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Characterization of Thallium Sulfide Layers on the Surface of the Polyethylene Film Formed by the Use of Higher Polythionic Acid

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When the films of low density polyethylene first sulfured in the solution of higher polythionic, $H_2S_{33}O_6$, acid then are treated with the alkalified solution of thallium (I) sulfate, the layers of thallium sulfide of various composition in the surface of polyethylene film were formed. The stoichiometrical composition of layers according to the data of chemical analysis varies from $Tl_{0.3}S$ to $Tl_{2.5}S$. A phase composition of the layers obtained studied by the methods of X-ray photoelectron spectroscopy and X-ray diffraction. The data of Tl $4f_{7/2}$, O 1s and S 2p spectra showed that thallium is bonded with sulfur into TlS and Tl_2S, but the Tl_2SO_4 and $Tl(OH)_3$ are adsorbed on the layers surface too. Five thallium sulfide phases, TlS, Tl_2S, Tl_2S_2, Tl_4S_3 and Tl_2S_5 were identified in the composition of the layers by X-ray diffraction but the peaks of TlS phase predominate in the diffractograms.

Keywords: high polythionic acid, polyethylene, layer of thallium sulfide.

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]. Electrical conductivity of thallium sulfide 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 sorbed by PE and thallium (I) ions present in a solution of thallium (I) salt [4]:

$$3xTl^+ + 1/8S_8 \rightarrow Tl_{2x}S + xTl^{3+}. \quad (1)$$

Molecules of the elemental sulfur forms during known [5] decomposition of higher polythionic acids:

$$H_2S_nO_6 \rightarrow H_2S_{n-x}O_6 + xS. \quad (2)$$

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 on the surface of PE were obtained.

One of the most commonly used technique available for surface analysis of composite materials is X-ray photoelectron spectroscopy (XPS). This technique is a widely utilized for determining chemical composition of coatings and thin layers. For the determination of phase composition of thallium sulfide layers an X-ray diffraction analysis is most suitable.

The aim of the present study was to obtain layers of thallium sulfide of various composition, and to investigate the chemical and phase composition of formed layers of thallium sulfide on the surface of polyethylene film by the methods of XPS and X-ray diffraction analysis.

EXPERIMENTAL

The layers of thallium sulfide were deposited on PE film of low density (GOST 10354–82) produced at Vilnius Plastic Plant “Plasta”. Its thickness was 0.22 ± 0.01 mm. Before sulfuration the surface of the PE film was cleaned in 4 % solution of cationic surfactant, degreased in benzene and washed in distilled water.

Samples of PE in size 15 × 75 mm were sulfured in a 0.002 mol/dm^3 stirred $H_2S_{33}O_6$ solution, which was prepared by the method given in [6]. The concentration of diffused into PE sulfur was determined by the atomic absorption spectrophotometer “Perkin Elmer 503” [7] indirectly by the measurements of Ba^{2+} ions concentration after sulfur deposition in the form of $BaSO_4$.

Then samples of sulfured PE were treated by unstirred 0.1 mol/dm^3 Tl_2SO_4 (pH 2.8) solution having addition of KOH (of 0.015 mol/dm^3). When using alkalified TI (I) salt solution thallium sulfide layers on the surface of PE were obtained. The amount of thallium was determined by atomic absorption spectroscopy method [7] using a Perkin-Elmer 503 atomic absorption spectrophotometer.

XPS spectra of thallium sulfide layers were recorded by a spectrometer “ESCALAB MKII” (VG Scientific, radiation Mg K_α – 1253.6 eV, capacity 300 W). Vacuum in the analysing chamber was kept at level of $1.33 \cdot 10^{-8}$ Pa, the distribution of elements in the depth was determined by sputtering with an Ar^+ gun with the ion energy of about 1.0 keV. The samples were etched in a preparation chamber with the vacuum $9.3 \cdot 10^{-3}$ Pa and current 20 μA;

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duration of etching was 10 s. Maximum accuracy of the method is ± 0.1 at. %.

To investigate the layers obtained by the XPS method the photoelectron spectra of Tl $4f_{7/2}$, O 1s and S 2p were recorded. Empirical sensitivity factors for these elements were taken from the literature [8 – 10] and the spectra obtained were compared with the standart ones [11].

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 PE samples with the layers of Tl_xS_y were treated using programs “Search Match”, “ConvX”, “Xfit” to eliminate the peaks of PE.

RESULTS AND DISCUSSIONS

Having studied the kinetics of sorption-diffusion of sulfur from a solution of higher polythionic acid $H_2S_{33}O_6$ into a PE film, it was determined that the sulfur concentration in the samples (c_S, mg/cm^3) after its treatment in a solution of higher polythionic acid at the temperatures of 60 and 80 °C consequently increases. The obtained saturated sulfur concentration at a temperature of 60 °C is 8.6 mg/cm^3, and at a temperature of 80 °C – 10.1 mg/cm^3 [4]. Thus at a higher temperature the higher sulfur concentration is obtained in the PE. Two reasons may be responsible for that: firstly, the decomposition of polythionic acid proceeds faster at higher temperature and a bigger amount of elemental sulfur separates; secondly, the molecules of sulfur more easy penetrates into a volume of the polymer because of the higher temperature expansion of the amorphous phase at a higher temperature.

Polyolefins and among them the PE sorbs sulfur by the amorphous phase at the state of high elasticity [12].

Looking for the formation of thallium sulfide layers in the surface of sulfured PE films, they were treated 10 min with the alkalified Tl_2SO_4 solution at the temperature of 80 °C. The influence of experimental conditions on the thallium sulfide layers in the PE surface formation process was studied. It was found that the amount of thallium in the sulfide layer increases with the prolongation of PE sulfuration in the $H_2S_{33}O_6$ solution duration at all temperatures studied, and a different constant amount of thallium on the surface of PE at each temperature is reached [4]. The value of thallium amount increases significantly with an increase of the $H_2S_{33}O_6$ solution temperature. The amount of thallium in the layer is in direct dependence on the concentration of sulfur in the PE film, i.e. the amount of thallium in the layer increases with an increase of sulfur concentration. That is completely understandably since at a higher diffused into the PE sulfur concentration the bigger amount of Tl^+ ions may be involved into an oxidation-reduction reaction with the sulfur molecules.

The molar Tl/S ratios in the thallium sulfide layers on the PE surface having measured the amounts of sulfur and thallium in the PE films were calculated. Their values are presented in the Table 1.

It was found that a value of Tl/S ratio increases with an increase of the initial PE sulfuration stage duration and the temperature of $H_2S_{33}O_6$ solution used for the PE sulfuration. By changing the conditions of sulfuration, it is possible to obtain the layers of thallium sulfide of very different stoichiometrical composition in the surface matrica layer of PE: stoichiometry may vary from $Tl_{0.3}S$ to $Tl_{2.5}S$. Thus, when the duration of sulfured PE treatment with the alkalified solution of Tl (I) sulfate at a temperature of 80 °C is 10 min and the PE was initially sulfured in the $H_2S_{33}O_6$ solution at a temperature of 60 or 80 °C, the stoichiometrical composition of the thallium sulfide layers obtained was close (according to data of chemical analysis) to TlS or Tl_2S. When the sulfur concentration in a PE film is lower and when the PE was initially sulfured at a temperature of 60 °C, significantly lower amount of thallium was found in the sulfide layer. It seems that a reaction product – thallium sulfide hinders the further diffusion of Tl^+ ions into the depth of a polymer.

Table 1. The molar ratios Tl/S (S = 1) in the thallium sulfide layers in the surface of PE first treated in $H_2S_{33}O_6$ solution and then – in Tl (I) salt solution at 80 °C for 10 min

Duration of sulfuration, min	Temperature of solution	
	60 °C	80 °C
9	0.3	0.5
24	0.3	0.6
65	0.6	2.5
120	1.1	2.1

More precise composition of thallium sulfide layers was studied by the method of X-ray photoelectron spectroscopy. On the basis of Tl $4f_{7/2}$, O 1s and S 2p spectra data it was determined, that a layer composed of different thallium, sulfur and oxygen compounds forms on the surface of a polymer when the PE films were initially kept during different period of time in the sulfuration solution at a temperature of 60 or 80 °C and then treated with the alkalified solution of thallium(I) sulfate.

The following compounds were identified: TlS, Tl_2S, Tl_2SO_4 and $Tl(OH)_3$. The results are presented in the Table 2.

A study of the distribution of the elements Tl, S, O in the Tl_xS_y layers showed that an oxygen takes a major part on the surface of all PE films (30 – 57 at. %). All processes of Tl_xS_y layers on the PE surface formation proceeds in the natural environment, therefore it is impossible to avoid an influence of environment on the chemical composition of the layers obtained. Such large amount of oxygen may be caused by the chemical absorption and because of little soluble in water thallium (I) sulfate absorption in the surface layer, and the formation of insoluble thallium (III) hydroxide. Since the metal sulfides in the polymer surface matrix using an sorption-diffusion method forms in the form of dendrites, some amount of little soluble Tl_2SO_4 may remain in between the dendrites. Thallium (III) ions forms also during the oxidation-reduction reaction when the thallium (I) ions react with the elemental sulfur (equation 1), and these form insoluble $Tl(OH)_3$ with the HO^- groups present in the alkalified solution of Tl_2SO_4. The amount of oxygen reduces significantly (to 6 – 19 at. %) when the layer surface is etched by the Ar^+

Table 2. The data of XPS analysis of the layers of Tl_xS_y in the surface of PE

Conditions of a sulfuration in a solution of $H_2S_{33}O_6$	Etching conditions	Element	Content, at. %	Binding energy, eV	Composition of layer
τ = 15 min t = 60 °C	Surface	O	47.2	530.7+532.3	TlS, Tl_2S, $Tl(OH)_3$, Tl_2SO_4
		Tl	31.4	118.3	
		S	21.4	161.4+167.6	
	Etched 10 s – 20 μA	O	19.7	530.7	TlS, Tl_2S, $Tl(OH)_3$
		Tl	49.7	118.1	
		S	30.6	161.3+167.6	
τ = 30 min t = 60 °C	Surface	O	57.3	530.2+531.8	TlS, Tl_2S, $Tl(OH)_3$, Tl_2SO_4
		Tl	21.9	118.1	
		S	20.8	161.3+167.8	
	Etched 10 s – 20 μA	O	11.6	530.7	TlS, Tl_2S, $Tl(OH)_3$
		Tl	56.5	118.0	
		S	31.9	160.8	
τ = 60 min t = 60 °C	Surface	O	44.2	530.7+532.1	TlS, Tl_2S, $Tl(OH)_3$, Tl_2SO_4
		Tl	32.3	118.2	
		S	23.5	161.3+167.7	
	Etched 10 s – 20 μA	O	15.9	531.1	TlS, Tl_2S, $Tl(OH)_3$
		Tl	49.3	118.1	
		S	34.8	161.0+167.7	
τ = 120 min t = 60 °C	Surface	O	38.0	530.8+532.2	TlS, Tl_2S, $Tl(OH)_3$, Tl_2SO_4
		Tl	33.9	118.1	
		S	28.1	161+163.5+167.6	
	Etched 10 s – 20 μA	O	6.2	531.1	TlS, Tl_2S, $Tl(OH)_3$
		Tl	52.1	118.2	
		S	41.7	161+167.8	
τ = 15 min t = 80 °C	Surface	O	34.2	530.7+533.0	Tl_2S, TlS, $Tl(OH)_3$, Tl_2SO_4
		Tl	32.3	118.2	
		S	33.5	161.3+167.6	
	Etched 10 s – 20 μA	O	15.1	530.6	Tl_2S, TlS, $Tl(OH)_3$
		Tl	45.7	118.1	
		S	39.2	161.3+167.8	
τ = 30 min t = 80 °C	Surface	O	37.4	530.8+533.2	Tl_2S, TlS, $Tl(OH)_3$, Tl_2SO_4
		Tl	38.6	118.3	
		S	24.0	161.3+167.8	
	Etched 10 s – 20 μA	O	10.1	531.2	Tl_2S, TlS, $Tl(OH)_3$
		Tl	57.7	118.3	
		S	32.2	161.1	
τ = 60 min t = 80 °C	Surface	O	30.3	531.2	Tl_2S, TlS, $Tl(OH)_3$
		Tl	42.2	118.3	
		S	27.5	161.3+167.8	
	Etched 10 s – 20 μA	O	9.3	531.2	Tl_2S, TlS, $Tl(OH)_3$
		Tl	54.8	118.1	
		S	35.9	161.1	
τ = 120 min t = 80 °C	Surface	O	34.3	530.8	Tl_2S, TlS, $Tl(OH)_3$
		Tl	38.9	118.3	
		S	26.8	161.3+167.8	
	Etched 10 s – 20 μA	O	12.4	531.2	Tl_2S, TlS, $Tl(OH)_3$
		Tl	50.1	118.2	
		S	37.5	161.3+ 167.6	

ions. That proves that oxygen in the compounds mentioned is present only on the surface.

The data of XPS analysis show that the composition of Tl_xS_y layers formed at the different conditions is very similar (Table 2). Only the amount of sulfur found on the surface of PE film sulfured at a temperature of 80 °C is higher by 12 at. %. A reason of that may be a bigger amount of sulfur absorbed in the surface of PE at a higher temperature. When the PE film with the sulfide layer is etched by the Ar^+ ions, the amounts of the elements changed: the amount of oxygen reduces but the amount of thallium increases significantly (up to 57.7 at. %) and also of sulfur (up to 41.7 at. %). The formation of thallium sulfides of various composition is indicated by the spectra of the elements too. The peaks in the S 2p spectra (Figs. 1 and 2) corresponding to the bond energies 161.3, 161.5, 167.8 eV show the formation of thallium sulfides TlS and Tl_2S in the Tl_xS_y layer. That confirms a bond energy of thallium sulfides ~ 118 eV present in the spectra of Tl $4f_{7/2}$. Consequently, the thallium (I) sulfide, Tl_2S, and a mixed sulfide, TlS, ($Tl^I[Tl^{III}S_2]$) are present in the layers.

The data of XPS analysis gives only approximate x and y values in the Tl_xS_y layers obtained. X-ray diffraction analysis gives more accurate identification of thallium sulfides formed on the surface of PE [13 – 15]. Results of this analysis are presented in Figures 3 and 4.

The peak of monoclinic TlS phase predominate in the diffractograms of obtained Tl_xS_y layers when a PE films were sulfured in the solution of $H_2S_{33}O_6$ during 15, 60 and 120 min. at the temperature of 60 °C (Fig. 3). That is in accordance with the results of chemical analysis (Table 1). Especially strong in the layers diffractograms is the TlS phase peak at $2\Theta = 24.0°$ (corresponding to $d = 3.7$ Å). The another peak of TlS phase at $2\Theta = 36.2°$ (corresponding to $d = 2.5$ Å) is observed in the diffractograms of these samples also. The peaks of another two thallium sulfide phases in the diffractograms of PE samples initially

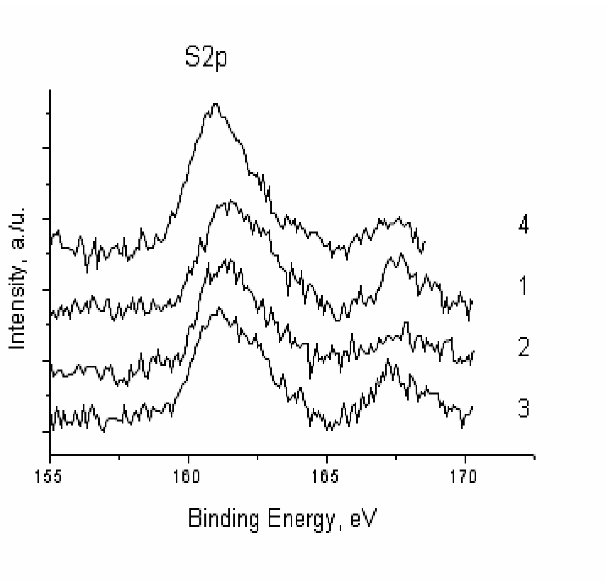

Fig. 1. XPS spectra for S 2p. PE initially treated with a solution of $H_2S_{33}O_6$ at 60 °C different time and then with a Tl (I) salt solution at 80 °C for 10 min. Sulfuration time (min): 1 – 15, 2 – 30, 3 – 60, 4 – 120

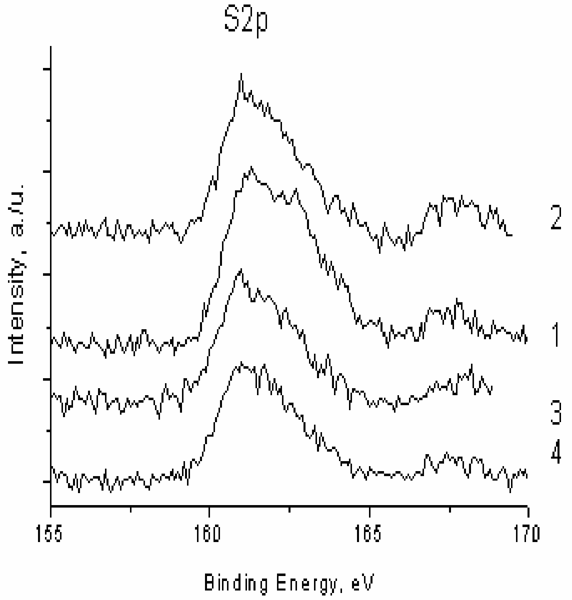

Fig. 2. XPS spectra for S 2p. PE initially treated with a solution of $H_2S_{33}O_6$ at 80 °C different time and then with a Tl (I) salt solution at 80 °C for 10 min. Sulfuration time (min): 1 – 15, 2 – 30, 3 – 60, 4 – 120

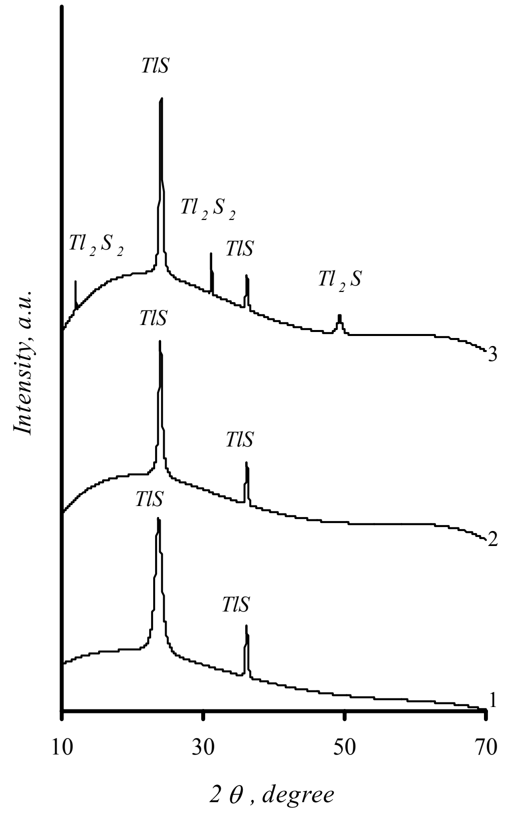

Fig. 3. X-ray diffraction patterns of a thallium sulfide layers in the surface of PE. PE initially treated with a solution of $H_2S_{33}O_6$ at 60 °C different time and then with a Tl (I) salt solution at 80 °C for 10 min. Sulfuration time (min): 1 – 15, 2 – 60, 3 – 120

sulfured during 120 min are observed (Fig. 3, curve 3): of tetragonal Tl_2S_2 at $2\Theta = 11.9°$ and $31.2°$ (corresponding to $d = 7.4$ Å and 2.9 Å) and of rhombohedral Tl_2S at $2\Theta = 49.3°$ (corresponding to $d = 1.9$ Å).

Only two peaks of TlS phase at $2\Theta = 24.0$ and $36.2°$ (Fig. 4, curve 1) in the diffractogram of PE sample initially sulfured during 15 min at the temperature of 80°C are observed. If the duration of PE initial sulfuration is increased (30, 60 and 120 min), the peak of S_8 at $2\Theta = 22.9°$ (corresponding $d = 3.9$ Å) (Fig. 4, curves 2 – 4) is observed. Thus, when sulfur concentration in PE is higher, i.e. if a polymer was initially sulfured at a higher temperature, some amount of nonreacted sulfur remains in the samples. The numerous peaks of three thallium sulfide phases in the diffractograms of these samples are observed: of monoclinic TlS, tetragonal Tl_2S_2 and of rhombohedral Tl_2S. The TlS peak at $2\Theta = 24.0°$ and of Tl_2S_2 at $2\Theta = 31.2°$ (corresponding $d = 2.9$ Å) are most intensive. These peaks in the diffractograms of PE samples sulfured during longer period of time are more intensive. The peak of Tl_2S phase at $2\Theta = 49.3°$ (corresponding $d = 1.9$ Å) appears in a diffractogram of PE sample initially sulfured 60 min (Fig. 4, curve 3) and this peak in the diffractogram of PE sulfured during 120 min (Fig. 4, curve 4) is significantly more intensive. Not intensive peaks of already mentioned thallium sulfide phases in the two latter diffractograms are observed too: of TlS at $2\Theta = 46.5°$, $51.9°$ and $53.0°$ (corresponding $d = 2.0$ Å, 1.8 Å and 1.7 Å) and of Tl_2S_2 at $2\Theta = 11.9°$ (corresponding $d = 7.4$ Å).

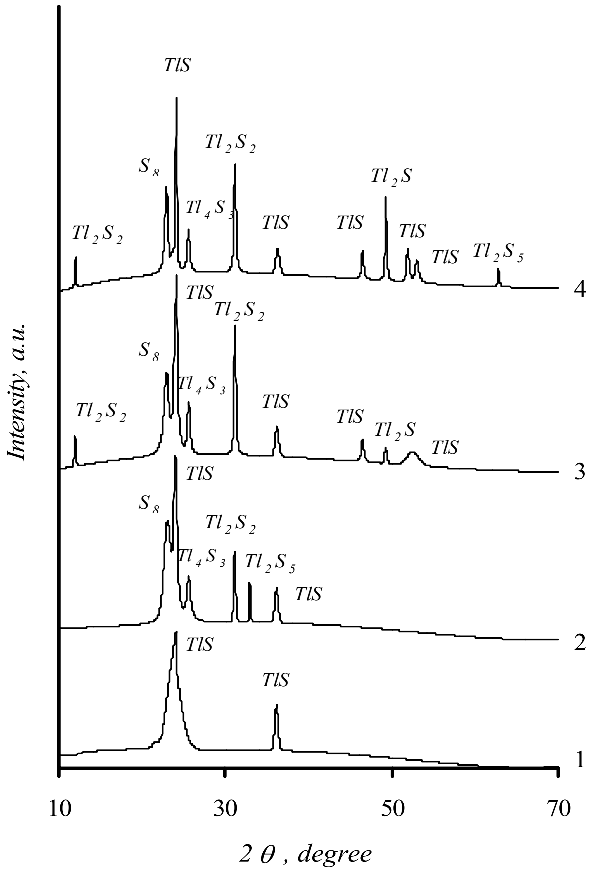

Fig. 4. X-ray diffraction patterns of a thallium sulfide layers in the surface of PE. PE initially treated with a solution of $H_2S_{33}O_6$ at 80 °C different time and then with a Tl (I) salt solution at 80 °C for 10 min. Sulfuration time (min): 1 – 15, 2 – 30, 3 – 60, 4 – 120

The peak of a new phase, Tl_4S_3, at $2\Theta = 24.7°$ (corresponding $d = 3.6$ Å) appears in the diffractograms of thallium sulfide layers in PE initially sulfured 30 – 120 min (Fig. 4, curves 2 – 4). This phase is a mixed Tl (I) and Tl (III) sulfide – $Tl_3^{I}[Tl^{III}S_3]$. The peak of another one thallium sulfide phase – of orthorhombic Tl_2S_5 at $2\Theta = 32.9°$ (corresponding $d = 2.7$ Å) in the diffractogram of sulfide layer in PE initially sulfured 30 min (Fig. 4, curve 2) is observed. Not intensive peak of Tl_2S_5 phase at $2\Theta = 62.7$ ° (corresponding $d = 1.5$ Å) is observed in diffractogram when the duration of PE initial sulfuration is prolonged until 120 min (Fig. 4, curve 4). This phase is thallium polysulfide – Tl_2SS_4.

Thus, five phases – TlS, Tl_2S, Tl_2S_2, Tl_4S_3 and Tl_2S_5 were identified by the X-ray diffraction analysis of the thallium sulfide layers formed in the PE surface. The peak of TlS phase at $2\Theta = 24.0°$ is most intensive in diffractograms recorded.

CONCLUSIONS

1. The layers of thallium sulfide formed on the surface of polyethylene film first sulfured in a solution of higher polythionic acid, $H_2S_{33}O_6$, and later treated with the alkalified solution of thallium (I) sulfate were studied by chemical, X-ray photoelectron spectroscopy and X-ray diffraction methods.
2. The stoichiometrical composition of thallium sulfide layer is dependent on the conditions of polyethylene initial sulfuration in the solution of higher polythionic acid. It varies from $Tl_{0.3}S$ to $Tl_{2.5}S$.
3. Thallium compounds TlS, Tl_2S, Tl_2SO_4 ir $Tl(OH)_3$ were identified in the layer of thallium sulfide in the surface of polyethylene by X-ray photoelectron spectroscopy.
4. Five thallium sulfide phases, TlS, Tl_2S, Tl_2S_2, Tl_4S_3 and Tl_2S_5 were identified in the composition of the layers by X-ray diffraction but the peaks of TlS phase predominate in the diffractograms.

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