visible range [5, 6]. Cu_2Se is used as a window layer for solar cells, for photovoltaic cells of Shoty-diodes [7, 8], as radiation filters [9]. Cu_xSe thin film s was prevously focused mostly on their possible use in solar cells and superionic conductors [10, 11].

Hydrophilic and hydrophobic polymers are capable of absorbing ions of various electrolytes from aqueous solutions [12]. Therefore, this fact enabled us to form copper sulfide layers on polyamide and polyethylene by a sorption-diffusion method [13, 14]. In the first stage, polythionates, $S_n(SO_3)_2^{2-}$, i. e. compounds containing divalent sulfur atom chains are introduced into PA [15], and in the second stage, PA 6 is treated with a solution of Cu(I–II) salt.

Selenides, being very similar to sulphides, in their properties, are considerably better semiconductors. Therefore it was important to investigate the formation of these layers. However, selenides and polyselenides are soluble in water and readily oxidise in air, and this complicates the treatment of these compounds considerably. Selenopolytionates are considerably more stable than selenide. We have investigated the possibility to use selenopolythionates because of their higher stability to form selenide layers.

Selenopolythionates ($Se_xS_yO_6^{2-}$, where x = 1 – 7, y = 2 – 7) were investigated at Kaunas University of Technology for a number of years, but their practical application was rather limited. In this study the simplest selenopolythionate – selenotrithionate ($Se(SO_3)_2^{2-}$) of homological series $SeS_xO_6^{2-}$, where x = 2, 3, 4, was chosen for the modification polyamide 6 (PA 6) films.

The aim of present work was to prove that anions of selenotrithionate ($Se(SO_3)_2^{2-}$) have been sorbed by PA 6 film from the water solutions of potassium selenotrithionate, $K_2Se(SO_3)_2$, and to investigate the changes of sorbed selenotrithionate anions during polymer seleniumization process as well as to determine the possibility to form the copper selenide layers on the surface of seleniumized polymer.

EXPERIMENTAL

The films of polyamide 6 (specification TY 6-05-1775-76, grade PK-4) 15 mm × 70 mm in size of 70 μm thickness were used. This PA 6 film is close to a non-porous 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). Before the chalcogenation, 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.

The PA 6 films thus prepared were treated in a thermostatic vessel using a continually stirred $K_2Se(SO_3)_2$ solution. The 0.05 mol/dm^3 solutions of $K_2Se(SO_3)_2$ in 0.1 mol/dm^3 HCl at 60 °C were used. At the certain time

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intervals, the samples were removed, rinsed with distilled water, dried over $CaCl_2$, and then used in the analysis and further experiments. The total duration of experiments was 4 h.

The salt of potassium selenotrithionate, $K_2Se(SO_3)_2$, was prepared and chemically analyzed according to procedures presented in [16].

The concentration of selenium in a PA 6 film was determined using the method of atomic absorption spectrophotometry [17]. A modified PA 6 film were dissolved in concentrated nitric acid and selenium, present in the resulting solution, was determined by the atomic absorption spectrometer "Perkin-Elmer-503"; wavelength $\lambda = 196$ nm, diffractive gap – 5 (2.0 nm), electrodeless discharge lamp, air-acetylene flame. For the standard conditions described above, the sensitivity is about 0.5 μg/ml Se for 1 % absorption.

The concentration of sulfur in PA 6 film was determined nephelometrically as described in reference [18]. The photometer colorimeter KFK-3 (Russia) for the determination of the optical density of the solution at the wavelength 405.0 nm was used. For the preparation of this solution the chalcogenized PA 6 film was treated simultaneously like for the preparation of selenium determination by the atomic absorption spectrometry. 10 cm^3 of the solution was diluted to 50 cm^3. Then to 20 cm^3 of resulting solution the 5 cm^3 of 0.1 N HCl solution was added and evaporated to dryness. This procedure was used for the complete elimination of NO_3^- anions, which interfer the further analysis, and it was repeated few times. Then the residual precipitate was dissolved in water, 5 $cm^3$of 0.1 $mol\cdot dm^{-3}$ $BaCl_2$ solution added and the mixture diluted to 25 cm^3. If the sulfur was present in the solution, the resulting mixture becomes turbid ($BaSO_4$). Using the data of solution optical density measurements and the calibratrion curve, the concentration of sulphate ions in the solution and finally – the concentration of sulfur in the initial chalcogenized PA 6 film was calculated.

The samples of seleniumized PA were treated with a solution of Cu(I–II) salt at 80 °C for 10 min. A Cu Cu(I–II) salt solution was made from crystalline $CuSO_4\cdot 5H_2O$ and hydroquinone as described in Refs [19, 20]. It is a mixture of Cu salts, containing 0.34 mol/dm^3 of Cu(II) and 0.06 mol/dm^3 of Cu(I) [20]. After the treatment with the solution of Cu(I–II) salts, the samples of polymers were rinsed with distilled water, dried over anhydrous $CaCl_2$ and used in further experiments.

Surface of the PA 6 films were characterized with atomic force microscope (AFM) measurements were made with a Quesant Corp., QScope-250 instrument. The dry films were investigated by AFM in the contact mode using commercial (Nano Technology Instruments – Europe BV) Si cantilevers CSG10 series with a force constant 0.2 Nm^{-1} and tip curvature 10 nm. The images were anlyzed and images metrology was made using SPIP (Image Metrology) and Quesant Corp. software.

The UV and Visible (200 nm – 500 nm) and IR (400 cm^{-1} – 1400 cm^{-1}) spectra were obtained on a Spectronic^R Genesys^{TM} and Perkin–Elmer GX spectrophotometers. UV and Visible spectra were recorded with compensation of the absorption of PA.

X-ray diffraction analysis of seleniumized PA 6 films and copper selenide layers on the polymer surface was performed with a DRON-6 diffractometer provided with a special device for beam limitation at low and medium diffraction angles using graphite-monochromatized Cu-Kα radiation source ($\lambda = 1.54178$ Å) under a voltage of 30 kV and a current of 30 mA. The XRD patterns were recorded with a step size of 0.05° from $2\theta = 28°$ to 70°. X-ray diffractograms of modified PA 6 films were treated using the program Search Match.

The resistance at constant current of the copper selenide layers formed on PA 6 films samples seleniumized 0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5 and 4.0 h was measured using an E7-8 numerical measuring instrument with special electrodes.

RESULTS AND DISCUSSION

Depending on the duration of treating the PA 6 films with the solution of the selenotrithionate, the colour of PA 6 films change from colourless, light yellow, through intensive yellow, orange and red. The acid decomposition of selenotrithionate is known to take place through intermediate formation of $Se_n(SO_3)_2^{2-}$ ions [21], the colour of which varies from yellowish, characteristic of diselenotetrathionate $Se_2(SO_3)_2^{2-}$ to dark red characteristic of selenopolythionates possessing 5 ÷ 7 or even more selenium atoms per molecule. This confirm the sorption of ions of selenopolythionates by polymer. After colourless or light yellow PA 6 films were treated with hydrochloric or nitric acids, they, as anticipated, turn reddish due to the liberation of elemental red colloidal selenium by equation [21]:

$$Se(SO_3)_2^{2-} + 2H^+ \rightarrow Se\downarrow + SO_2 + H_2SO_4, \qquad (1)$$

When seleniumized PA 6 films were treated with solution of $AgNO_3$, the colourless surface of polymer acquired a black colour due to the formation of Ag_2Se by equation [22]:

$$Se(SO_3)_2^{2-} + 2Ag^+ + H_2O \rightarrow Ag_2Se\downarrow + 2H_2SO_4, \qquad (2)$$

The sorbed anions of $Se(SO_3)_2^{2-}$ in polymer were also characterized by optical methods of IR and UV absorption spectra.

The nature of selenium-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 selenotrithionate.

The UV absorption spectra of PA 6 films seleniumized for different periods of time in a solution of $K_2Se(SO_3)_2$ are shown in Figure 1. The absorption maxima of freshly prepared solution of $K_2Se(SO_3)_2$ is observed at 250 nm (curve 2). The same absorption maxima are observed in spectra of PA 6 films, treated with solution of $K_2Se(SO_3)_2$. The intensity of these absorption maxima in the UV spectra, as expected, increases with an increase of the duration of a polymer treatment with a solution of potassium selenotrithionate (curves 1, 3 – 5). When PA 6 films were seleniumized longer as 1.5 hour, the new absorption maxima spring up. For example, new absorption maxima at 280 nm of PA 6 seleniumized 2 h are observed (curve 6). When PA 6 film was seleniumized 3 h

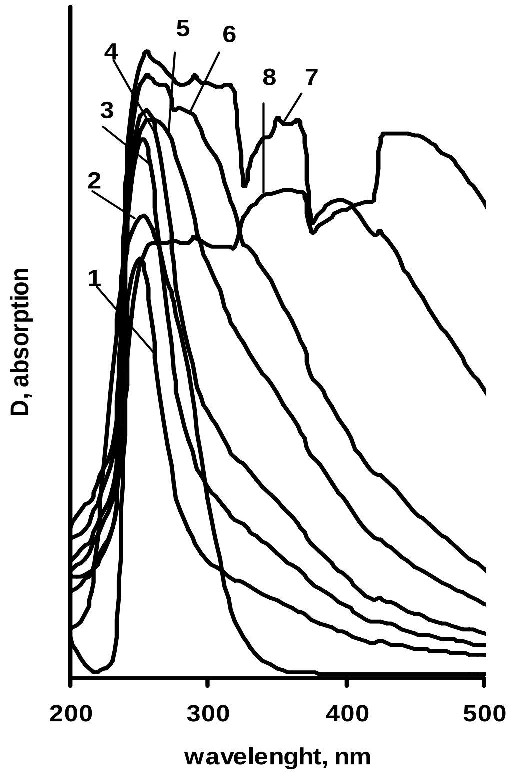


Fig. 1. UV absorption spectra of PA 6 films seleniumized with a solution of $K_2Se(SO_3)_2$ at different periods of time. Duration of PA 6 seleniumization, h: 1 – 0.25, 2 – $K_2Se(SO_3)_2$, 3 – 0.5, 4 – 1.0, 5 – 1.5, 6 – 2.0, 7 – 3.0, 8 – 4

(curve 7), the absorption maxima 280 nm drifted to right at 290 nm and three new absorption maxima at 350, 395 and 425 nm of PA 6 are observed. When PA 6 film was seleniumized 4 h (curve 8), the absorption maxima besides 255 nm specific for anion of $Se(SO_3)_2^{2-}$ disappear and three absorption maxima at 290, 360 and 425 nm of PA 6 are observed. The changes of UV absorbtion spectra with increase of duration of PA 6 films in solution of $K_2Se(SO_3)_2$ show that the sorbed anion of $Se(SO_3)_2^{2-}$ decompose by equation (1).

The IR absorption spectra of PA 6 films seleniumized for different periods of time in a solution of $K_2Se(SO_3)_2$ are shown in Figure 2. The absorption deformation of O–S–O vibrations of the affined particles of $Se(SO_3)_2^{2-}$ are displayed in the range of the wavenumber (400 – 1400) cm^{-1}. The absorption deformation of O–S–O vibrations of the affined particles of $Se(SO_3)_2^{2-}$ are displayed in the range of the wavenumber (400 – 1400) cm^{-1}. It was found that the peaks of most intensive bands in the IR spectra of PA 6 films seleniumized in a $K_2Se(SO_3)_2$ solution, recorded by the compensation method (PA 6 absorption eliminated) were in the interval of the wavenumber (520 – 640) cm^{-1}, (964 – 1047) cm^{-1} and (1132 – 1271) cm^{-1} (Fig. 2). On the backgrounds of the literature data of IR spectra of $K_2Se(SO_3)_2$ the peaks in the first interval were assigned to the asymmetric deformation O–S–O vibrations, δ_{as}(O–S––O), in the second interval – to the symmetric valence S–O vibrations, ν_s(S–O), in the third interval – to the asymmetric valence S–O vibrations, ν_{as}(S–O) [23]. No similar peaks were evident for the PA 6 films treated longer with solution of $K_2Se(SO_3)_2$. For example, IR spectra of PA 6 film seleniumized 15 min in solution of selenotrithionate in the interval of the wavenumber (520 – 640) cm^{-1} has four sharp absorption peaks at 520, 578, 600 and 640 cm^{-1}; in the interval of the wavenumber (964 – 1047) cm^{-1} – three absortion peaks at 1008, 1037 and 1047 cm^{-1}, in third interval of the wavenumber (1132 – 1271) cm^{-1} – two absorption peaks at 1190 cm^{-1} and 1218 cm^{-1} (curve 1). When PA 6 film was seleniumized 1.5 h the two strong absorbtion peaks remained in mention IR spectra at 520 cm^{-1} and 600 cm^{-1} – in the first interval, at 1008 cm^{-1} and 1047 cm^{-1}, – in the next interval and in the third interval – the different as in the intensity of the absorbtion peaks at 1190 cm^{-1} and 1218 cm^{-1} become less (curve 2). When PA 6 film was seleniumized 4 h the absorbtion peaks didn't change in two first absorbtion intervals, but in the third interval only one absorbtion peak at 1218 cm^{-1} remains (curve 3). The intensity of these peaks decreased with increasing the duration of treatment, indicating the decomposition of sorbed anions of $Se(SO_3)_2^{2-}$ in polymer.

The results of investigation PA 6 films with IR and UV absorption spectra confirm that the sorbtion of $Se(SO_3)_2^{2-}$ ions by PA 6 films occurs the polymer treatment with a solution of $K_2Se(SO_3)_2$ and sorbed ions decomposed with time.

The changes of PA 6 films surface before and during treatment in solution of $K_2Se(SO_3)_2$ were investigated by the atomic force microscopy (AFM) (Fig. 3). The surface of PA 6 films after 30 min selenization became less rough then the initial PA 6 film (Fig. 3, a and b) because of adsorption of the anions of $Se(SO_3)_2^{2-}$. The separate islands of selenium are formed on PA 6 film surface after 1.5 h selenization, when the decomposition of the solution of $K_2Se(SO_3)_2$ starts (Fig. 3, c). It is occurs when adsorbed by polymer anions of $Se(SO_3)_2^{2-}$ also decomposed and the elemental selenium remains on polymer surface. Therefore, the part of elemental selenium formed during the decomposition of solution of $K_2Se(SO_3)_2$ sorbs on PA 6 surface and of this time the PA 6 films became reddish. The island of selenium spread denser on surface of PA 6 when the seleniumization time increased up to 2.5 h (Fig. 3, d). Therefore, the thickness of film increases with increase of the seleniumization time of PA 6 films. The film thickness varies strong between the islands of selenium, forming landscape with the islands of a height 1 μm and smaller, tenths of nanometer scale islands in between.

Several studies indicate that red amorphous selenium is truly amorphous [24 – 26] and it‘s no found of the evidence of crystallinity in X-ray diffraction photographs. The red amorphous selenium and grey hexagonal selenium to be directly related to one another, because of grey hexagonal, "metallic" selenium is thermodynamically the most stable form of the element and can by formed by warming any other modification [27]. The form of red amorphous selenium is stable at room temperature, but it transforms to hexagonal selenium on heating to 60 °C – 80 °C [28]. For this the PA 6 film treated 4 h with solution of $K_2Se(SO_3)_2$ was kept in thermostat 2 h at 80 °C. The both samples were investigated by XRD analysis.

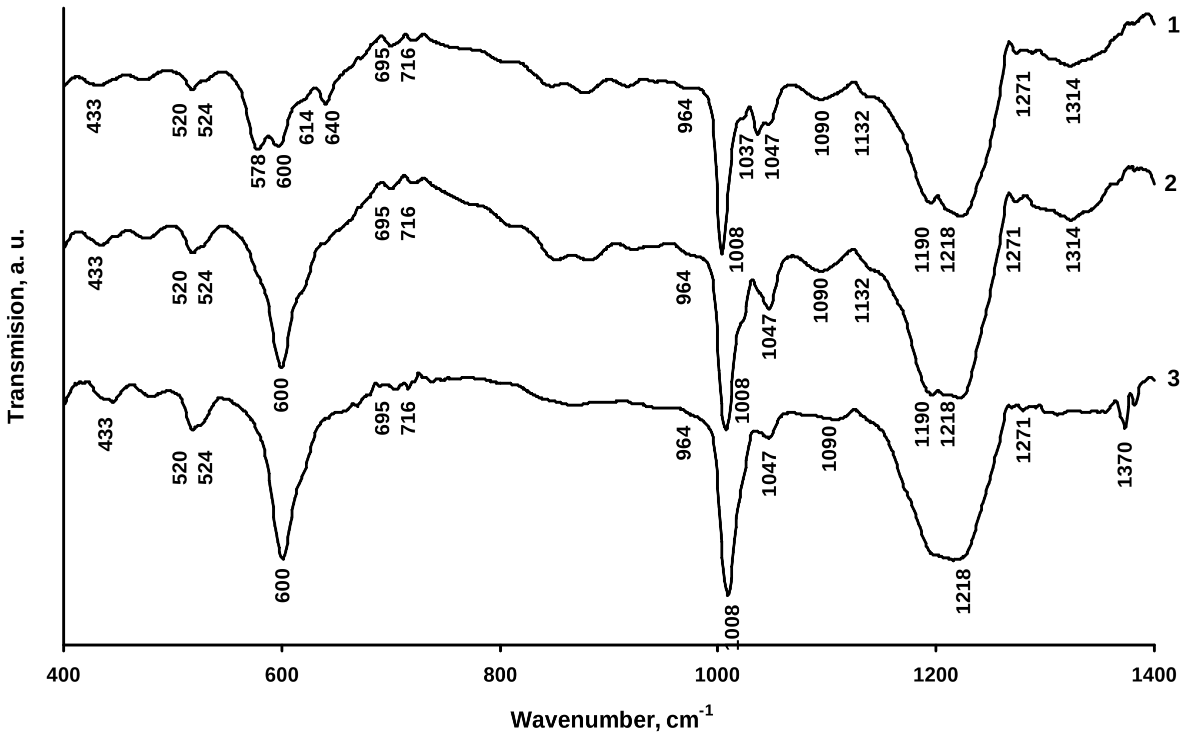
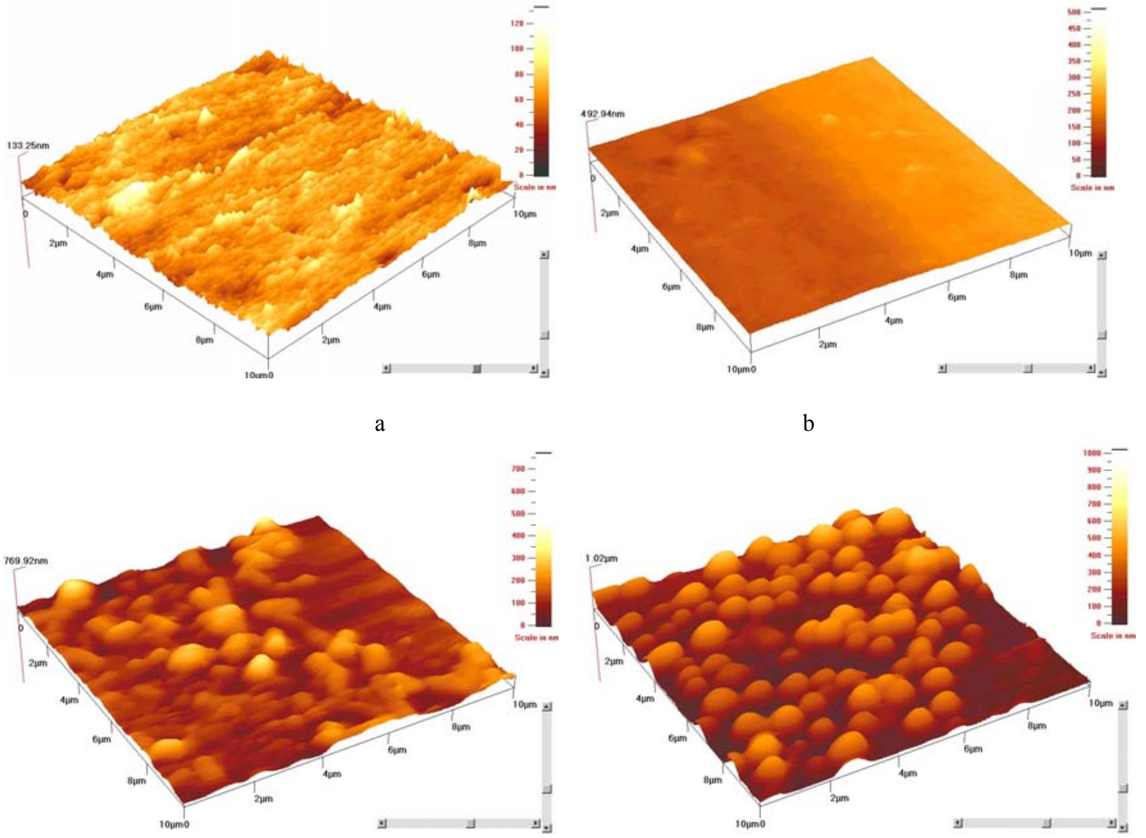


Fig. 2. IR absorption spectra of PA 6 films seleniumized with a $K_2Se(SO_3)_2$ solution at different periods of time. Duration of PA 6 seleniumization, h: 1 – 0.25; 2 – 1.50; 3 – 4.00



a b

c d

Fig. 3. AFM images: a – the initial PA 6 films; the seleniumized PA 6 films in solution of $K_2Se(SO_3)_2$ at different periods of time. Duration of PA 6 seleniumization, h: b – 0.5, c – 1.5, d – 2.5

Structural studies of the PA 6 films seleniumized by sorption-diffusion method are limited by the crystallinity of polymer. The intensities of their peaks at $2\Theta \sim 20°$ and 24° exceed intensity of selenium peaks few times. Therefore the range of $2\Theta \geq 8.0°$ was investigated more detail. As expected the XRD pattern of PA 6 film treated 4 h with solution of $K_2Se(SO_3)_2$ did not record because of the reason mentioned above. The fact that the red amorphous selenium on surface of PA 6 film has been transformed to crystal modification of selenium after 2 h heating at 80 °C, was confirmed by X-ray diffraction analysis of PA 6 films (Table 1).

Table 1. The data of the X-ray diffraction pattern of PA 6 film seleniumized in solution of $K_2Se(SO_3)_2$ 4 h and then 2 h thermostated at 80 °C

d, Å	Intensity, %	Phases
3.0982	88	Se (Pdf 75-1162) [29]
2.9270	28	Se (Pdf 75-1162) [29]
2.8178	100	Se (Pdf 75-1162) [29]
2.3086	12	Se (Pdf 75-1162) [29]
2.2142	6	Se (Pdf 73-2121) [28]
1.9883	5	Se (Pdf 73-2121) [30]
1.7838	22	Se (Pdf 75-1162) [29]

The peaks at $2\Theta = 28.73$, 30.52, 31.73, 38.98 and 51.17° (corresponding to $d = 3.0982$, 2.9270, 2.8178, 2.3086 and 1.7878 Å respectively) could be assigned to the phase of monoclinic selenium (Pdf 75-1162) [29], in which d are 3.0952, 2.9257, 2.8144, 2.3086 and 1.7850 Å) and the peaks at $2\Theta = 40.71$ and 45.59° (corresponding to $d = 2.2147$ and 1.9883 Å respectively) could be assigned to the phase of monoclinic selenium (Pdf 73-2121) [30], in which d are 2.2122 Å and 1.9843 Å).

The data of X-ray diffraction are in good agreement with the results of AFM studies because confirmed the liberation of red amorphous selenium on PA 6 films during seleniumization process.

The anions of $Se(SO_3)_2^{2-}$ in PA 6 film were determined quantitatively as well. For this, the concentration of selenium (m_{Se}) in 1 g of PA 6 film and the change of 1 g PA 6 film mass (Δm) during selenization were determined. Figure 4 shows that the concentration of selenium in PA 6 film increasing gradually with time, while that of the change of 1 g PA 6 film mass, although increasing at the initial stage, starts dropping after 1.5 h. The ratio of 1 g of the PA 6 film mass change with the selenium concentration in it $\Delta m/m_{Se}$ is close to 3 ($3.06 \div 3.00$.) up to ~1.5 h, i. e. as has been anticipated in the case of selenotrithionate ions M $SeS_2O_6^{2-}$/ M Se = 239.09/78.96 = 3.03. Later on, the ratio of $\Delta m/m_{Se}$ decreases gradually and reaches only 1.12 after 4 hours. The reduction of the ratio $\Delta m/m_{Se}$ is comparable with the decomposition of anions of $Se(SO_3)_2^{2-}$ and the liberation of elemental red colloidal selenium by mentioned above equation (1) SO_2 as well as SO_4^{2-} ions are gradually removed from the PA 6 film, only elemental selenium of fine dispersion remaining in it.

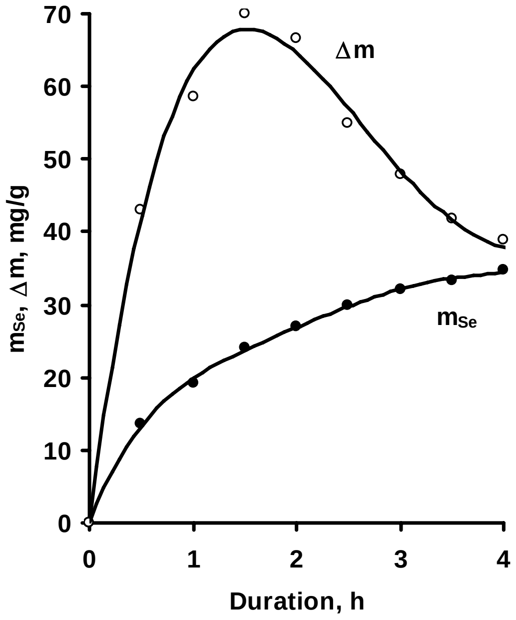


Fig. 4. Changes of PA 6 film mass (Δm) and selenium concentration in it (m_{Se}) with time on treating with $K_2Se(SO_3)_2$ solution

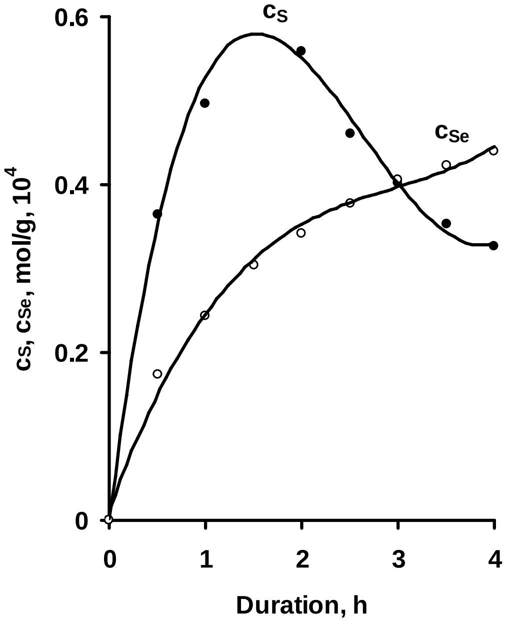


Fig. 5. Changes molar rate of sulfur (c_S) and selenium concentration (c_{Se}) in seleniumized PA 6 films in solution of $K_2Se(SO_3)_2$ at different periods of time

The changes of selenium (c_{Se}) and sulphur (c_S) molar ratio calculated to 1 g of polymer confirmed the decomposition of sorbed anions of $Se(SO_3)_2^{2-}$ in PA 6 films. Figure 5 shows that the molar ratio of selenium in a PA 6 film increases gradually with time, while that the molar ratio of sulphur, although increases up to 1.5 h and then decreases. Therefore, at the beginning of the process ($1 \div 1.5$ hours), the molar ratio of c_{Se}/c_S in the PA 6 film is more-less close to two, i. e. is similar that in an anion of selenotrithionate. However, later the ratio decreases to 0.74. This can be explained by the decomposition of $Se(SO_3)_2^{2-}$ ion mentioned above.

Thus, the results obtained have proved, that the selenium from selenotrithionate solutions gets into the PA 6 film as $Se(SO_3)_2^{2-}$ ions, which decompose with time in the film due to the autocatalytic decomposition.

The second aim of this work was to prove the suitability of seleniumized PA 6 films with solution of $K_2Se(SO_3)_2$ for formation the copper selenide layers on polymer. For this the seleniumized PA 6 films were treated with Cu(I–II) salts solution. Changes of a PA 6 films appearance after its treatment with the Cu(I–II) salt solution also indicate the formation of copper selenide layers on the surface of a polymer. Colour of tapes from colourless, light yellow, orange or red transforms into brown, then – into black, and acquires a metallic lustre. Electrical measurements finally indicate that layers from dielectric become conducting and sheet resistance of Cu_xSe layers on PA 6 films varies in the interval of (56.8 – 135.0) Ω/□. The fact, that the formation of Cu_xSe takes place by keeping seleniumized PA 6 samples in the solution of Cu (I–II) salts, was confirmed by the X-ray diffraction analysis of the Cu_xSe layers formed (Table 2). The peaks at $2\Theta = 32.6°$ and 49.1° (corresponding to $d = 2.7484$ Å and 1.8384 Å respectively) could be assigned to the phase of *orthorombic* copper selenide ($CuSe_2$) (Pdf 74-280) [31], in which d are 2.7474 Å and 1.8376 Å), the peaks at $2\Theta = 38.12°$ and 41.0° (corresponding to $d = 2.3483$ Å and 2.1999 Å respectively) could be assigned to the phase of *monoclinic* copper selenide (Cu_2Se) (Pdf 27-1131) [32], in which d are 2.3480 Å and 2.1990 Å) and peaks at $2\Theta = 44.9°$ (corresponding to $d = 2.033$ Å respectively) could be assigned to the phase of *cubic* berzelianite ($Cu_{2\text{-}x}Se$) (Pdf 6-680) [33], in which d are 2.030 Å).

Table 2. The data of the X-ray diffraction pattern of PA 6 film 1.5 h seleniumized in solution of $K_2Se(SO_3)_2$ and after its treated with the Cu(I–II) salt solution

d, Å	Intensity, %	Phases
2.7484	50	$CuSe_2$ (Pdf 74-280) [31]
2.3483	100	Cu_2Se (Pdf 27-1131) [32]
2.1999	57	Cu_2Se (Pdf 27-1131) [32]
2.0330	63	$Cu_{x\text{-}2}Se$ (Pdf 6-680) [33]
1.8384	40	$CuSe_2$ (Pdf 74-280) [31]

The XRD analysis of modified PA 6 films proved the possibility to apply of the $Se(SO_3)_2^{2-}$ anions as the precursors for formation the electroconductive copper selenide layers on this polymer.

CONCLUSIONS

1. The sorption-diffusion of selenotrithionate ions, $Se(SO_3)_2^{2-}$, from 0.05 mol/dm^{-3} solution of potassium trithionate, $K_2Se(SO_3)_2$, in HCl by polyamide 6 films has been studied by means of IR (400 cm^{-1} – 1400 cm^{-1}) and UV (200 nm – 500 nm) absorption spectra and chemical methods.
2. The peaks in the IR spectra of the selenotrithionate anions sorbed into a polyamide were found in the intervals (520 – 640) cm^{-1}, (964 – 1047) cm^{-1} and (1132 – 1271) cm^{-1} and assigned to the δ_{as}(O–S–O, ν_s(S–O) and ν_{as}(S–O) respectively. One absorption maxima at ~250 nm was observed in the UV absorption spectra as shoulders up to 1.5 h of polymer seleniumization. Later new absorption maxima sprig up because of decomposition sorbed anions of $Se(SO_3)_2^{2-}$. The spectral data confirm that selenium is sorbed by PA films in the form of selenotrithionate ions.
3. The changes of molar ratio of Se:S in seleniumized PA 6 films with time confirm spectral data that selenium is sorbed by PA films in the form of selenotrithionate ions and the decomposition starts. The chemical analyzis of seleniumized PA 6 films confirmed that sorbed anions of $Se(SO_3)_2^{2-}$ began to decompose in polymer after 1.5 hour from the start of selenization. The elemental selenium remains in polyamide 6 films therefore other decomposition products SO_2 and SO_4^{2-} ions gradually remove from the polymer.
4. The surface of PA 6 films during treatment in the solution of $K_2Se(SO_3)_2$ has been changed. The surface of seleniumized PA 6 films with time became less rough then the initial polymer film. The separate islands of red amorphous selenium are formed on polymer surface and with time the island of selenium spread denser on surface of PA 6 films.
5. The use of selenotrithionate solution as selenization precursor enables the formation on the surface of PA 6 films the copper selenide layer. XRD analysis of the surface of PA 6 films after its seleniumization and treatment with solution of Cu(I–II) salts showed the formation layer composed of *orthorombic* and *monoclinic* copper selenides ($CuSe_2$ and Cu_2Se) and *cubic* berzelianite ($Cu_{2-x}Se$). The PA 6 films after modification changes from dielectric to conductive. The sheet resistance values of modified PA 6 films surface varied in the interval of (56.8 – 135.0) Ω/□.

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REFERENCES

1. **Žebrauskas, A., Mikalauskienė, A.** The Copper Sulfide Coatings Resistivity Dependence on Deposition and Annealing *Chemija* 3 1993: pp. 84 – 89 (in Russian).
2. Patent LT 4235, 1997 (in Lithuanian).
3. Patent LT 4402, 1998 (in Lithuanian).
4. Patent LT 5119, 2004 (in Lithuanian).
5. **Okimura, H., Matsumae, T., Makabe, R.** Electrical Properties of $Cu_{2-x}Se$ Thin Films and Their Application for Solar Cells *Thin Solid Films* 71 (1) 1980: pp. 53 – 59.
6. **Bhuse, V. M., Hankare, P. P., Garadkar, K. M., Khomane, A. S.** A Simple, Convenient, Low Temperature Route to Grow Polycrystalline Copper Selenide Thin Films *Materials Chemistry and Physics* 80 (1) 2003: 82 – 88.
7. **Haram Santosh, K., Santhanam, K. S. V.** Photoelectrochemical Responses of Orthorhombic and Cubic Copper Selenides *Journal of Electroanalytical Chemistry* 396 (1 – 2) 1995: pp. 63 – 68.

8. **O'Brien, R. N., Santhanam, K. S. V.** Laser Interferometry of Electroless Deposition of Copper Selenide *Journal of Electroanalytical Chemistry* 260 (1) 1989: pp. 231 – 235.
9. **Garcia, V. M., Nair, P. K., Nair, M. T. S.** Copper Selenide Thin Films by Chemical Bath Deposition *Journal of Crystal Growth* 203 (1 – 2) 1999: pp. 113 – 124.
10. **Lakshmikumar, S. T.** Selenization of Cu and In Thin Films for the Preparation of Selenide Photo-absorber Layers in Solar Cells Using Se Vapour Source *Solar Energy Materials and Solar Cells* 32 (1) 1994: pp. 7 – 19.
11. **Lévy-Clément Claude, Neumann-Spallart, M., Haram, S. K., Santhanam, K. S. V.** Chemical Bath Deposition of Cubic Copper (I) Selenide and its Room Temperature Transformation to the Orthorhombic Phase *Thin Solid Films* 302 (1 – 2) 1997: pp. 12 – 16.
12. **Zaikov, G. E., Yordanskiy, A. L., Markin, V. S.** Diffusion of Electrolytes into the Polymers. Moscow, 1984 (in Russian).
13. **Ancutienė, I., Janickis, V., Ivanauskas, R., Stokiene, R., Kreiveniene, N.** Preparation and Some Properties of Conductive Copper Sulfide, Cu_xS, Nanofilms Formed on the Polymers Surface by the Use of Polythionic Acids *Polish Journal of Chemistry* 81 (3) 2007: pp: 381 – 391.
14. **Ancutienė, I., Janickis, V., Ivanauskas, R.** Formation and Characterization of Conductive Thin Layers of Copper Sulfide (Cu_xS) on the Surface of Polyethylene and Polyamide by the Use of Higher Polythionic Acids *Applied Surface Science* 252 (12) 2006: pp: 4218 – 4225.
15. **Foss, O.** Advances in Inorganic Chemistry and Radiochemistry. Emeleus H. J., Sharpe A. G. (ed.). New York: Academic Press 2 1960: pp. 237 – 278.
16. **Rathke, B. J.** Zur Kenntnis der Chemischen Achnlichkeit von Schwefel und Selen; Selenodithionige Saure, – Selentrithionsaure *Journal fur Practishe Chemic* 95 1865: pp. 1 – 48 (in German).
17. An Atomic Absorption, Analytical Methods for Atomic Absorption Spectrometry Perkin–Elmer-503, Perkin Elmer, 1973.
18. **Williams John, W.** Handbook of Anion Determination. Khimija, Moscow, 1982 (in Russian).
19. **Janickis, V., Maciulevičius, R., Ivanauskas, R., Ancutienė, I.** Chemical Deposition of Copper Sulfide Films in the Surface of Polyamide by the Use of Higher Polythionic Acids *Colloid and Polymer Science* 281 2003: pp. 84 – 89.
20. **Ancutienė, I., Janickis, V., Grevys, S.** Modification of Polyethylene Film Sulphurized in a Solution of Higher Polythionic Acids by Layers of Copper Sulphides *Chemija* 2 1997: pp. 3 – 10.
21. **Zelionkaitė, V. I., Janickij, I. V., Šuliakienė, I.** The Decomposition of Selenotrithionate *Transactions of Lithuanian Academy of Sciences. Chemistry and Chemical technology* 3 1963: pp. 93 – 101. (in Russian).
22. **Heuer, O.** Beitrag zur Kenntis der Selenopolythionate *Doctor. Thesis* Hannover, 1926. (in German).
23. **Janickis, V. J., Janickis, J. V.** IR Absorption Spectra of Potassium Selenopolythionates *Transactions of Lithuanian Academy of Sciences Ser. B* 6 (157) 1986: pp. 43 – 49 (in Russian).
24. **Gattow, G. Z.** Die Bildungsenthalpie von SeO_2 und die Umwandlungswärmen der Selen-Modifikationen *Zeitschrift für Anorganische und Allgemeine Chemie* 317 (3 – 4) 1962: pp. 245 – 260 (in German).
25. **Gattow, G., Heinrich, G.** Thermochemie des Selens. II. Die Umwandlungen der Kristallinen Selen-Modifikationen *Zeitschrift für Anorganische und Allgemeine Chemie* 331 (5 – 6) 1964: pp. 256 – 274 (in German)
26. **Gattow, G., Heinrich, G.** Thermochemie des Selens. III. Die Umwandlungen der Amorphen Selen-Modifikationen *Zeitschrift für Anorganische und Allgemeine Chemie* 331 (5 – 6) 1964: pp. 275 – 288 (in German).
27. **Greenwood, N. N., Earnshaw, A.** Chemistry of the Elements. Pergamon Press, Oxford, 1985.
28. **Charles Cooper, W., Westbury, R. A.** The Structure of Selenium. In: Ralph A. Zingaro and W. Charles Cooper (Eds.) *Selenium* Van Nostrand Reinhold Company, New York, 1974: 835 p.
29. **Burbank, R. D.** The Crystal Structure of α-monoclinic Selenium *Acta Crystallographica* 4 (2) 1951: pp. 140 – 148.
30. **Marsh, R. E., Pauling, L., McCullough, J. D.** The Crystal Structure of β Selenium *Acta Crystallographica* 6 (1) 1953: pp. 71 – 75.
31. **Gattow, G. Z.** Über Kupfer-Chalkogen-Verbindungen. VII. Die Kristallstruktur von $CuSe_2$ *Zeitschrift für Anorganische und Allgemeine Chemie* 340 (5 – 6) 1965: pp. 312 – 318 (in German).
32. **Murray, W., Heyding, R. O.** Private Communication. Queen’s University, Kingston Ontario, Canada, 1974.
33. **Earley, J. W.** Description and Synthesis of the Selenide Minerals *American Mineralogist* 35 (5 – 6) 1950: pp. 337 – 364.