

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

Remigijus IVANAUSKAS*

Department of Inorganic Chemistry, Kaunas University of Technology, Radvilėnų 19, LT-50254 Kaunas, Lithuania

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Using of UV, VIS and IR absorption spectra it is shown that the selenotrihionate anions ($\text{Se}(\text{SO}_3)_2^{2-}$) are sorbed-diffused into a polyamide 6 films if they are treated with the solution ($0.05 \text{ mol}\cdot\text{dm}^{-3}$) potassium selenotrihionate $\text{K}_2\text{Se}(\text{SO}_3)_2$ in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ 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 selenotrihionate have proved that sorbed $\text{Se}(\text{SO}_3)_2^{2-}$ 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 selenotrihionate 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 $\text{Se}(\text{SO}_3)_2^{2-}$ 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 ($56.8 \text{ }\Omega/\square$ – $135.0 \text{ }\Omega/\square$).

Keywords: selenotrihionate, 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 electrolycally conductive or semi-conductive films of binary inorganic compounds, particularly 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 previously 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, $\text{S}_n(\text{SO}_3)_2^{2-}$, 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. Seleno-

polythionates are considerably more stable than selenide. We have investigated the possibility to use selenopolythionates because of their higher stability to form selenide layers.

Selenopolythionates ($\text{Se}_x\text{S}_y\text{O}_6^{2-}$, 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 – selenotrihionate ($\text{Se}(\text{SO}_3)_2^{2-}$) of homological series $\text{SeS}_x\text{O}_6^{2-}$, 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 selenotrihionate ($\text{Se}(\text{SO}_3)_2^{2-}$) have been sorbed by PA 6 film from the water solutions of potassium selenotrihionate, $\text{K}_2\text{Se}(\text{SO}_3)_2$, and to investigate the changes of sorbed selenotrihionate 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) $15 \text{ mm} \times 70 \text{ mm}$ in size of $70 \text{ }\mu\text{m}$ 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 $\text{K}_2\text{Se}(\text{SO}_3)_2$ solution. The $0.05 \text{ mol}/\text{dm}^3$ solutions of $\text{K}_2\text{Se}(\text{SO}_3)_2$ in $0.1 \text{ mol}/\text{dm}^3$ HCl at 60°C were used. At the certain time

* Corresponding author. Tel.: +370-37-300172; fax: +370-37-300152.
E-mail address: remigijus.ivanauskas@ktu.lt (R. Ivanauskas)

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 selenotriethionate, $\text{K}_2\text{Se}(\text{SO}_3)_2$, 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 $\lambda = 196 \text{ nm}$, diffractive gap – 5 (2.0 nm), electrodeless discharge lamp, air-acetylene flame. For the standard conditions described above, the sensitivity is about $0.5 \mu\text{g/ml Se}$ 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 interfere the further analysis, and it was repeated few times. Then the residual precipitate was dissolved in water, 5 cm^3 of $0.1 \text{ mol}\cdot\text{dm}^{-3}$ 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 calibration 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 $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ 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 analyzed 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 GenesysTM 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-K α radiation source ($\lambda = 1.54178 \text{ \AA}$) 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 $2\theta = 28^\circ$ to 70° . X-ray diffractograms of modified PA 6 films were treated using the program Search Match.

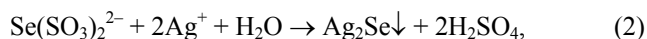
The resistance at constant current of the copper selenide layers formed on PA 6 films samples seleniumized 0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5 and 4.0 h was measured using an E7-8 numerical measuring instrument with special electrodes.

RESULTS AND DISCUSSION

Depending on the duration of treating the PA 6 films with the solution of the selenotriethionate, the colour of PA 6 films change from colourless, light yellow, through intensive yellow, orange and red. The acid decomposition of selenotriethionate is known to take place through intermediate formation of $\text{Se}_n(\text{SO}_3)_2^{2-}$ ions [21], the colour of which varies from yellowish, characteristic of diselenotetrathionate $\text{Se}_2(\text{SO}_3)_2^{2-}$ to dark red characteristic of selenopolythionates possessing 5 ÷ 7 or even more selenium atoms per molecule. This confirms 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]:



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]:



The sorbed anions of $\text{Se}(\text{SO}_3)_2^{2-}$ 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 selenotriethionate.

The UV absorption spectra of PA 6 films seleniumized for different periods of time in a solution of $\text{K}_2\text{Se}(\text{SO}_3)_2$ are shown in Figure 1. The absorption maxima of freshly prepared solution of $\text{K}_2\text{Se}(\text{SO}_3)_2$ is observed at 250 nm (curve 2). The same absorption maxima are observed in spectra of PA 6 films, treated with solution of $\text{K}_2\text{Se}(\text{SO}_3)_2$. 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 selenotriethionate (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

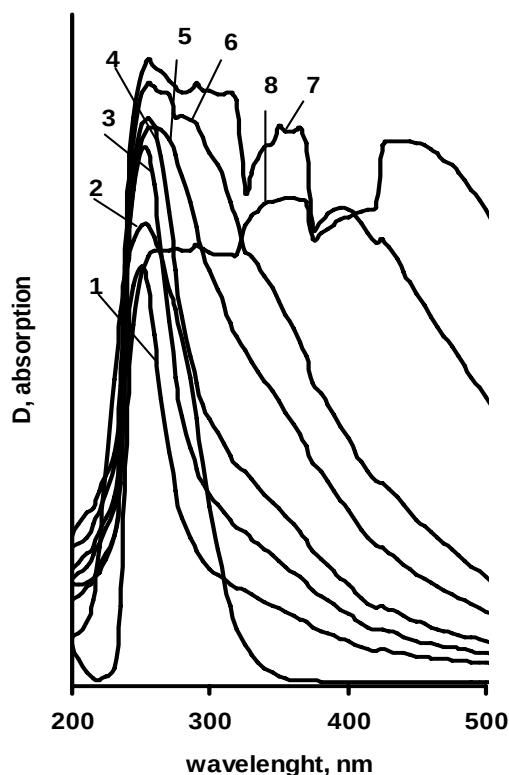


Fig. 1. UV absorption spectra of PA 6 films selenized with a solution of $K_2Se(SO_3)_2$ at different periods of time. Duration of PA 6 selenization, h: 1 – 0.25, 2 – $K_2Se(SO_3)_2$, 3 – 0.5, 4 – 1.0, 5 – 1.5, 6 – 2.0, 7 – 3.0, 8 – 4

(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 selenized 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 absorption 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 selenized 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 ($400–1400\text{ cm}^{-1}$). 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 ($400–1400\text{ cm}^{-1}$). It was found that the peaks of most intensive bands in the IR spectra of PA 6 films selenized in a $K_2Se(SO_3)_2$ solution, recorded by the compensation method (PA 6 absorption eliminated) were in the interval of the wavenumber ($520–640\text{ cm}^{-1}$, ($964–1047\text{ cm}^{-1}$ and ($1132–1271\text{ cm}^{-1}$ (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, $\delta_{as}(O-S-O)$, in the second interval – to the symmetric valence S–O vibrations, $\nu_s(S-O)$, in the third interval – to the asymmetric valence S–O vibrations, $\nu_{as}(S-O)$ [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 selenized 15 min in solution of selenotritionate in the interval of the wavenumber ($520–640\text{ cm}^{-1}$) has four sharp absorption peaks at 520, 578, 600 and 640 cm^{-1} ; in the interval of the wavenumber ($964–1047\text{ cm}^{-1}$) – three absorption peaks at 1008, 1037 and 1047 cm^{-1} , in third interval of the wavenumber ($1132–1271\text{ cm}^{-1}$) – two absorption peaks at 1190 cm^{-1} and 1218 cm^{-1} (curve 1). When PA 6 film was selenized 1.5 h the two strong absorption 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 absorption peaks at 1190 cm^{-1} and 1218 cm^{-1} become less (curve 2). When PA 6 film was selenized 4 h the absorption peaks didn't change in two first absorption intervals, but in the third interval only one absorption 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 sorption 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 $1\text{ }\mu\text{m}$ 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 be 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 $60^\circ\text{C}–80^\circ\text{C}$ [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.

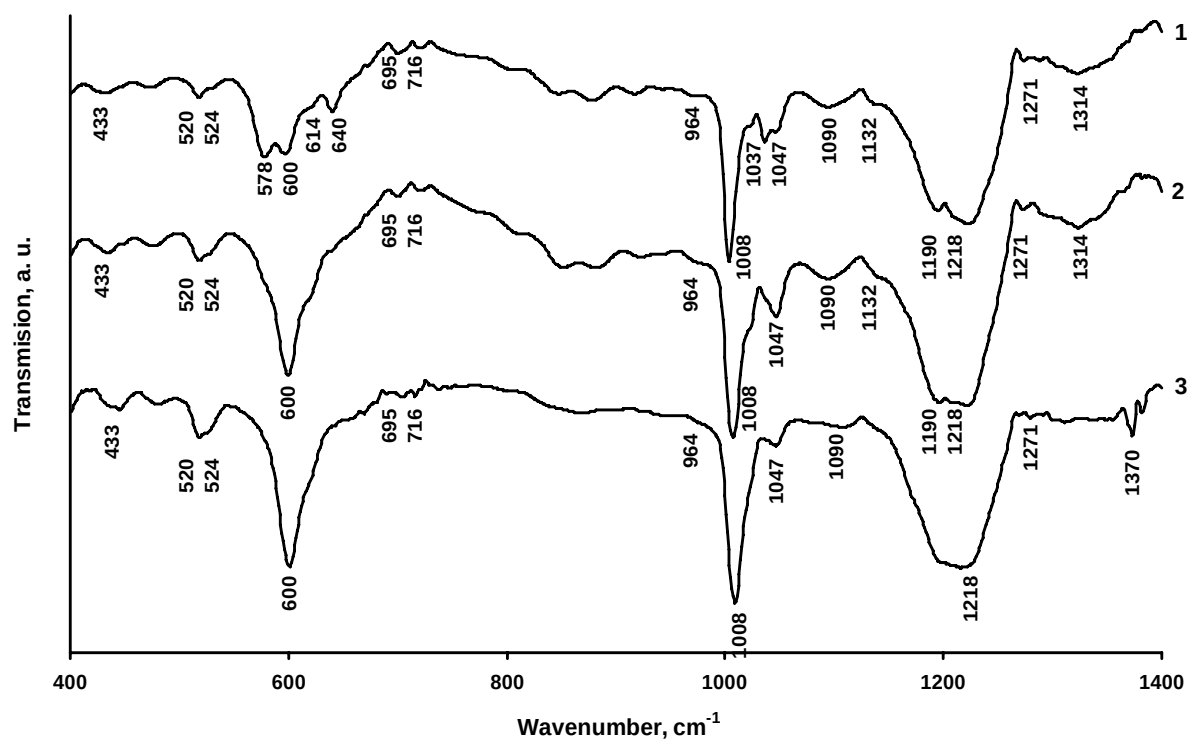


Fig. 2. IR absorption spectra of PA 6 films seleniumized with a $K_2Se(SO_3)_2$ solution at different periods of time. Duration of PA 6 seleniumization, h: 1 – 0.25; 2 – 1.50; 3 – 4.00

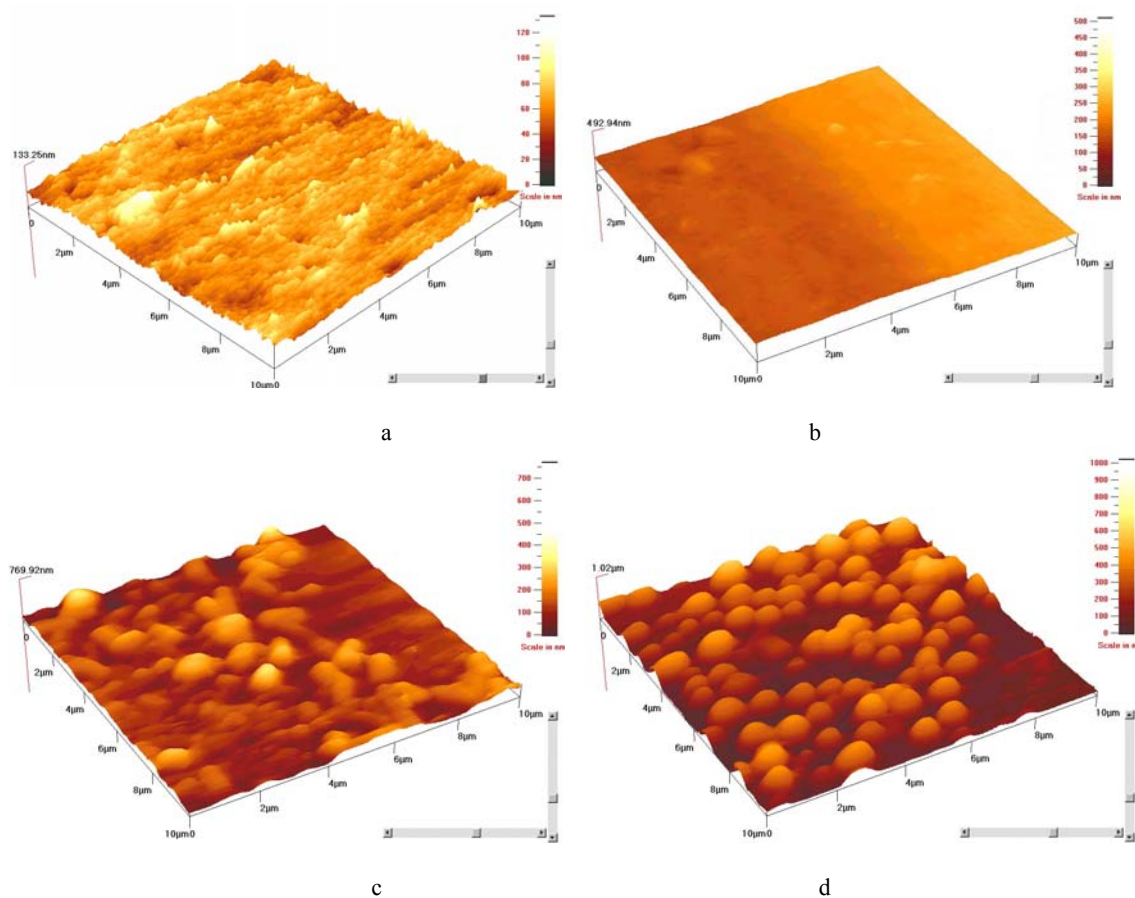


Fig. 3. AFM images: a – the initial PA 6 films; the seleniumized PA 6 films in solution of $K_2Se(SO_3)_2$ at different periods of time. Duration of PA 6 seleniumization, h: b – 0.5, c – 1.5, d – 2.5

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 $2\theta \sim 20^\circ$ and 24° exceed intensity of selenium peaks few times. Therefore the range of $2\theta \geq 8.0^\circ$ 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 $80^\circ C$, 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 $80^\circ C$

$d, \text{\AA}$	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 $1.7878 \text{ \AA}$ 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 $1.7850 \text{ \AA}$ and the peaks at $2\theta = 40.71$ and 45.59° (corresponding to $d = 2.2147$ and $1.9883 \text{ \AA}$ respectively) could be assigned to the phase of monoclinic selenium (Pdf 73-2121) [30], in which d are $2.2122 \text{ \AA}$ and $1.9843 \text{ \AA}$.

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 seleniumization 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 selenotrichionate 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.

The changes of selenium (c_{Se}) and sulphur (c_S) molar ratio calculated to 1 g of polymer confirmed the decompo-

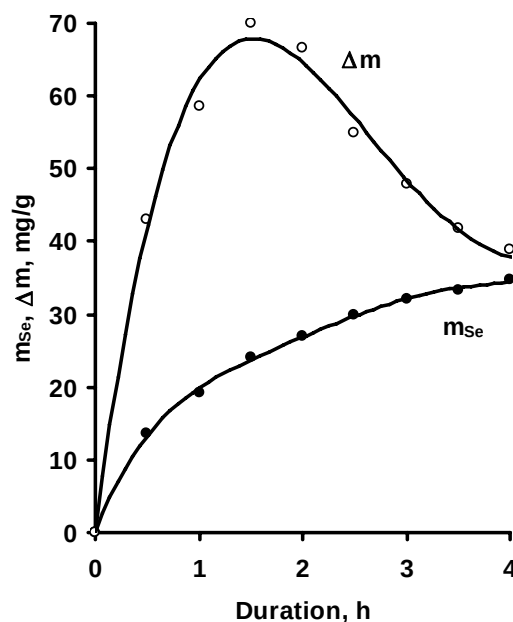


Fig. 4. Changes of PA 6 film mass (Δm) and selenium concentration in it (m_{Se}) with time on treating with $K_2Se(SO_3)_2$ solution

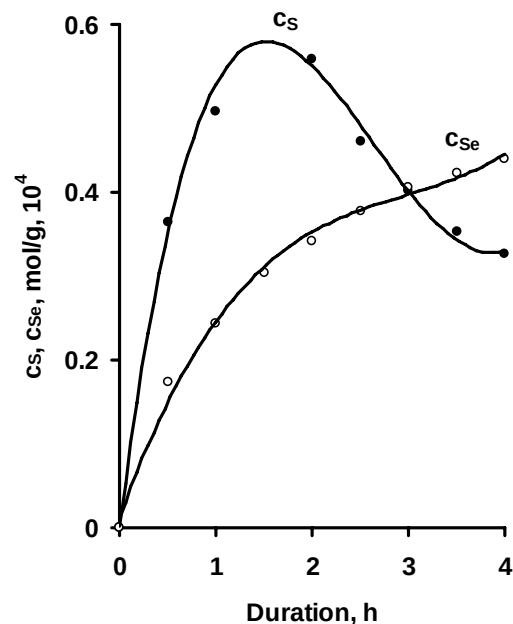


Fig. 5. Changes molar rate of sulfur (c_S) and selenium concentration (c_{Se}) in seleniumized PA 6 films in solution of $K_2Se(SO_3)_2$ at different periods of time

sition 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 selenotrichionate. 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 selenotritrithionate solutions gets into the PA 6 film as $\text{Se}(\text{SO}_3)_2^{2-}$ 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 $\text{K}_2\text{Se}(\text{SO}_3)_2$ 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) $\Omega/\square$. 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 $2\theta = 32.6^\circ$ and 49.1° (corresponding to $d = 2.7484 \text{ \AA}$ and $1.8384 \text{ \AA}$ respectively) could be assigned to the phase of *orthorhombic* copper selenide (CuSe_2) (Pdf 74-280) [31], in which d are $2.7474 \text{ \AA}$ and $1.8376 \text{ \AA}$, the peaks at $2\theta = 38.12^\circ$ and 41.0° (corresponding to $d = 2.3483 \text{ \AA}$ and $2.1999 \text{ \AA}$ respectively) could be assigned to the phase of *monoclinic* copper selenide (Cu_2Se) (Pdf 27-1131) [32], in which d are $2.3480 \text{ \AA}$ and $2.1990 \text{ \AA}$ and peaks at $2\theta = 44.9^\circ$ (corresponding to $d = 2.033 \text{ \AA}$ respectively) could be assigned to the phase of *cubic* berzelianite (Cu_{2-x}Se) (Pdf 6-680) [33], in which d are $2.030 \text{ \AA}$.

Table 2. The data of the X-ray diffraction pattern of PA 6 film 1.5 h seleniumized in solution of $\text{K}_2\text{Se}(\text{SO}_3)_2$ and after its treated with the Cu(I–II) salt solution

$d, \text{ \AA}$	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-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 $\text{Se}(\text{SO}_3)_2^{2-}$ anions as the precursors for formation the electroconductive copper selenide layers on this polymer.

CONCLUSIONS

1. The sorption-diffusion of selenotritrithionate ions, $\text{Se}(\text{SO}_3)_2^{2-}$, from 0.05 mol/dm^3 solution of potassium trithionate, $\text{K}_2\text{Se}(\text{SO}_3)_2$, 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 selenotritrithionate 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 $\delta_{\text{as}}(\text{O}-\text{S}-\text{O})$,

$\nu_{\text{s}}(\text{S}-\text{O})$ and $\nu_{\text{as}}(\text{S}-\text{O})$ respectively. One absorption maxima at $\sim 250 \text{ nm}$ 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 $\text{Se}(\text{SO}_3)_2^{2-}$. The spectral data confirm that selenium is sorbed by PA films in the form of selenotritrithionate 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 selenotritrithionate ions and the decomposition starts. The chemical analyzis of seleniumized PA 6 films confirmed that sorbed anions of $\text{Se}(\text{SO}_3)_2^{2-}$ 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 $\text{K}_2\text{Se}(\text{SO}_3)_2$ 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 selenotritrithionate 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 *orthorhombic* 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) $\Omega/\square$.

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