

Comparison of Polythionates as Precursors for the Formation of Thallium Sulfide Layers

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The processes of obtaining layers of thallium, sulfides, Tl_xS_y , by the sorption-diffusion method on polyamide 6 using solutions of lower polythionates – sodium trithionate and tetrathionate, $Na_2S_3O_6$, $Na_2S_4O_6$, potassium pentathionate, $K_2S_5O_6$, and of dodecathionic acid, $H_2S_{12}O_6$, as precursors of sulfur are compared. The concentration of sorbed sulfur increases with increasing the duration of treatment, the concentration and temperature of precursor solution. It rather significantly also depends on the nature – sulfurity of polythionate, i.e. on the number of sulfur atoms in the polythionate anion: effectiveness of sulfurization using solutions of dodecathionic acid is significantly higher than that of lower polythionates. Thallium sulfide layers are formed on the surface of polyamide after the treatment of sulfurized polymer with $Tl(I)$ salt solution. The concentration of thallium in the layer increases with the increase of initial sulfurization duration and in case of $H_2S_{12}O_6$ solution used – on the temperature of this process. The results of X-ray diffraction analysis confirmed the formation of thallium sulfide layers in the surface of polyamide 6. The phase composition of layer changes depending on the conditions of initial treatment in a $H_2S_{12}O_6$ solution. Five thallium sulfide phases, two forms of TlS , Tl_2S_2 , Tl_4S_3 and Tl_2S_5 were identified in the composition of the layers treated for different time with a solution of dodecathionic acid at the temperature of 20 °C and 30 °C and then with $Tl(I)$ salt solution by X-ray diffraction but the maxima of TlS and Tl_2S_5 phases predominate in the diffractograms.

Keywords: polythionates, polyamide, sorption-diffusion, thallium sulfide layers.

INTRODUCTION

The layers of thallium sulfides show a great variety of stoichiometry, valuable physical properties and find applications in photoconductive devices and solar batteries [1–3].

Chemical bath deposition (CBD) method is most often used in deposition of electrically conductive layers of gallium, indium and thallium sulfides on various substrates. Nair with co-workers and other researchers [4–8] during number of years are studying the mechanism of formation of electrically conductive layers by CBD method and optical and electrical properties of the layers obtained. Thin semiconductive coatings of GaS , In_2S_3 , Tl_2S , Tl_4S_3 were deposited on various dielectrics. Polycrystalline layers are obtained by this method and, that the layer would acquire specific for some sulfide properties, the coatings obtained must be treated thermally at the certain temperature in the air or nitrogen atmosphere.

The studies carried out at the department of Inorganic chemistry of Kaunas university of technology [9, 10] showed that polythionates and the solutions of polythionic acids, $H_2S_nO_6$ ($n = 3–45$), are suitable for the sulfurization of polymeric substances [11] using sorption-diffusion method; after sorption of the sulfurization agent, the polymer substance is treated with a thallium(I) salt aqueous solution. By this method the thallium sulfide layers on polyethylene surface have been obtained [12]. On continuation of studies on polythionates use as sulfurization agents for the modification of polymers, in a number of works for the polycapromide polyamide 6 sulfurization and formation on its surface layers of

thallium sulfide (Tl_xS_y) we used acidified solutions of lower polythionates – trithionate, $S_3O_6^{2-}$, [13] tetrathionate, $S_4O_6^{2-}$, [13] pentathionate, $S_5O_6^{2-}$, [14, 15] – and solution of dodecathionic acid, $H_2S_{12}O_6$ [16, 17]. Some results, received using different sulfurization precursors were reviewed in recent publication [18], but the results have not been compared.

The aim of present work was to compare the results received by us during studies of processes of interaction of the chalcogenization agents – sodium trithionate and tetrathionate, $Na_2S_3O_6$, $Na_2S_4O_6$, potassium pentathionate, $K_2S_5O_6$, and dodecathionic acid, $H_2S_{12}O_6$, – with the semi-hydrophylic polymeric material – polyamide 6 film (PA) and also of sulfurized polymer treatment with a thallium(I) salt solution on the formation of thallium sulfide, Tl_xS_y , layers.

EXPERIMENTAL

A PA 6 film (specification TY 6-05-1775-76, grade PK-4, 70 μm thick) produced in Russia was used. Prior to the experiments pieces of the film 15 mm $\times$ 70 mm in size had been boiled in distilled water for 2 h to remove the remainder of the monomer. Then they were dried with filter paper and kept in a desiccator over $CaCl_2$ for 24 h.

Distilled water, chemically and analytically pure reagents were used to produce solutions.

The salts of polythionates – sodium trithionate monohydrate, $Na_2S_3O_6 \cdot H_2O$, sodium tetrathionate dihydrate, $Na_2S_4O_6 \cdot 2H_2O$, and potassium pentathionate hemitrihydrate, $K_2S_5O_6 \cdot 1.5H_2O$, – were prepared employing methods described in [19–21]. The prepared salts were kept in the dark, in a desiccator over concentrated sulfuric acid.

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For polymer sulfurization, $0.1 \text{ mol}\cdot\text{dm}^{-3}$ and $0.2 \text{ mol}\cdot\text{dm}^{-3}$ acidified with HCl ($0.1 \text{ mol}\cdot\text{dm}^{-3}$) $\text{Na}_2\text{S}_3\text{O}_6$ and $\text{Na}_2\text{S}_4\text{O}_6$ solutions at a temperature of 30°C and 50°C , and $(0.025 - 0.2) \text{ mol}\cdot\text{dm}^{-3}$ acidified with HCl ($0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl, $\text{pH} \sim 1.5$) solutions of $\text{K}_2\text{S}_5\text{O}_6$ at a temperature $0^\circ\text{C} - 20^\circ\text{C}$ were used.

$0.002 \text{ mol}\cdot\text{dm}^{-3}$ solution of dodecathionic acid was prepared and the average number of sulfur atoms in the polythionic acid molecule was determined by the methods given in [22]. For PA sulfurization, $\text{H}_2\text{S}_{12}\text{O}_6$ solutions at a temperature of $20^\circ\text{C} - 50^\circ\text{C}$ were used.

For the formation of Ti_xS_y layers, sulfurized PA film samples were treated with unstirred $0.1 \text{ mol}\cdot\text{dm}^{-3}$ Ti_2SO_4 ($\text{pH} 2.8$) solution containing KOH ($0.015 \text{ mol}\cdot\text{dm}^{-3}$) [23, 24] during 10 min. at a temperature of 80°C . When using alkalified Ti(I) salt solution, thallium sulfide layers on the surface of PA were obtained. After treatment with the solution of Ti(I) salt, PA samples were rinsed with distilled water, dried over anhydrous CaCl_2 and used in further experiments.

Sulfur concentrations (C_s , $\text{mg}\cdot\text{g}^{-1}$) in PA film samples were determined potentiometrically [25]. First sample of a sulfurized PA film was treated under heating with $(10 - 15) \text{ ml}$ of $10 \text{ mol}\cdot\text{dm}^{-3}$ KOH solution and diluted with the same amount of distilled water. Standard calomel and platinum electrodes were used for the potentiometric titration of the solution obtained in KOH with 0.05 N solution of iodine under stirring. For potentiometric measurements, a pH-meter ($\text{pH}-673 \text{ M}$ millivoltmeter) was used.

The concentrations of thallium (C_{Ti} , $\text{mg}\cdot\text{g}^{-1}$) in PA films were determined by the atomic absorption spectroscopy method using a Perkin-Elmer 503 atomic absorption spectrophotometer [26]. PA films modified by Ti_xS_y layers were dissolved in 2 cm^3 of concentrated HNO_3 , diluted with distilled water and boiled for 30 min (complete degradation of PA film). Then the solution was diluted up to 25 cm^3 and analysed.

X-ray diffraction analysis of thallium sulfide layers was performed employing a ДРОН-6 X-ray diffractometer (Russia) (supply unit ПYP 5.50), radiation CuK_α , Ni filter, monochromator angular, electric current in a tube $30 \mu\text{A}$, working voltage 30 kV . X-ray diffraction data were analysed with Search Match, Xfit, ConvX as well as Excel computer programs.

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 a potassium pentathionate [14] and dodecathionic acid [16] solutions. These investigations have confirmed that polythionate anions sorb-diffuse into PA treated with the solutions of polythionates.

The concentration of sulfur (Fig. 1) in PA sorbed from $\text{Na}_2\text{S}_3\text{O}_6$, $\text{Na}_2\text{S}_4\text{O}_6$, $\text{K}_2\text{S}_5\text{O}_6$ and $\text{H}_2\text{S}_{12}\text{O}_6$ solutions increases with increasing the duration of treatment, the concentration and temperature of precursor solution. It rather significantly also depends on the nature – sulfurity of polythionate, i. e. on the number of sulfur atoms in the polythionate anion.

It is quite obvious that the concentrations of sulfur in the samples during the exposure in the solution of $\text{H}_2\text{S}_{12}\text{O}_6$ at the temperatures of 20°C and 30°C in the range $\sim(6 - 95) \text{ mg}\cdot\text{g}^{-1}$ might be obtained by varying the temperature of the solution of $\text{H}_2\text{S}_{12}\text{O}_6$ and the duration of treatment (Fig. 1, curves 8 and 9). These values of sulfur concentration obtained in PA by the use of $\text{H}_2\text{S}_{12}\text{O}_6$ are significantly higher than those (at most $\sim 9.5 \text{ mg}\cdot\text{g}^{-1}$) obtained in the studies where the sorption of lower polythionates ions from $\text{Na}_2\text{S}_3\text{O}_6$, $\text{Na}_2\text{S}_4\text{O}_6$ and $\text{K}_2\text{S}_5\text{O}_6$ solutions of a significantly higher concentration ($0.2 \text{ mol}\cdot\text{dm}^{-3}$) but in corresponding conditions into PA films was studied [13, 14].

We have no kinetic data on the sorption of pentathionate ions, $\text{S}_5\text{O}_6^{2-}$, from $\text{K}_2\text{S}_5\text{O}_6$ solutions at the temperatures higher than 20°C because of significant decrease of pentathionate stability in water solution at higher temperature. The stability of $\text{K}_2\text{S}_5\text{O}_6$ solutions decreases also increasing the concentration of solution. Therefore, in Fig. 1 only kinetic data of sulfur sorption from $0.1 \text{ mol}\cdot\text{dm}^{-3}$ solution of $\text{K}_2\text{S}_5\text{O}_6$ at the temperature of 10°C and 20°C (curves 3 and 6) and from $0.2 \text{ mol}\cdot\text{dm}^{-3}$ solution of $\text{K}_2\text{S}_5\text{O}_6$ at the temperature of 10°C (curve 4) is presented. Nevertheless, while increasing the concentration of $\text{K}_2\text{S}_5\text{O}_6$ solution from $0.1 \text{ mol}\cdot\text{dm}^{-3}$ to $0.2 \text{ mol}\cdot\text{dm}^{-3}$ sulfur concentrations reached in PA are about 1.5 times higher at the same temperature (10°C) of sulfurization solution (Fig. 1, curves 3 and 4). In the same extent increases sulfur concentration in PA increasing the concentration of $\text{Na}_2\text{S}_4\text{O}_6$ solution from $0.1 \text{ mol}\cdot\text{dm}^{-3}$ to $0.2 \text{ mol}\cdot\text{dm}^{-3}$ at a temperature of 50°C of sulfurization solution (Fig. 1, curves 1 and 2).

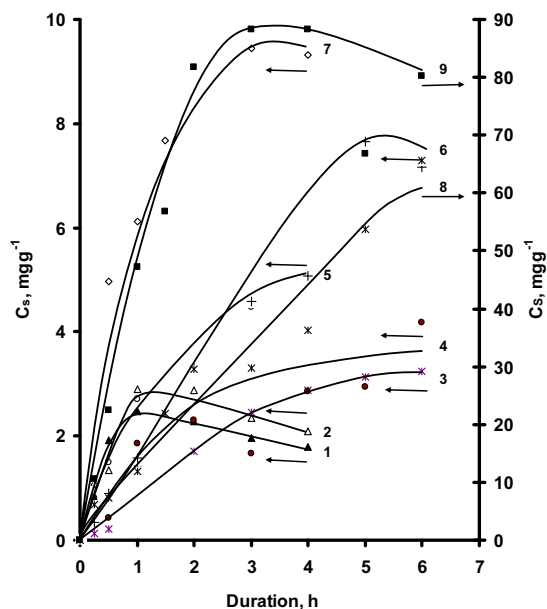


Fig. 1. Change of sulfur concentration in PA with time during its treatment with solutions of polythionates at different concentrations and temperatures. The polythionate, its solution concentration ($\text{mol}\cdot\text{dm}^{-3}$) and temperature ($^\circ\text{C}$): 1 – $\text{Na}_2\text{S}_4\text{O}_6$, 0.1, 50; 2 – $\text{Na}_2\text{S}_4\text{O}_6$, 0.2, 50; 3 – $\text{K}_2\text{S}_5\text{O}_6$, 0.1, 10; 4 – $\text{K}_2\text{S}_5\text{O}_6$, 0.2, 10; 5 – $\text{Na}_2\text{S}_3\text{O}_6$, 0.2, 30; 6 – $\text{K}_2\text{S}_5\text{O}_6$, 0.1, 20; 7 – $\text{Na}_2\text{S}_3\text{O}_6$, 0.2, 50; 8 – $\text{H}_2\text{S}_{12}\text{O}_6$, 0.002, 20; 9 – $\text{H}_2\text{S}_{12}\text{O}_6$, 0.002, 30

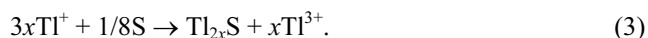
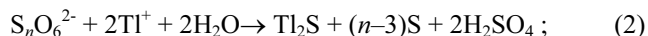
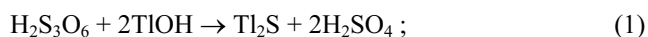
Increase of the temperature of sulfurization precursor solution increases the concentration of sulfur sorbed by PA. Increase of the temperature of 0.2 mol·dm⁻³ solution of Na₂S₃O₆ from 30 °C to 50 °C leads to increase of sorbed sulfur concentration from ~5 mg·g⁻¹ to 9.5 mg·g⁻¹ (Fig. 1, curves 5 and 7); increase of the temperature of 0.1 mol·dm⁻³ solution of K₂S₅O₆ from 10 °C to 20 °C leads to increase of sorbed sulfur from ~3 mg·g⁻¹ to 7.5 mg·g⁻¹ (Fig. 1, curves 3 and 6); increase of the temperature of 0.002 mol·dm⁻³ solution of H₂S₁₂O₆ from 20 °C to 30 °C leads to increase of sorbed sulfur from ~65 mg·g⁻¹ to 95 mg·g⁻¹ (Fig. 1, curves 8 and 9). Thus, the nature (degree of sulfurity) of polythionate anion and the conditions of PA sulfurization (concentration and temperature of sulfur precursor solution) decide the concentration of sulfur, sorbed-diffused into PA.

It is difficult to compare in-between sulfurization effectiveness of lower polythionates since potassium pentathionate is stable in solution at low temperatures (10 °C–20 °C); sodium tetrathionate and sodium trithionate solutions at higher temperatures (30 °C–50 °C) are still more-less stable. Nevertheless, the highest values of diffused into PA sulfur concentrations using low temperature K₂S₅O₆ solutions and Na₂S₃O₆ solutions at higher temperature are approximately similar.

Effectiveness of Na₂S₄O₆ solutions as PA sulfurization agents is lower compared with Na₂S₃O₆ and K₂S₅O₆ solutions because of the former lower stability.

Thus the obtained results provided the conditions for the formation of thallium sulfide, Tl_xS_y, layers on the surface of the PA.

In order to form thallium sulfide layers on the surface of sulfurized PA films, they were treated with the Tl(I) salt solution. As a result of the redox reactions of polythionates anions, S_{3,4,5,12}O₆²⁻, containing sulfur atoms of low oxidation state, sorbed on-diffused into a polymer with Tl(I) ions, the layers of thallium sulfides on the surface of PA were formed. The examples of possible reactions may be proposed by the equations of polythionate interaction with Tl containing particles:



The conditions of a polymer initial sulfurization and the nature of PA sulfurization precursor determine the concentration of thallium and the composition of sulfide layer: the concentration of thallium in the polyamide 6 film increases with the increase of initial sulfurization duration and varies in cases of lower polythionates used (Na₂S₃O₆, Na₂S₄O₆, K₂S₅O₆, up to ~2 h of sulfurization) from ~1.5 mg·g⁻¹ to ~5 mg·g⁻¹ and in cases when the solutions of dodecathionic acid were used – from ~20 mg·g⁻¹ to ~280 mg·g⁻¹ (Fig. 2). Thus the concentrations of thallium in PA reached using H₂S₁₂O₆ solutions for the polymer sulfurization are significantly higher than those reached using solutions of lower polythionates.

The concentration of thallium in the sulfide layer increases with an increase in the sulfur concentration reached at the temperatures of sulfurization 20 °C and 30 °C using H₂S₁₂O₆ solution. That is completely

understandable since with a higher concentration of sulfur sorbed-diffused into the PA a larger amount of Tl⁺ ions may be involved in an reaction with the sulfur species. The molar Tl/S ratio in the thallium sulfide layers on the PA surface was calculated from the concentrations measured in the PA films. It was found that the Tl/S ratio does not depend much on the time of initial PA sulfurization but decreases with the increase in temperature of the H₂S₁₂O₆ solution. By changing the conditions of sulfurization, it was possible to obtain thallium sulfide layers in the surface matrix layer of PA of stoichiometrical composition varying from ~Tl_{0.15}S to Tl_{1.2}S. When the time of treatment in the alkaline solution of Tl(I) at 80 °C was 10 min after the initial sulfurization in H₂S₁₂O₆ solution at 20 °C during 0.5 h–4.0 h, the stoichiometrical composition of the thallium sulfide layers was close to TlS; after the initial sulfurization at 30 °C during 0.25 h–3.0 h – the stoichiometrical composition was close to Tl₂S.

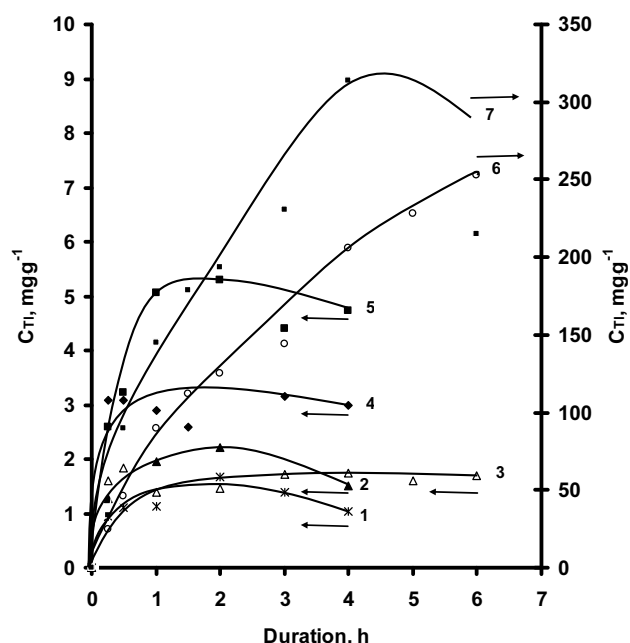


Fig. 2. Dependence of thallium concentration in sulfide layer on PA film on sulfurization duration when treating it with polythionates solutions at different concentrations and temperatures (°C): 1 – Na₂S₄O₆, 0.2, 50; 2 – Na₂S₄O₆, 0.1, 50; 3 – K₂S₅O₆, 0.1, 20; 4 – Na₂S₃O₆, 0.2, 50; 5 – Na₂S₃O₆, 0.2, 30; 6 – H₂S₁₂O₆, 0.002, 20; 7 – H₂S₁₂O₆, 0.002, 30

X-ray diffraction analysis gives more accurate identification of thallium sulfides formed on the surface of PA [27–29]. Unfortunately the Tl_xS layers formed using the solutions of lower polythionates were too thin and not suitable for their phase composition determination by X-ray diffraction methods. The results of X-ray diffraction analysis of Tl_xS_y layers formed using the solutions of dodecathionic acid are presented in Fig. 3.

The 7 peaks of high and middle intensity of α-TlS phase at 2θ = 31.20, 32.44, 41.76, 47.32, 53.28, 56.70 and 58.86, 9 peaks of middle and low intensity of orthorhombic Tl₂S₅ phase at 2θ = 28.76, 32.94, 34.40, 37.20, 40.70, 49.20, 51.16, 51.98 and 69.16, and one peak of middle intensity of monoclinic β-Tl₄S₃ phase at 2θ = 28.50 in the

diffraction pattern of PA sample initially sulfurized 0.5 h at the temperature of 30 °C are observed (Fig. 3, curve 2). That is in accordance with the results of chemical analysis (TI/S ~0.6). If the duration of PA initial sulfurization at the same temperature is increased to 1 h, only 4 peaks of α -TIS phase at $2\theta = 31.20, 41.76, 46.56, 53.28$ and 30 peaks of various intensity of orthorhombic Ti_2S_5 phase are observed (Fig. 3, curve 3). That again is in not bad accordance with the results of chemical analysis (TI/S ~0.48).

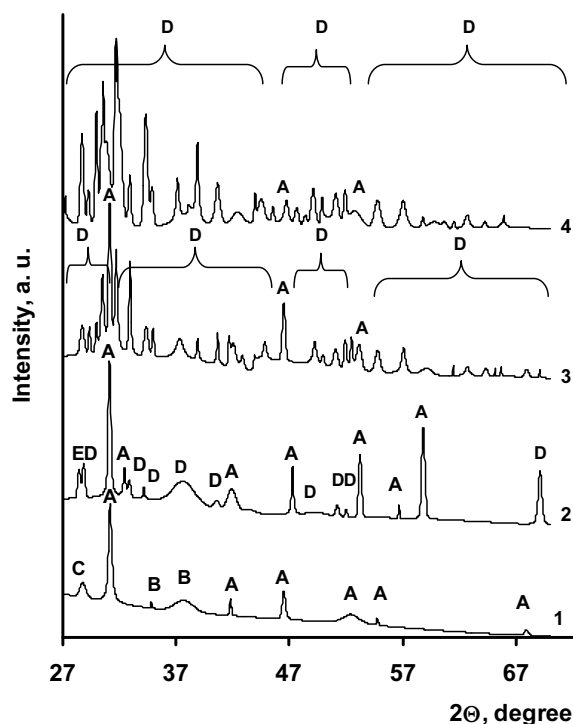


Fig. 3. X-ray diffraction patterns of thallium sulfides layers in the surface of PA. PA initially treated with a solution of $\text{H}_2\text{S}_{12}\text{O}_6$ and then with a Tl(I) salt solution at 80 °C for 10 min. PA sulfurization duration (h) and temperature (°C): 1 – 3.0, 20; 2 – 0.5, 30; 3 – 1.0, 30; 4 – 3, 30. A – α -TIS, B – tetragonal Ti_2S_2 , C – monoclinic TIS, D – orthorhombic Ti_2S_5 , E – β - Ti_4S_3

The influence of the deposition temperature when the duration of initial sulfurization was the same (3 h) on the composition of deposited thallium sulfide layers was investigated by X-ray diffraction of the layers formed from 20 °C and 30 °C solutions. The 6 peaks of various intensity of α -TIS phase at $2\theta = 31.20, 41.78, 46.56$ and 52.70 , only 2 peaks of low intensity of tetragonal Ti_2S_2 phase at $2\theta = 34.86$ and 37.90 , and one peak of low intensity of monoclinic TIS phase at $2\theta = 28.94$ in the diffraction pattern of PA sample initially sulfurized at the temperature of 20 °C are observed (Fig. 3, curve 1). That is in accordance with the results of chemical analysis (TI/S ~0.8). If the temperature of PA initial sulfurization is increased to 30 °C, only 2 peaks of low intensity of α -TIS phase at $2\theta = 46.56$ and 52.70 , and 32 peaks of various intensity of orthorhombic Ti_2S_5 phase are observed (Fig. 3, curve 4). That again is in accordance with the results of chemical analysis (TI/S ~0.6).

Thus, five phases, two forms of TIS, Ti_2S_2 , Ti_2S_5 and Ti_4S_3 were identified by X-ray diffraction analysis in thallium sulfide layers on the surface of PA. If the duration

of PA initial sulfurization is short (0.5 h–1.0 h) and the temperature is relatively low (20 °C), the phases of α -TIS and orthorhombic Ti_2S_5 predominate in the diffraction patterns of the Ti_xS_y layers. The phase composition of these layers approaches to the composition of orthorhombic Ti_2S_5 phase if the duration and temperature of the initial polymer sulfurization is increased.

From the data it was concluded, that the changing the conditions of PA sulfurization and the nature of sulfurization precursor leads to the formation of thallium sulfide layers of different composition.

CONCLUSIONS

1. Solutions of polythionates of different sulfurity – sodium trithionate and tetrathionate, $\text{Na}_2\text{S}_3\text{O}_6$, $\text{Na}_2\text{S}_4\text{O}_6$, potassium pentathionate, $\text{K}_2\text{S}_5\text{O}_6$, and dodecathionic acid, $\text{H}_2\text{S}_{12}\text{O}_6$, as precursors of sulfur for the formation of layers of thallium sulfides, Ti_xS_y , on the surface of semihydrophilic polymer polyamide 6 (PA) were compared. The concentration of sorbed sulfur increases with the increase of the duration of treatment, concentration and temperature of polythionates solutions. It rather significantly also depends on the nature – sulfurity of polythionate, – i. e. on the number of sulfur atoms in the polythionate anion. The concentrations of sulfur obtained in PA by the use of $\text{H}_2\text{S}_{12}\text{O}_6$ are significantly higher ($6 \text{ mg} \cdot \text{g}^{-1}$ – $95 \text{ mg} \cdot \text{g}^{-1}$) than those (at most $\sim 9.5 \text{ mg} \cdot \text{g}^{-1}$) obtained when the solutions of lower polythionates ($\text{Na}_2\text{S}_3\text{O}_6$, $\text{Na}_2\text{S}_4\text{O}_6$, $\text{K}_2\text{S}_5\text{O}_6$) of a significantly higher concentration but in similar conditions has been used for PA sulfurization.

2. The layers of thallium sulfide of various composition are formed on the surface of PA after treatment of sulfurized polymer with the water solution of Tl(I) salt. The concentration of thallium in Ti_xS_y layers is dependent on the concentration of sulfur in PA, i. e. on conditions of initial polymer sulfurization and on the nature of polythionate used.

3. XRD results confirmed the formation of thallium sulfide layers on the surface of PA. The composition of Ti_xS_y layers depends on the conditions of this process. Two forms of TIS, Ti_2S_2 , Ti_2S_5 and Ti_4S_3 phases were identified by X-ray diffraction analysis in thallium sulfide layers on the surface of PA formed using $\text{H}_2\text{S}_{12}\text{O}_6$ solution. If the duration of the initial PA sulfurization was short (0.5 h–1.0 h) and the temperature was relatively low (20 °C), the α -TIS and orthorhombic Ti_2S_5 phases prevailed in the diffraction patterns of the Ti_xS_y layers. The phase composition of these layers approached the composition of the orthorhombic Ti_2S_5 phase, if the duration and temperature of the initial polymer sulfurization had been increased.

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