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The Modification of Polyamide 6 Films by the Thallium Sulfide Layers Using Dodecationic Acid

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By a study of IR and UV absorption spectra it is shown that the dodecathionate anions are sorbed-diffused into a polyamide 6 films if they are treated with the water solution (0.002 mol·dm^{-3}, 20 °C – 50 °C) of dodecathionic acid, $H_2S_{12}O_6$. The values of sulfur concentration obtained in polyamide 6 (up to ∼250 mg·g^{-1}) are significantly higher than those obtained in the studies in which the sorption of lower polythionates – trithionate, $S_3O_6^{2-}$, tetrathionate, $S_4O_6^{2-}$, and pentathionate, $S_5O_6^{2-}$, – by polyamide 6 films has been studied. The concentration of sorbed dodecathionate ions increases with the increase of duration of treatment and temperature of a $H_2S_{12}O_6$ solution. The thallium sulfide, Tl_xS, layers are formed in the surface of polyamide 6 film if the sulfured polymer is treated with alkalified (0.015 mol·dm^{-3} NaOH) 0.1 mol·dm^{-3} solution of Tl_2SO_4 at 80 °C temperature: the anionic particles $S_{12}O_6^{2-}$ containing sulfur atoms of low oxidation state react with the Tl(I) ions. The conditions of a polymer initial sulfuration determine the amount of thallium and the composition of sulfide layer: the amount of thallium in the polyamide 6 film increases with the increase of duration and temperature of initial sulfuration, and varies from ∼25 mg·cm^{-2} to ∼250 mg·cm^{-2}; the stoichiometrical composition of Tl_xS layers on polyamide 6 formed according the data of chemical analysis varies from ∼$Tl_{0.15}S$ to $Tl_{1.2}S$. The results of X-ray structural 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 too. Four thallium sulfide phases, TlS, Tl_2S_2, Tl_4S_3 and Tl_2S_5 were identified in the composition of the layers by X-ray diffraction but the maxima of TlS and Tl_2S_5 phases predominate in the diffractograms. The regularities determined enable formation by sorption-diffusion method of thallium sulfide layers of desirable composition using the dodecathionic acid as a polyamide 6 sulfuration agent.

Keywords: dodecathionic acid, polyamide, sorption-diffusion, thallium sulfide layers.

INTRODUCTION

For a couple of decades, interest in the binary chalcogenide thin layers obtaining has lead to a large amount of research. These thin layers have a number of applications in various fields, 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]. Thallium sulfide's electrical conductivity changes with exposure to infrared light, therefore making this compound useful in photocells. The layers of thallium sulfides are commonly produced by the deposition method from solutions [3]. But its formation is more convenient by the use of sorption methods.

Sorption-diffusion is a simple and promising method for obtaining binary sulfide layers. Thallium sulfide layers are formed in the surface matrix of a polyethylene film (PE) as a result of the oxidation-reduction reaction between sulfur particles formed during decomposition of higher polythionic acids, $H_2S_xO_6$, [4] and sorbed by PE and thallium(I) ions present in a solution of thallium(I) salt [5, 6]. Depending on the initial sulfur concentration in PE and the conditions of the treatment with Tl(I) salt solution, red brownish or grey brown layers of thallium sulfide in the surface of PE were obtained.

Hydrophilic and semi-hydrophilic polymers are capable of absorbing ions of various electrolytes from aqueous solutions [7]. Over the last decade, a sorption method for the formation of thin copper sulfide, Cu_xS, and thallium sulfide, Tl_xS, layers on the surface of polyamide 6 (PA) based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_nO_6^{2-}$, has been under extensive investigation [8 – 17]. It was shown that during treatment the anions of lower polythionates – trithionate, tetrathionate and pentathionate, $S_3O_6^{2-} – S_5O_6^{2-}$, containing chains of divalent sulfur atoms of low oxidation state, $^{-}O_3S–S_x–SO_3^{-}$ [8–11], are sorbed by a polymer. Thin layers of copper or thallium sulfide are formed on a PA surface if a polymer sulfured in such conditions later is treated with a solution of copper(II/I) or thallium(I) salt [12 – 17]. The lower polythionates such as sodium trithionate, $Na_2S_3O_6 \cdot H_2O$, sodium tetrathionate, $Na_2S_4O_6 \cdot \cdot H_2O$, and potassium pentathionate, $K_2S_5O_6 \cdot 3/2H_2O$, were used for PA sulfuration in previous studies looking for the formation of Tl_xS layers on PA surface [15, 18, 19]. But the Tl_xS layers formed were too thin and not suitable for their phase composition determination by X-ray diffraction methods.

Few experiments using a solution of dodecathionic acid, $H_2S_{12}O_6$, for the PA sulfuration showed that significantly higher concentration of sorbed-diffused sulfur could be obtained in PA [12, 20] and the electrically conductive high quality copper sulfide films has been formed on PA surface.

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The aim of this study was to obtain high quality layers of thallium sulfide of various composition on the surface of PA film using as a precursor the solution of dodecathionic acid, and to investigate their composition by chemical and X-ray diffraction methods. X-ray diffraction has been showed [5, 21, 22] to be suitable for the determination of phase composition of Tl_xS layers on the surface of PE formed.

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 (15×70) 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 dessicator over $CaCl_2$ for 24 h.

PA films were sulfured in a thermostatic vessel up to 6 h at a temperature of 20 °C – 50 °C using a continually stirred 0.002 $mol \cdot dm^{-3}$ solution of $H_2S_{12}O_6$ prepared by the method given in [23]. At certain time intervals, the PA film samples were removed from $H_2S_{12}O_6$ solution, rinsed with distilled water, dried with filtration paper, left over $CaCl_2$ for 24 h and then used in further experiments and analysis.

Sulfur concentrations (Cs) in PA film samples were determined potentiometrically [24]. Firstly a sample of a sulfured PA film was treated under heating with 10 ml – 15 ml of 10 $mol \cdot dm^3$ KOH 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 the potentiometric measurements, a pH-meter – pH-673 M millivoltmeter was used.

Then samples of sulfured PA were treated by unstirred 0.1 $mol \cdot dm^{-3}$ Tl_2SO_4 (pH 2.8) solution having addition of KOH (of 0.015 $mol \cdot dm^{-3}$) during 10 min. at the temperature of 80 °C. When using alkalified Tl(I) salt solution thallium sulfide layers on the surface of PA were obtained. The amount of thallium was determined by atomic absorption spectroscopy method [25] using a Perkin-Elmer 503 atomic absorption spectrophotometer. The UV, VIS (200 nm – 400 nm) and IR (400 cm^{-1} – 1300 cm^{-1}) spectra were obtained with the aid of Spectronic^R Genesys^{TM} and Perkin−Elmer GX spectrometers, system FT−IR.

The phase composition of the thallium sulfide layers was investigated by means of X-ray diffraction using a DRON-6 diffractometer (radiation Cu K_α, voltage 30 kV). X-ray diffractograms of PA samples with the layers of Tl_xS_y were treated using programs „Search Match", „ConvX", „Xfit".

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 dodecathionic acid solution.

It was found that the peaks of most intensive bands in the IR spectra of PA samples sulfured in a $H_2S_{12}O_6$ solution, recorded by the compensation method (PA absorption eliminated) were in the intervals 420 – 473, 503 – 558, 612 – 724, 838 – 1100, 1144 – 1293 cm^{-1} (Fig. 1). According to the literature data [10, 11, 26] the peaks in the first interval were assigned to the valence vibrations in the S–S bond ($\nu_{S–S}$), in the second interval – 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). These results confirm that the sorption of dodecathionate ions by a PA occurs during the polymer treatment with a solution of $H_2S_{12}O_6$.

The UV absorption spectra of PA samples sulfured for different periods of time in a solution of $H_2S_{12}O_6$ are shown in Figure 2. Four absorption maxima are observed in these spectra: at ~225 nm as a shoulder, at ~250 nm as a peak, at ~290 nm and ~322 nm – 332 nm as a shoulders. According to the data of the study of the UV absorption spectra of polythionates [11, 27 – 29], the absorption maxima of polythionate ions as shoulders and peaks are at ~215, ~250, ~290 and ~340 nm. Thus, UV absorption spectra recorded by us confirm again that sulfur is sorbed by PA films in the form of polythionate ions. Intensity of the absorption maxima in the spectra, as expected, increase with an increases in the duration of a polymer treatment in a solution of dodecathionic acid.

In this work the kinetics of sorption-diffusion of sulfur from the solution of dodecathionic acid into PA film was investigated (Fig. 3). It was found that the concentration of sulfur in the samples (C_s, $mg \cdot g^{-1}$) during exposure in the solution of $H_2S_{12}O_6$ at 20, 30, 40 or 50 °C increases continuously with a time. Sulfur concentrations in the range ~10 $mg \cdot g^{-1}$ – 250 $mg \cdot g^{-1}$ might be obtained by varying the temperature of the solution of $H_2S_{12}O_6$. The results of the kinetics presented show that a higher sulfur concentration was obtained at a higher temperature.

It is obvious that the values of sulfur concentration obtained in PA are significantly higher than those obtained in the studies in which the sorption of pentathionate ions from the $K_2S_5O_6$ solution of 50 times higher concentration – by PA films has been studied (curve 1). Thus, the results obtained provided conditions for the formation of thallium sulfide, Tl_xS, layers on the surface of PA.

In order to form thallium sulfide layers on the surface of sulfured PA films, they were treated for 10 min with the alkaline Tl_2SO_4 solution at 80 °C. It was found that the amount of thallium in the sulfide layer increased with the time of PA sulfuration in the $H_2S_{12}O_6$ solution at all temperatures studied, and a different amount of thallium in the surface of PA at each temperature is reached (Fig. 4). The amount of thallium increases significantly with increase in temperature of the $H_2S_{12}O_6$ solution from 20 °C to 40 °C. But the amount of thallium in the sulfide layer on the surface of PA initially sulfured at 50 °C is lower than in the sulfide layer when PA film was sulfured at 40 °C. The reason of that is formation of not homogeneous sulfide layer on the surface of greatly destructed PA and it causes some mechanical losses of thallium sulfide.

The amount of thallium in the layer increases with an increase in the sulfur concentration reached at the temperatures of sulfuration 20 °C – 40 °C. That is completely understandable since with a higher concentration of sulfur

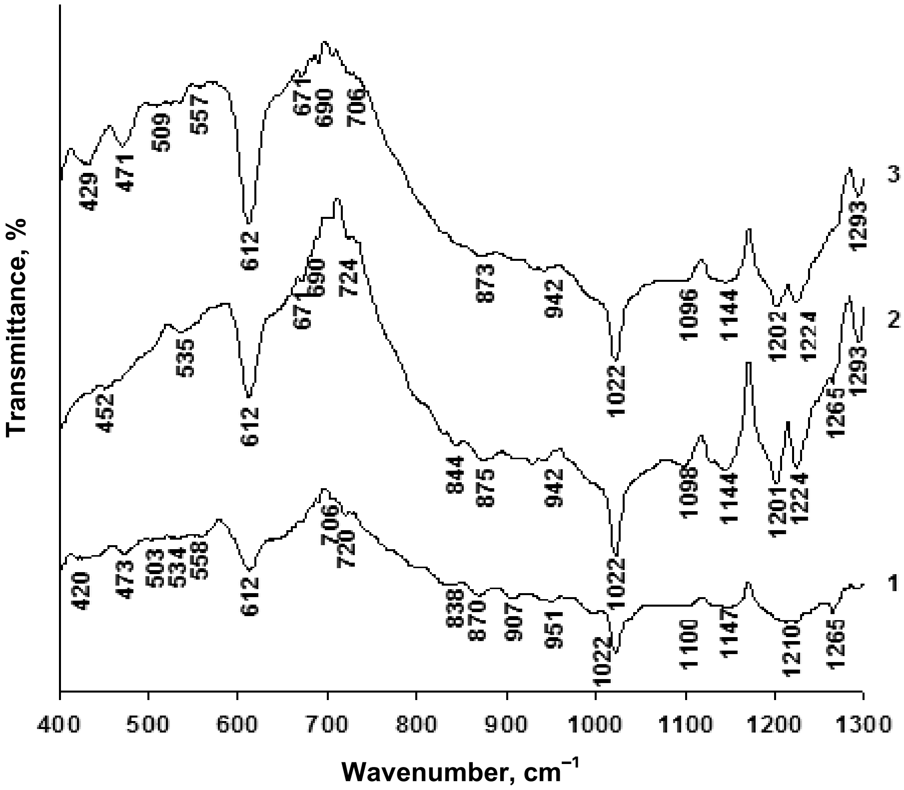

Fig. 1. IR absorption spectra of a PA films treated with 0.002 mol·dm^{-3} solution of $H_2S_{12}O_6$ at 20 °C different time. Sulfuration time, h: 1 – 0.25; 2 – 0.5; 3 – 2.0

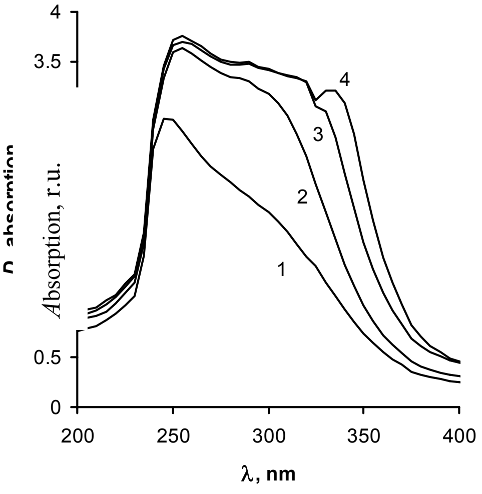

Fig. 2. UV absorption spectra of PA films treated with 0.002 mol·dm^{-3} solution of $H_2S_{12}O_6$ at 20 °C different time. Sulfuration time, h: 1 – 0.25; 2 – 0.5; 3 – 1.0; 4 – 2.0

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 amounts measured in the PA films. It was found that the Tl/S ratio (Table 1) does not depend much on the time of initial PA sulfuration but in all cases decreases with the increase in temperature of the $H_2S_{12}O_6$ solution. By changing the conditions of sulfuration, it was possible to obtain thallium sulfide layers on 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 sulfuration in $H_2S_{12}O_6$ solution at 20 °C during 0.5 h – 4.0 h, according to the chemical analysis, the stoichiometrical composition of the thallium sulfide layers obtained was close to TlS; after the initial

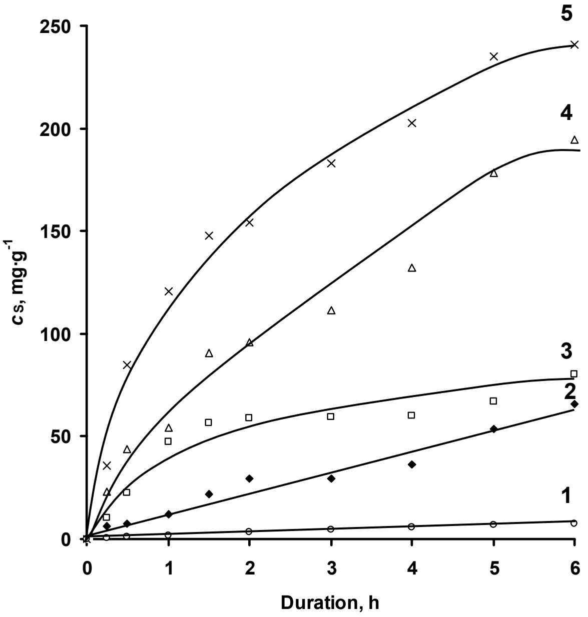

Fig. 3. Change of sulfur concentration in PA with time during its treatment with acidified (0.1 mol·dm^{-3} HCl) 0.1 mol·dm^{-3} $K_2S_5O_6$ solution at 20 °C (1) and with 0.002 mol·dm^{-3} solution of $H_2S_{12}O_6$ at different temperatures. Temperature, °C: 2 – 20; 3 – 30; 4 – 40; 5 – 50

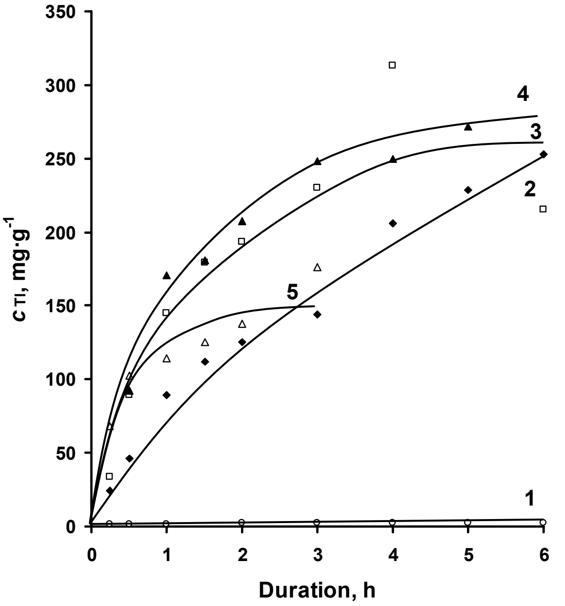

Fig. 4. Depence of the amount of thallium in sulfide layer on PA film on sulfuration duration when treating it with acidified (0.1 mol·dm^{-3} HCl) 0.05 mol·dm^{-3} $K_2S_5O_6$ solution at 20 °C (1) and with 0.002 mol·dm^{-3} solution of $H_2S_{12}O_6$ at different temperatures. The temperature (°C) of $H_2S_{12}O_6$ solution: 2 – 20; 3 – 30; 4 – 40; 5 – 50

sulfuration at 30 °C during 0.25 h – 3.0 h – the stoichiometrical composition was close to Tl_2S; after the initial sulfuration at 40 °C up to 4.0 h – the stoichiometrical composition was about $Tl_{0.3}S$ and after the sulfuration at 50 °C – close to $Tl_{0.15}S$. The decrease of the molar ratio Tl/S with the increase in the temperature of the sulfuration solution may be explained by the fact that the concentration of sorbed-diffused into PA sulfur grows with increase of sulfuration temperature to significantly higher extent compared with the extent of thallium amount increase with the grow of $H_2S_{12}O_6$ solution temperature. It appears that the reaction product – thallium sulfide hinders the further diffusion of Tl^+ ions into the polymer.

X-ray diffraction analysis gives more accurate identification of thallium sulfides formed on the surface of PA [30 – 32]. Results of this analysis are presented in Figures 5 and 6.

The 7 peaks of high and middle intensity of *α*–TlS [30–1331] phase at $2\theta = 31.20$, 32.44, 41.76, 47.32, 53.28, 56.70 and 58.86, 9 peaks of middle and low intensity of orthorhombic Tl_2S_5 [71–358] phase, which is thallium polysulfide – Tl_2SS_4, at $2\theta = 28.76$, 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*-Tl_4S_3 [43–1067] phase, which is the mixed sulfide $Tl_3^{I}[Tl^{III}S_3]$ of Tl(I) and Tl(III), at $2\theta = 28.50$ in the diffractogram of PA sample initially sulphured 0.5 h at the temperature of 30 °C are observed (Fig. 5, curve 1). That is in accordance with the results of chemical analysis (Table, Tl/S ~0.6). If the duration of PA initial sulfuration at the same temperature is increased to 1 h, only 4 peaks of *α*-TlS [30–1331] phase at $2\theta = 31.20$, 41.76, 46.56, 53.28 and 30 peaks of various intensity of orthorhombic Tl_2S_5 [71–358] phase are observed (Fig. 5, curve 2; Table 2). That again is in not bad accordance with the results of chemical analysis (Table 1, Tl/S ~0.48). If the duration of PA initial sulfuration is increased to 6 h, only 1 peak of *α*-TlS [30–1331] phase at $2\theta = 46.56$ and even 34 peaks of various intensity of orthorhombic Tl_2S_5 phase are observed (Fig. 5, curve 4; Table 2). That agrees well with the results of chemical analysis (Table, Tl/S ~0.4). These peaks of orthorhombic Tl_2S_5 [71–358] phase in the diffractograms of PA samples sulphured during longer period of time are more intensive. That is in accordance with the tendency of reduction of Tl/S molar ratio 0.63 – 0.48 – 0.42 in the Tl_xS layers on PA formed (Table) with the prolongation of initial PA sulfuration time 0.5 – 1.0 – 6.0 h.

The influence of the deposition temperature when the duration of initial sulfuration was the same (3 h) on the structure of deposited thallium sulfide layers was investigated by X-ray diffraction of the layers formed from 20, 30, 40 and 50 °C solutions. The 6 peaks of various intensity of *α*-TlS phase at $2\theta = 31.20$, 41.78, 46.56 and 52.70, only 2 peaks of low intensity of tetragonal Tl_2S_2 [82–2050] phase at $2\theta = 34.86$ and 37.90, and one peak of low intensity of monoclinic TlS [82–438] phase at $2\theta = 28.94$ in the diffractogram of PA sample initially sulphured at the temperature of 20 °C are observed (Fig. 6, curve 1).That is in accordance with the results of chemical analysis (Table 1, Tl/S ~0.8). If the temperature of PA initial sulfuration is increased to 30 °C, only 2 peaks of low intensity of *α*-TlS [30–1331] phase at $2\theta = 46.56$ and 52.70, and 32 peaks of various intensity of orthorhombic Tl_2S_5 [71–358] phase are observed (Fig. 6, curve 2; Table 2). That again is in accordance with the results of chemical analysis (Table 1, Tl/S ~0.6). If the temperature of sulfuration is increased to 40 °C, the same 2 peaks of *α*-TlS [30–1331] phase at $2\theta = 46.56$ and 52.70, and 21 peaks of various intensity of orthorhombic Tl_2S_5 [71– 358] phase are observed (Fig. 6, curve 3; Table 2). That agrees well with the results of chemical analysis (Table, Tl/S~0.4). And when the temperature of sulfuration is increased to 50 °C, only peaks (3 peaks of very high

Table 1. The molar ratios Tl/S (S = 1) in the thallium sulfide layers in the surface of PA first treated in $H_2S_{12}O_6$ solution and then – in Tl(I) salt solution

Temperature of $H_2S_{12}O_6$ solution, °C	Duration of sulfuration, h								
	0.25	0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0
20	0.63:1	1:1	1.19:1	0.81:1	0.66:1	0.76:1	0.89:1	0.66:1	0.60:1
30	0.49:1	0.63:1	0.48:1	0.49:1	0.52:1	0.61:1	0.81:1	–	0.42:1
40	–	0.33:10.1	0.28:1	0.31:1	0.34:1	0.35:1	0.30:1	0.21:1	–
50	0.31:1	9:1	0.15:1	0.13:1	0.14:1	0.15:1			

Table 2. The 2 θ values of orthorhombic Tl_2S_5 phase in the X-ray diffraction pattems of Tl_xS layers in the surface of PA

No. Fig. and curve	2 θ, degree
Fig. 5, curve 2	28.76, 29.28, 29.98, 30.56, 31.72, 32.94, 34.40, 34.92, 37.20, 38.90, 40.70, 42.10, 42.88, 44.02, 44.70, 49.20, 49.98, 51.16, 51.98, 52.54, 54.92, 57.20, 58.90, 61.60, 62.78, 64.50, 65.16, 65.84, 68.14, 69.16
Fig. 5, curve 4	27.76, 28.76, 29.28, 30.56, 31.72, 32.94, 34.40, 34.92, 37.2, 38.36, 38.90, 40.70, 42.88, 44.70, 45.62, 46.28, 47.74, 48.56, 49.20, 50.16, 51.16, 51.98, 52.48, 54.02, 54.92, 56.82, 57.20, 58.90, 61.60, 62.78, 63.84, 65.84, 68.14, 69.16
Fig. 6, curve 2	27.74, 28.76, 29.28, 29.98, 30.56, 31.72, 32.94, 34.40, 34.92, 37.20, 38.90, 40.70, 42.46, 44.02, 44.70, 45.62, 47.74, 48.56, 49.20, 49.98, 51.16, 51.98, 54.92, 57.20, 58.90, 60.06, 60.86, 61.60, 62.78, 64.50, 65.84
Fig. 6, curve 3	28.76, 30.56, 31.72, 34.40, 37.20, 38.36, 38.90, 40.70, 42.10, 42.88, 44.70, 49.20, 51.16, 51.98, 54.92, 57.20, 58.90, 61.60, 62.78, 64.50, 65.84

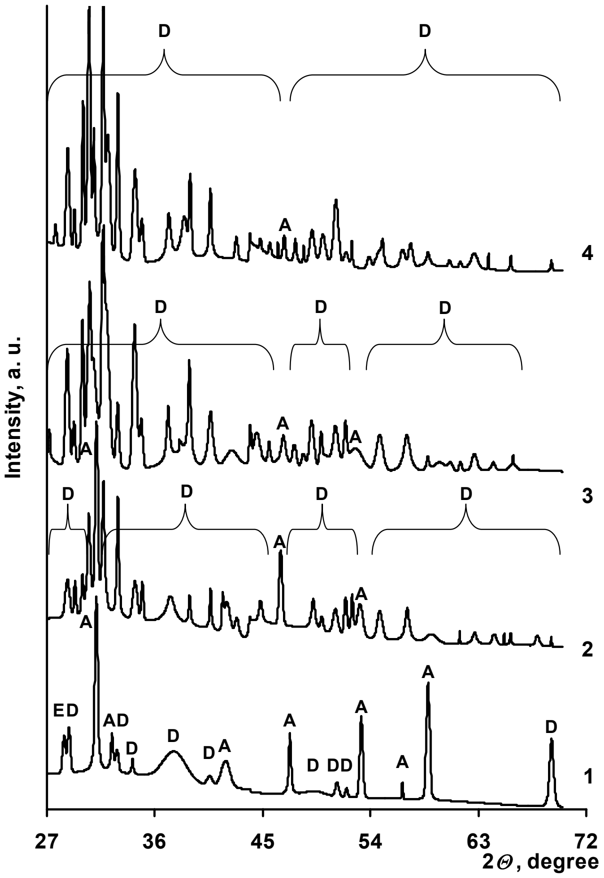

Fig. 5. X-ray diffraction patterns of thallium sulphide layers in the surface of PA. PA initially treated with a solution of $H_2S_{12}O_6$ at 30 °C different time and then with a Tl(I) salt solution at 80 °C for 10 min. Sulfuration time, h: 1 – 0.5; 2 – 1.0; 3 – 3.0; 4 – 6.0. A – α-TlS [30–1331]; D – orthorhombic Tl_2S_5 [71–358]; E – β-Tl_4S_3 [43–1067]

intensity among them) of orthorhombic Tl_2S_5 [71–358] phase at $2\theta = 28.76$, 29.98, 30.56, 31.72, 32.94, 34.40, 37.20, 38.36, 40.70, 51.16, 51.98, 57.20, 58.90, 69.16 and 2 clear peaks of middle intensity of rhombohedral elemental sulphur S [24–1206] at $2\theta = 47.32$ and 53.30 are observed (Fig. 6, curve 4). Thus, when sulphur concentration in PA is high, i.e. if a polymer was initially sulphured at a higher temperature, some amount of nonreacted sulphur remains in the sample. That agrees well with the results of chemical analysis (Table 1, Tl/S ~0.2).

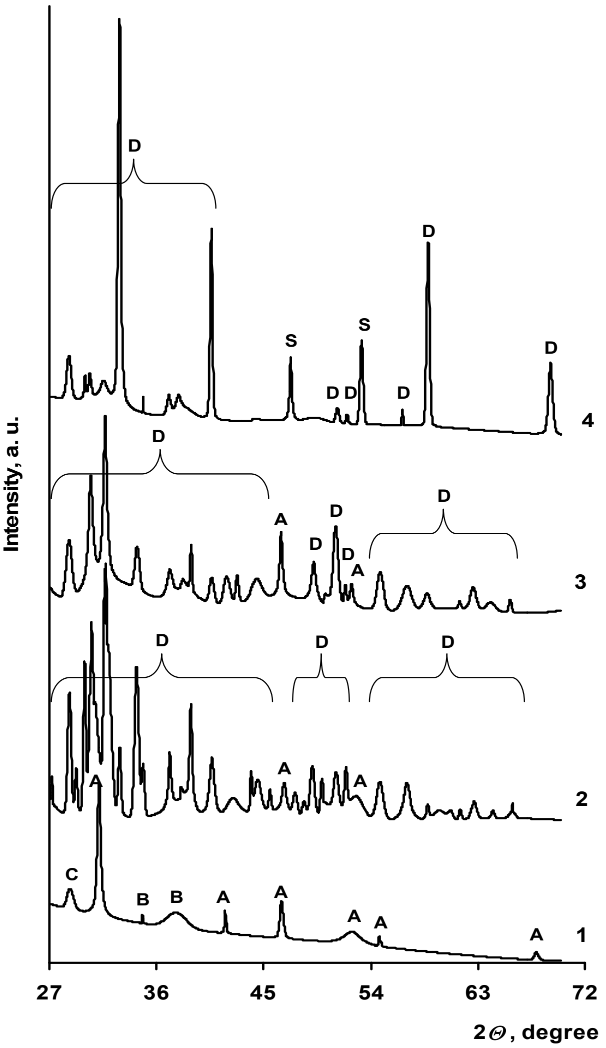

Fig. 6. X-ray diffraction patterns of thallium sulphide layers in the surface of PA. PA initially treated with a solution of $H_2S_{12}O_6$ for 3 h at different temperature and then with a Tl(I) salt solution at 80 °C for 10 min. Temperature, °C: 1 – 20; 2 – 30; 3 – 40; 4 – 50. A – α-TlS [30–1331], B – tetragonal Tl_2S_2 [82–2050], C – monoclinic TlS [82–2050], D – orthorhombic Tl_2S_5 [71–358], S – elemental sulfur S [24–1206]

Thus, four phases, TlS [30–1331], Tl_2S_2 [82–2050], Tl_2S_5 [71–358] and Tl_4S_3 [43–1067] were identified by

X-ray diffraction analysis in thallium sulfide layers on the surface of PA. If the duration of PA initial sulfuration is short (0.5 h – 1.0 h) and the temperature is relatively low (20 °C), the phases of α-TlS [30–1331] and orthorhombic Tl_2S_5 predominates in the diffractograms of the Tl_xS layers. The phase composition of these layers approaches to the composition of orthorhombic Tl_2S_5 [71–358] phase if the duration and temperature of the initial polymer sulfuration is increased.

From the data it was concluded, that the changing the conditions of PA sulfuration leads to the formation different composition of thallium sulpfide layers.

CONCLUSIONS

1. The sorption of dodecathionate ions, $S_{12}O_6^{2-}$, from 0.002 mol·dm^{-3} water solution of dodecathionic acid, $H_2S_{12}O_6$, 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 dodecathionate anions sorbed into a polyamide were found in the intervals 420–473, 503–558, 612–724, 838–1100, 1144–1293 cm^{-1}and assigned to the $\nu_{S–S}$, δ_{as}(O–S–O), δ_s(O–S–O), v_s(S–O) and v_{as}(S–O), respectively. Four absorption maxima were observed in the UV absorption spectra: at ~225 nm as a shoulder, at ~250 nm as a peak, at ~290 nm and ~322 nm – 332 nm – as a shoulders. The spectral data confirm that sulfur is sorbed by PA films in the form of dodecathionate ions.
3. The concentration of sulfur sorbed by a polymer increases with increasing the duration of polymer treatment in $H_2S_{12}O_6$ solution and the temperature of this solution. The layers of thallium sulfide forms in the surface of polyamide 6 film when the sulfured in dodecathionic acid solution polymer later treated with an alkaline solution of thallium(I) sulfate.
4. The amount of thallium in the sulfide layers increases with the increase of concentration of sulfur in polyamide. The chemical composition of thallium sulfide layers depends on the conditions of the sulfuration process and varies between $Tl_{0.15}S$ and $Tl_{1.2}S$.
5. Four thallium sulfide phases TlS, Tl_2S_2, Tl_4S_3 and Tl_2S_5 have been identified in the layers by X-ray diffraction. The maxima of TlS and Tl_2S_5 phases predominate in the diffractograms.
6. The regularities determined enable formation by sorption-diffusion method of thallium sulfide layers of desirable composition using the dodecathionic acid as a polyamide 6 sulfuration agent.

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