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The Modification of Polyethylene by the Thallium Sulphide Layers

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Thallium sulfide layers were formed on the surface of low-density polyethylene (PE) when the PE layer have been sulfured in a solution of higher polythionic acid $H_2S_{33}O_6$, and then immersed in the alkaline solution of thallium (I) sulfate. Sulphur concentration increased on PE surface with the increase of the sulphurisation time. The amount of thallium in the Tl_xS_y layers was dependent on a sulphur concentration sorbed-diffused into PE, the concentration and temperature of thallium sulfate solutions. The values of thallium content in the sulphide layer increased with increasing the duration of sulphured polyethylene treatment with Tl_2SO_4. Three phases TlS, Tl_2S, Tl_2S_2 were identified by X-ray diffraction analysis in thallium sulphide layers. The data of Tl $4f_{7/2}$, O 1s and S 2p spectra showed that thallium is bonded with sulphur into TlS and Tl_2S, but the Tl_2SO_4, S_8, Tl_2O_3 and $Tl(OH)_3$ are adsorbed on the layers surface too. Scanning Electron (SEM) and Atomic Force (AFM) microscopies were used to characterize surface morphology of thallium sulphide layers. The films deposited on the PE surface have a non-homogeneous structure and consist of separated islands. The process of their growth on PE surface starts from nucleation sites creating islands of TlS with a diameter in tenths of microns.

Keywords: polyethylene, higher polythionic acid, sulphurisation, thallium sulphide layer.

INTRODUCTION

Nano-structured composite materials are intensively studied during the last decade as new possibilities for advanced devices. The layers of thallium chalcogenides formed on the surface of polymeric materials can be useful for the specific photonic applications [1 – 3]. The layers of thallium sulphides show a great variety of stoichiometry, valuable physical properties and find applications in photoconductive devices and solar batteries [4 – 6].

The great number of these compounds and thus the large variety of their physical properties are determined by possible different oxidation states (+1 and +3) of thallium atoms in the compounds. In the thallium–sulphur system, many types of sulphides have been reported: Tl_2S, Tl_4S_3, TlS, TlS_2, Tl_2S_5, Tl_2S_9. Here, TlS and Tl_4S_3 are double sulphides: $Tl^I[Tl^{III}S_2]$ and $Tl^I_3[Tl^{III}S_3]$, respectively, whereas TlS_2, Tl_2S_5, Tl_2S_9 may be considered as polysulphides Tl_xSS_n (for example, Tl_2SS_8 with elemental composition: Tl_2S_9). It is known that TlS, Tl_2S and Tl_4S_3 are photoconductors [4, 6 – 7].

The effort to deposit thallium sulphide layers on polymeric materials were described in early works [8, 9]. Sorption-diffusion method for obtaining thallium sulphide layers is a simple and promising method in which, after sorption of the sulphurisation agent, the polymer substance is treated with a thallium salt aqueous solution. The solutions of polythionic acids, $H_2S_nO_6$ (n = 9 – 45), are suitable for sulphurisation of the majority of polymers. Recently, it has been reported [8] that thallium sulphide

layers on the surface of polyethylene (PE) can be deposited using a solution of higher polythionic acids.

The aim of present work was to put in the whole and to discuss the results received by us during systematic studies of processes of interaction of the sulphurisation agent, $H_2S_nO_6$, with the hydrophobic polymeric material – polyethylene film (PE) and also of sulfured polymer treatment with a thallium(I) salt solution on the formation of thallium sulphide layers. The chemical and phase composition of the Tl_xS_y layers were studied by the methods of atomic absorption spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy (XPS). Scanning Electron (SEM) and Atomic Force (AFM) microscopies were used to characterize surface morphology of thallium sulphide layers.

EXPERIMENTAL

The layers of thallium sulphide were deposited on a low density PE film of 0.22 mm ±0.01 mm thickness (GOST 10354-82), made in Vilnius plastics factory "Plasta". Before sulphuration the surface of the PE samples 15 mm × 75 mm in size was cleaned in a 4 % solution of cationic surfactant (Perwocell WOF–100), degreased in toluene, washed in distilled water and dried [10]. Then the PE samples were sulphured in 0.002 $mol\cdot dm^{-3}$ solutions of polythionic acids, $H_2S_nO_6$ (n = 21, 33, 45) at the temperatures 25, 40, 60 and 80 °C. At different periods of time the samples were removed, washed in distilled water and dried. Distilled water, reagents of the grades "especially pure", "chemically pure" and "analytically pure" were used in the experiments. The concentration of the sulphur diffused into the PE samples was determined by a spectrometric cyanide method [11] using a Specord UV/VIS spectrophotometer (λ = 450 nm).

The sulphurised samples were then treated in unstirred 0.1 $mol\cdot dm^{-3}$ – 0.01 $mol\cdot dm^{-3}$ solution of Tl_2SO_4 (pH 2.8) with addition of 0.015 $mol\cdot dm^{-3}$ KOH. Thallium sulphide layers on the surface of the PE were obtained using this alkaline Tl(I) salt solution for 2 min – 20 min at the temperatures of 40, 60 or 80 °C. The amount of thallium in a PE sample was determined using an atomic absorption spectrophotometer Perkin-Elmer 503 (λ = 276 nm) [12].

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The phase composition of the thallium sulphide layers was investigated by means of X-ray diffraction using a DRON-6 diffractometer (radiation Cu K_{α}, voltage 30 kV). The experimental XRD pattern analysis was performed using Crystallografica software and PDF date base [13-16].

XPS spectra of thallium sulphide layers were investigated by a spectrometer "ESCALAB MKII" (VG Scientific, radiation Mg K_{α} – 1253.6 eV). vacuum in the analysing chamber was kept at level of $1.33\cdot10^{-8}$ Pa, the distribution of elements in 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 $9.3\cdot10^{-3}$ Pa and current 20 μA; duration of etching was 10 s. Maximum accuracy of the method is ±0.1 at.%. The photoelectron spectra of Tl $4f_{7/2}$, O 1s and S 2p were recorded. Empirical sensitivity for these elements were taken from the [15, 17 – 18] and the spectra obtained was compared with the standard ones [19].

Surface and cross-section morphologies of the films were characterized with a scanning electron microscope (XL-30 S, Philips), atomic force microscope (AFM) measurements were made with a Quesant Corp., QScope-250 instrument. The dry samples 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.

ANALYSIS AND RESULTS

It is known that the molecules of the elemental sulphur form during the decomposition of higher polythionic acids [20]. In this work formation of Tl_xS_y layers on PE surface were realized in two steps. The first step, an adsorption of elemental sulphur on the PE surface from the solutions of higher polythionic acids, $H_2S_nO_6$ (n = 21, 33, 45), was studied at temperature 60 °C.

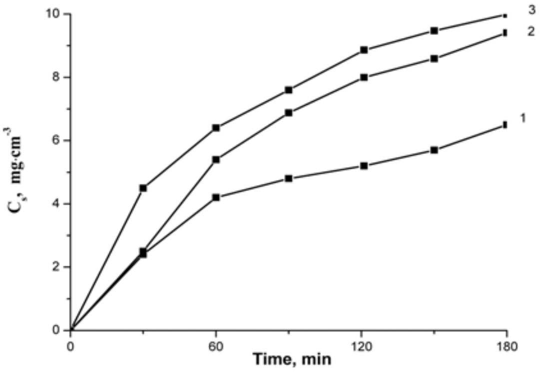

Fig. 1. Dependence of the content of sulphur in layer on PE film on sulphurisation time under treatment it with solutions of $H_2S_nO_6$ at 60 °C. The average number of sulphur number atoms (*n*) in polythionic acid molecule: 1–21; 2–33; 3–45

We found that the concentration of sulphur (c_S, mg·cm^{-3}) in the PE samples increases with an increase of sulphur number atoms in the molecule of $H_2S_nO_6$ and of the time of PE treatment in higher polythionic acids solutions. The kinetic curves of sulphur content changes in the PE are shown in Fig. 1.

At the beginning of sulphurisation process c_S in PE increased, later on, though after 3 h the saturated sulphur concentration out of reach. Thus these results revealed that solutions of higher polythionic acid, $H_2S_{33}O_6$, are suitable to be applied for PE sulphurisation during further research, as further increase of sulphurisation degree (number of sulphur atoms in a molecule, n) does not make more distinguished influence upon the effectiveness of PE sulphurisation.

Figure 2 presents changes of sulphur concentration in PE films after its treatment in a solution of higher polythionic acid $H_2S_{33}O_6$ at the different temperatures.

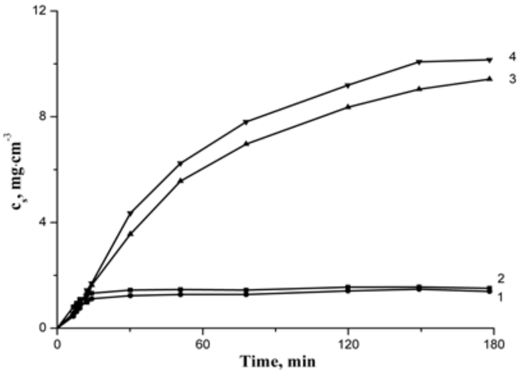

Fig. 2. Dependence of the content of sulphur in layer on PE film on sulphurization time under treatment it with solutions of $H_2S_{33}O_6$. The temperature (°C) of $H_2S_{33}O_6$ solution: 1 – 25, 2 – 40, 3 – 60, 4 – 80

The saturated sulphur concentration in PE samples at a temperature of 25 °C was reached after 1 h.

(1.1 mg·cm^{-3}), and at a temperature of 40 °C it was reached after 2 h of treatment (1.6 mg·cm^{-3}). In the PE samples treated in a $H_2S_{33}O_6$ solution at 60 °C and 80 °C a saturated sulphur concentration was reached after 3 h only – its values were 8.6 mg·cm^{-3} and 10.1 mg·cm^{-3} [21]. Thus at a higher temperature the higher sulphur 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 elelmental sulphur separates; secondly, molecules of sulphur more easily diffuse into the polymer because of the greater expansion of the amorphous phase at the higher temperature. The amorphous phase of polyolefins including PE sorbs sulphur well in the high elastic state [22].

Thus, an increase of the sulphurisation solution temperature leads to a significant increase of the concentration of sulphur diffused into PE films we performed PE sulphurisation at 60 °C temperature during further research.

In the second step, the PE film samples were sulphured during different periods of time to induce formation of thallium sulphide layers the surfaces were treated for 10 min with the alkaline solution of thallium (I) sulfate at 80 °C. Thallium sulphide layers in the surface of PE film were formed by a sorption-diffusion method as a result of the oxidation-reduction reaction between sulphur by PE and Tl^+ ions present in a solution of thallium (I) salt:

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

Elemental sulphur diffused into the PE from solution of $H_2S_{33}O_6$ interacted with Tl^+ ions of thallium (I) salt solution. Depending on the initial sulphur concentration in the PE fim and the duration of the treatment with thallium (I) salt solution Tl_xS_y layers was obtained. The colour of PE films directly depends on the conditions of sulphurisation: the PE films, in which the concentration of diffused sulphur was small, become redly brownish after "thalliumisation", and the films, in which the concentration of sulphur was bigger after the reaction with Tl^+ ions become dust-colour or even blackish.

The kinetic curves of thallium content changes in the thallium sulphide layers formed are presented in Figures 3–7.

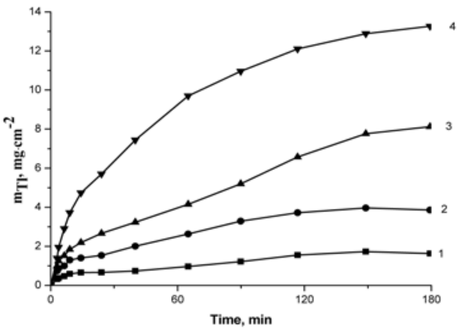

Fig. 3. Dependence of the content of thallium in sulphide layer on PE film on sulphurization time under treatment it with solutions of $H_2S_{33}O_6$ for different periods of time. The period of treatment with 0.1 M Tl_2SO_4 solution at 80 °C was 10 min. The temperature (ºC) of $H_2S_{33}O_6$ solution: 1 – 25, 2 – 40, 3 – 60, 4 – 80

Figure 3 presents the value of thallium content in the sulphide layers on PE surface that increases with sulphurisation time at all temperatures used. Different content of thallium in the sulphide layers was obtained at each temperature. A maximum value of thallium content reached at a particular temperature depends strongly on the temperature of sulphuration solution and increases significantly while increasing the temperature of $H_2S_{33}O_6$ solution. The content of thallium is dependent on a sulphur concentration in PE, i. e. its value increases with an increase of c_S.

In the work the influence of sulphured PE "thalliumisation" conditions on the content of thallium (m_{Tl}) in the sulphide layers was studied changing the temperature, concentration of thallium (I) salt solution and the duration of treatment.

Dependence of thallium content in the sulphide layer on PE surface on the temperature of Tl_2SO_4 solution

(40, 60 and 80 °C), when PE was sulphured at 60 °C temperature is shown in Figure 4.

When the PE was sulphured in a solution of $H_2S_{33}O_6$ at temperature 60 °C and then treated with alkalified 0.1 M Tl_2SO_4 solution at 40 °C, the value of thallium content was almost independent on the temperature of the sulphuration solution (1.67 mg·cm^{-2}). But if the sulphured PE samples were treated with Tl_2SO_4 solution at higher temperature (60 °C or 80 °C), the content thallium depended significantly on the temperature of the initial PE sulphuration stage.

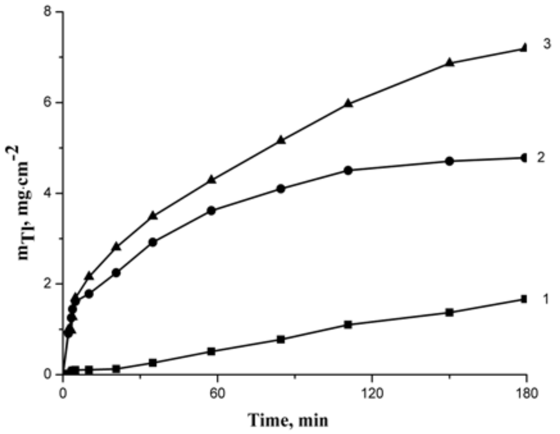

Fig. 4. Dependence of thallium content in sulphide layer on PE film on sulphurization time under treatment it with solution of $H_2S_{33}O_6$ at 60 °C for different periods of time. The period of treatment with 0.1 M Tl_2SO_4 solution was 10 min. The temperature (°C) of Tl_2SO_4 solution: 1 – 40, 2 – 60, 3 – 80

Figures 5 and 6 present the influence of Tl_2SO_4 solution concentration on the content of thallium in the Tl_xS_y layers.

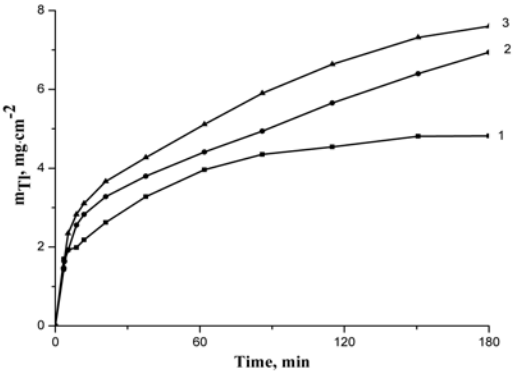

Fig. 5. Dependence of thallium content in sulphide layer on PE film on sulphurization time under treatment it with solution of $H_2S_{33}O_6$ at 60 °C for different periods of time. The period of treatment with 0.1 M Tl_2SO_4 solution at 80 °C was 10 min. The concentration (mol·dm^{-3}) of Tl_2SO_4 solution: 1 – 0.001, 2 – 0.05, 3 – 0.1

The content of thallium with the increase in thallium (I) salt solution concentration increases differently, since it strongly depends on the temperature of sulphuration stage. When the PE samples were sulphurated at a lower temperature (60 °C), the values of m_{Tl} were dependent on Tl_2SO_4 solution concentration (Fig. 5).

But if the PE samples had been initially sulphured at a higher temperature (80 °C), the concentration of thallium (I) salt solution significantly influenced the thallium content in the sulphide layers formed (Fig. 6).

The largest amounts of thallium in the sulphide layers were obtained using 0.1 M Tl_2SO_4 solution (Fig. 5, curve 3; Fig. 6, curve 3).

The prolongation of sulphured PE treatment in a Tl_2SO_4 solution leads to an increase of the amount of thallium in the sulphide layers (Fig. 7).

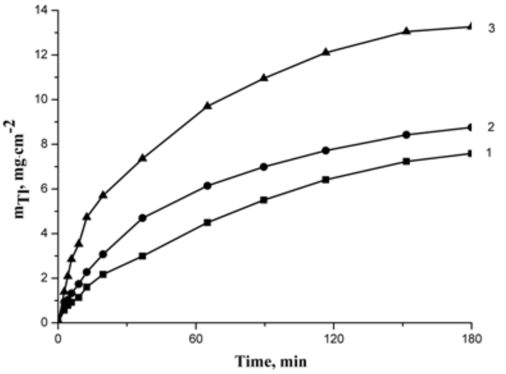

Fig. 6. Dependence of thallium content in sulphide layer on PE film on sulphurisation time under treatment it with solution of $H_2S_{33}O_6$ at 80 °C for different periods of time. The period of treatment with 0.1 M Tl_2SO_4 solution at 80 °C was 10 min. The concentration (mol·dm^{-3}) of Tl_2SO_4 solution: 1 – 0.001, 2 – 0.05, 3 – 0.1

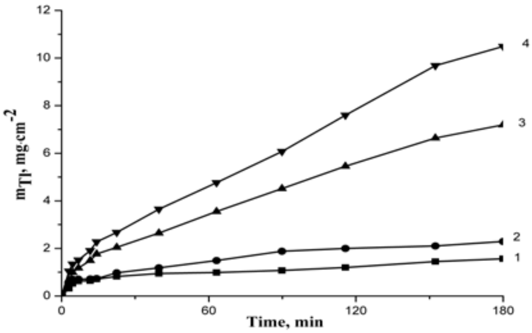

Fig. 7. Dependence of thallium content in sulphide layer on PE film on sulphurization time under treatment it with solution of $H_2S_{33}O_6$ at 60 °C for different periods of time. The sulphured PE treated with 0.1 M Tl_2SO_4 solution at 80 °C. Duration (min) of sulphured PE treatment with Tl_2SO_4 solution: 1 – 2, 2 – 5, 3 – 10, 4 – 20

When the PE samples had been sulphured longer in the $H_2S_{33}O_6$ solution at a temperature of 60 °C and the treated 2 min– 5 min with 0.1 M Tl_2SO_4 salt solution, the content of thallium in the sulphide layer changed little (Fig. 7, curves 1, 2). The content of thallium in the samples treated with thallium (I) salt solution for 10 min or 20 min increased all time (Fig. 7, curves 3, 4). The maximum contents of thallium have been obtained in the PE samples treated for 20 min with Tl_2SO_4 salt solution.

The phase composition of the Tl_xS_y layers obtained was confirmed by X-ray diffraction analysis. The XRD patterns of deposited thallium sulphide layers are presented in Figures 8 and 9.

The peak of monoclinic TlS phase predominates in the diffractograms of obtained Tl_xS_y layers when PE films were sulphurated in the solution of $H_2S_{33}O_6$ during 15, 60 and 120 min at 60 °C (Fig. 8). The results are in good agreement with the chemical analysis. The strong peak of TlS(223) phase is seen in diffractograms at $2\Theta = 24.18°$ (corresponding to interplanar spacing $d = 3.69$ Å). The peak of TlS(130) phase at $2\Theta = 25.6°$ (corresponding to $d = 3.48$ Å) is observed in the diffractograms of these samples also. The peaks of another two thallium sulphide phases in the diffractograms of PE samples initially sulphured during 120 min are observed (Fig. 8, curve 3): tetragonal Tl_2S_2 at $2\Theta = 11.9°$, 31.2° and 46.9° (corresponding to $d = 7.3$ Å, 2.87 Å and 1.955 Å) and rhombohedral Tl_2S at $2\Theta = 29.4°$ and 49.36° (corresponding to $d = 2.9$ Å, 1.79 Å).

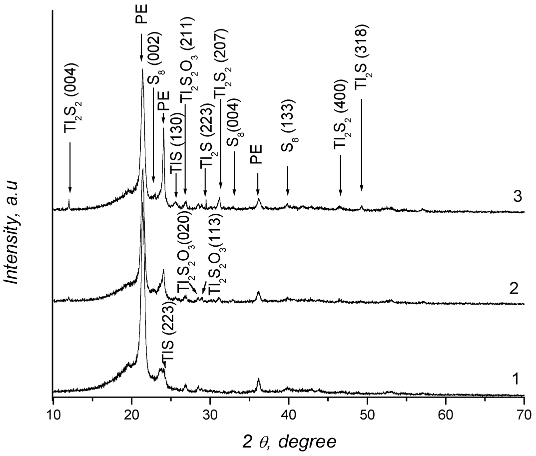

Fig. 8. X-ray diffraction patterns of thallium sulphide layers on the surface of PE. PE initially treated with a solution of $H_2S_{33}O_6$ at 60 °C for different times and then immersed in Tl_2SO_4 solution at 80 °C for 10 min. Sulphurization time (min): 1 – 15, 2 – 60, 3 – 120

The influence of the deposition temperature on the structure of deposited thallium sulphide layers was investigated by X-ray diffraction of the films deposited from 60 °C and 80 °C temperature solutions.

Two peaks of Tl_2S_2 phases at $2\Theta = 12.04°$ and 31.25° (corresponding to $d = 7.3$ Å, 2.87 Å) and TlS(130) phase at $2\Theta = 26.02°$ (corresponding to $d = 3.47$ Å) (Fig. 9, curve 1) in the diffractogram of PE sample initially sulphured during 15 min at the temperature of 80 °C are observed. If the duration of PE sulphuration is increased (60 min and 120 min), the peak of S_8(022) at $2\Theta = 23.02°$ (corresponding to $d = 3.78$ Å) (Fig. 9, curves 2 – 3) is observed. Thus, when sulphur concentration in PE is higher, i. e. if a polymer was initially sulphured at a higher temperature, some amount of nonreacted sulphur remains in the samples. The numerous peaks of three thallium sulphide phases are observed (Fig. 9, curve 3): of tetragonal Tl_2S_2 at $2\Theta = 46.52°$, 63.24° (corresponding to $d = 1.9$ Å, 1.47 Å), monoclinic TlS at $2\Theta = 52.58°$, 53.54° (corresponding to $d = 1.76$ Å, 1.72 Å), rhombohedral Tl_2S at $2\Theta = 49.36°$ (corresponding to $d = 1.79$ Å).

When PE was treated with a solution of $H_2S_{33}O_6$ at 60 °C and 80 °C for different times and then with Tl_2SO_4 solution at 80 °C for 10 min, five phases TlS, Tl_2S, Tl_2S_2, $Tl_2S_2O_3$, S_8 were identified by X-ray diffraction analysis in thallium sulphide layers.

The composition of thallium sulphide layers was studied by the method of X-ray photoelectronic spectroscopy. The surface of Tl_xS_y layers was etched by

Ar^+ ions up to 1 nm depth. 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, sulphur and oxygen compounds forms on the surface of PE. By means of this method the layers of thallium sulphides, obtained by sulphurisation the PE film in 60 °C or 80 °C temperature $H_2S_{33}O_6$ solution and then treating with Tl(I) salt solution, were analysed.

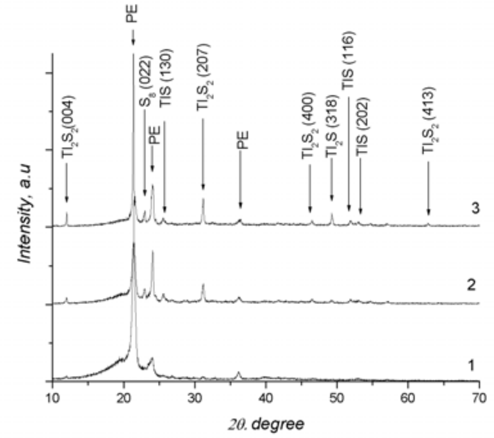

Fig. 9. X-ray diffraction patterns of thallium sulphide layers on the surface of PE. PE initially treated with a solution of $H_2S_{33}O_6$ at 80 °C for different times and then immersed in Tl_2SO_4 solution at 80 °C for 10 min. Sulphurisation time (min): 1 – 15, 2 – 60, 3 – 120

By means of the XPS method we identified that on the polymer surface the layer consisting of different thallium, sulphur and oxygen compounds was formed. The following compounds were identified: TlS, Tl_2S, Tl_2SO_4, $Tl(OH)_3$, S_8 and Tl_2O_3. The study of Tl, S, O element distribution in Tl_xS_y layers revealed that oxygen (30 at.% – 57 at.%) makes the largest part on the surface of all samples of PE film. During the formation of Tl_xS_y layers on the PE surface all processes take place in the open environment, so it is impossible to avoid environment influence upon chemical composition of obtained layers and on the surface of thallium sulphides layers oxygen can always be detected. As metal sulphides, when getting them in the matrix of polymers' surface by sorption-diffusion method, form in the shape of dendrites, so among the dendrites one can detect adsorbed hardly soluble Tl_2SO_4. In addition, if oxidation-reduction reaction when Tl^+ ions react with element sulphur occurs, Tl^{3+} ions that make insoluble $Tl(OH)_3$ together with present groups of HO^- in alkalified Tl_2SO_4. In deeper layers oxygen can be interlinked into Tl_2O_3. The layers of Tl_xS_y on polymer' surface composes in islets because the diffusion of sulphur and Tl^+ ions is possible only in amorphous areas of PE, atmospheric oxygen faces no difficulties to approach the latter.

When the surface of the layer is etched by Ar^+ ions, the amount of oxygen considerably decreases (0 at.% – 20 at.%). This proves that in the mentioned compounds the greater part of oxygen is found only on the surface.

The data of XPS analysis show that the composition of Tl_xS_y layers formed under different conditions is very similar. Thus the research performed by the XPS method confirm the results obtained by XRD research of Tl_xS_y layers – the formation of thallium sulphides of different stages in the layers of Tl_xS_y on the PE surface.

Figures 10 and 11 show the typical surface morphology of the deposited thallium sulphide thin films on the PE surface obtained by AFM and SEM.

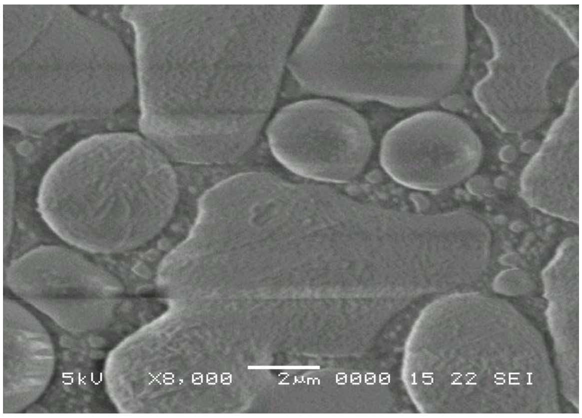

Fig. 10. SEM image of Tl_xS_y films on polyethylene. Image area (16×10) μm²

At the initial stage of the film growth on PE film the separate islands of the sulphur are formed with the roughness in the range of tenths of nanometers. When the deposition time increased the thickness of the film increased. The film thickness vary strongly between the islands, forming landscape with the islands of a height up to 10 μm and of small, tenths of nanometer scale islands in between. The sulphur film morphology is strongly influenced by the stresses on the surface of PE, which can occur as a result of the polymer crystallites structure disorientation during the PE rolling process and polymerization.

The mechanism of thallium sulphide layers formation is based on a sorbtion-difusion mechanism on the sulphur surface and does't influence strongly the morphology of the thallium sulphide film.

The films deposited on the PE substrate have not homogeneous structure and consist of islands with grains of several micrometer size and areas with separated submicrometer sized grains.

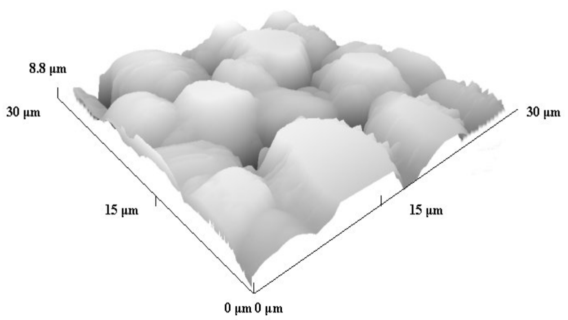

Fig. 11. AFM image of Tl_xS_y films on polyethylene. PE initially treated with a solution of $H_2S_{33}O_6$ at 60 °C for 120 min and then immersed in Tl_2SO_4 solution at 80 °C for 10 min

The inhomogeneous film structure is related to the PE film surface structure and islands of different PE crystallization direction (Fig. 11).

CONCLUSIONS

1. The polyethylene film can be effectively sulphurised in the solutions of higher polythionic acids. The concentration of sulphur in PE increases with the increase the time of PE treatment in $H_2S_nO_6$ solution, the temperature of sulphuration solution and sulphurisation degree (number of sulphur atoms in a molecule, n) of higher polythionic acids.
2. The temperature of solutions of higher polythionic acid and thallium (I) salt determines the content of thallium in the thallium sulphide layers formed: Tl content increases with increasing the temperatures.
3. The content of thallium depends on the concentration of Tl_2SO_4 solution. Its increase leads to an increase of thallium content, especially at a higher sulphur concentration initially diffused into the polymer.
4. The values of thallium content in the sulphide layer increases with increasing the duration of sulphured PE treatment with Tl(I) solution. The maximum contens of thallium have been obtained in PE samples treated for 20 min with Tl(I) salt solution.
5. Three thallium sulphide phases TlS, Tl_2S and Tl_2S_2 have been indentified in the layers by X-ray diffraction. TlS, Tl_2S, Tl_2SO_4, $Tl(OH)_3$, S_8 and Tl_2O_3 were indentified in the layers by means of X-ray photoelectron spectroscopy.
6. Deposition of thallium sulphide films from the solution of higher polythionic acid on PE produces the films with non-homogeneous, separated island type morphology. The growth of the film thickness up to 10 micrometers does not produce of dense homogeneous film. The film consists of separated islands with the average roughness up to 10 micrometers.

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