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The Modification of Polyethylene (PE) and Polyester Textile (PES) by the Conducting Copper Sulfide Layers

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It is shown that low density polyethylene film and polyester textile can be effectively sulfurized in the solutions of elemental rhombic (α) sulfur in carbon disulfide. The concentration of sulfur in polyethylene and polyester textile increases with the increase of temperature and concentration of sulfur solution in carbon disulfide. However, it little depends on the duration of treatment since the sulfur adsorption-diffusion on/into polymer takes place very fast – during the first 3 – 5 min of sulfurization. Copper sulfide layers in the surface of polyethylene and polyester textile were formed when these sulfurized polymeric materials were treated with the solution of copper (I–II) salts. The Cu_xS layers with the lowest electrical resistance and of good adhesion with the polymer were obtained when the polyethylene was sulfurized in the 5.7 mol/dm^3 and polyester textile – in 3 mol/dm^3 solution of sulfur in carbon disulfide at the temperature of 20 °C, and when the duration of sulfurization was 1 min – 3 min. The Cu_xS layers of the minimal sheet resistance 11.2 Ω/□ on polyethylene and surface resistivity $10^2 – 10^4$ Ω on polyester textile were formed when these sulfurized polymeric materials were treated with copper salts solution at the temperature of 80 °C. The phase composition of Cu_xS layers obtained was studied by means of potentiometric measurements and X-ray diffraction. The potentiometric measurements showed that the values of Cu_xS layers electrode potentials decrease with the prolongation of sulfurized polymeric material treatment time in the copper(I-II) salt solution at the temperature of 80 °C: from 230 mV to 145 mV – of Cu_xS on polyethylene and from 212 mV to 205 mV – of Cu_xS on polyester textile. That indicates the change of a value of x in the Cu_xS in the interval $1 < x < 2$. By X-ray analysis it was determined that copper sulfide layers in the surface of polyethylene consist of four phases: *yarrowite* $Cu_{1.12}S$, *spioncopite* $Cu_{1.4}S$, *digenite* $Cu_{1.8}S$ and *djurleite* $Cu_{1.95}S$. The copper sulfide layers on the surface of polyester textile consist of two phases: *yarrowite* $Cu_{1.12}S$ and *digenite* $Cu_{1.8}S$.

Keywords: polyethylene, polyester textile, sulfurization, copper sulfide layers.

INTRODUCTION

There has been increasing interest during the last few decades in the modification of polymers by formation on their surface of thin layers of compounds with important physical properties leads to obtaining of composites with different properties.

Thin films have a number of applications in various fields, including interference filters, polarizers, narrow band filters, solar cells, photoconductors, waveguide coatings, temperature control of satellites, photothermal solar coatings, magnetic film, superconducting films, microelectronics devices, diamond films, and high-temperature wear resistant films, etc. [1]. Numerous materials have been prepared in thin film form because of their potential technical value and scientific curiosity in their properties. Conducting copper sulfide thin layers have wide range of applications in various fields of science and technology. Copper sulfide is an interesting material for its metal – like electrical conductivity, chemical – sensing capability and ideal characteristics for solar energy absorption [2].

Currently, there are many research activities devoted to the development of thin layer fabrication methods and functional properties. Thus, there are a number of well-known deposition techniques, such as by vacuum evaporation, sputtering and chemical methods such as chemical vapour deposition, spray pyrolysis, electrodeposition, anodization, electroconversion, electroless, dip growth, successive ionic absorption and reaction, chemical bath deposition and suspension – gas interface techniques, etc. [1, 3].

Few methods of the formation of copper sulfide layers on the surface of dielectrics are investigated [4]. Copper sulfide layers form in the surface matrix of a dielectric as result of the chemical reaction between sorbed-diffused sulfur containing particles and cuprous or cupric ions. For the sulfurization of dielectrics various solutions were proposed, e. g. the aqueous solutions of sodium polysulfides, Na_2S_n ($n \approx 4.8$) [5] and of polythionic acids, $H_2S_nO_6$ ($n = 6 \div 45$) [6, 7]. Solutions of sodium polysulfides are highly alkaline and solutions of higher polythionic acids are acidic and complicated in preparation. The proposed agents are suitable for a limited number of dielectrics.

The sorption-diffusion methods for the formation of thin conducting layers of copper sulfide in the surface of polymers during last years at the Department of Inorganic Chemistry of KTU were studied. The preparation of sulfide thin films by this method has attracted much attention because of its simplicity, low cost, low temperatures of formation processes (20 °C – 80 °C) and availability of starting materials.

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 cycle – octa sulfur solutions in non-aqueous solvent – carbon disulfide, CS_2, with the hydrophobic polymeric materials – polyethylene film (PE) and polyester textile (PES), also processess of copper

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sulfide layers in the surface of PE and PES formation and the characterization of the copper sulfide layers obtained, since only separate fragments of these studies in our previous publications were described [8 – 13]. The chemical and phase composition of the Cu_xS layers, their electrical conductance were studied by the methods of atomic absorption spectroscopy, X-ray diffraction and by the measurements of electrode potential and electrical resistance.

EXPERIMENTAL

The layers of Cu_xS were deposited on a low density PE film of 0.14 mm ± 0.01 mm thickness (GOST 10354-82), made in Vilnius Plastics Factory "Plasta" and unimproved polyester textile "Marsas", made in Joint-Stock Company "Kauno audiniai". A surface density of PES was 0.125 kg/m^2. The density of polyethylene was measured by a flotation method, using a series of water/acetone mixtures at 20 °C. The samples were immersed in liquids of different density (0.910 g/cm^3 – 0.920 g/cm^3) seeking one in which they neither sink nor float. The samples of 15 mm^2 × 60 mm^2 or 30 mm^2 × 30 mm^2 in size were used. Before sulfurization they were processed as described in the previous works [8, 11]. Then PE or PES samples were sulfurized in 0.06 ÷ 22.2 mol/dm^3 solution of elemental rhombic sulfur in CS_2 at the temperature 20 °C ÷ 45 °C for the period of time from 0.5 min to 120 min. Then they were dried over $CaCl_2$ for 24 h. Distilled water, reagents of the grades "especially pure", "chemically pure" and "analytically pure" were used in the experiments. The concentration of sulfur in PE or PES was determined as described in [8, 11]. The sulfur into the samples was extracted with acetone, and the content in the extract was determined by a spectrometric cyanide method [14] using a КФК-3 photometer (λ = 450 nm).

For the formation of Cu_xS layers the samples of sulfurized PE or PES were treated with unstirred 0.4 mol/dm^3 water solution of $CuSO_4$ with a 0.1 mol/dm^3 addition of reductor (hydroquinone, $C_6H_4(OH)_2$). The composition of this solution as a mixture of univalent and divalent copper salts was established earlier [6]: it contains 0.34 mol/dm^3 of Cu (II) salt and 0.06 mol/dm^3 of Cu (I) salt. Sulfurized in the S_8 solution in CS_2, PE or PES samples were treated with the solution of copper (I-II) salt at the temperatures 40, 60 and 80 °C for the period from 0.25 min to 30 min. Then samples with the Cu_xS layers were washed with distilled water, dried over $CaCl_2$ and used in consequent experiments.

Cu_xS layer in the surface of PE or PES was dissolved in concentrated nitric acid and copper amount was determined by the atomic absorption spectrometer "Perkin–Elmer 503" (λ = 325 nm) [9].

The DC conductivity of the Cu_xS layers on PE was measured on an E7-8 numerical measuring instrument by special electrodes. The resistance of PES sample with Cu_xS layer was measured on a teraohmeter E6-13 by a described technique [15].

The electrode potential of PE and PES with Cu_xS layer was measured on a HI 9321 pH-meter potentiometer in a Cu_xS/aq $CuSO_4$ + H_2SO_4/Cu electrocell [16].

The phase composition of the copper sulfide layer was investigated by means of X-ray diffraction using a DRON-6 diffractometer (radiation Cu-K$_\alpha$). X-ray diffractograms of PE and PES samples with layers of Cu_xS were treated using the programs "Search Match", "ConvX", "Xfit", "Dplot95" and "Photo Styler" to eliminate the maxima of PE and PES.

ANALYSIS AND RESULTS

During the investigations of influence of non-polar solvent CS_2 to hydrophobic PE [17], it was very important to find out the effect of solvent for polymer: does it swell the polymer and how acts on its structure. By the measuring the density of PE samples before and after treatment with CS_2, it was determined that the density of samples after treatment in CS_2 solution for periods from 5 min to 120 min, increases on average from the initial density 0.916 g/cm^3 up to 0.919 g/cm^3. From that a conclusion can be drawn, that solvent CS_2 washes away the compounds of small molecular weight from the amorphous areas of polymer and this is a reason for conformational transformations in the polymer. Macromolecules take up position of better arrangement, therefore the density of PE samples increases [18].

At the beginning, PE samples were sulfurized in constantly stirred saturated sulfur solutions in CS_2 at the temperature 30, 35, 40 and 45 °C for the period of time from 0.5 min to 120 min. Noticed that concentration of sulfur (C_S) in the polyethylene increases. At the beginning of sulfurization process C_S in PE increases, later on, after the reaching the maximum value, it starts to decrease. In kinetic curves of sulfurization it is easy to see minima at the period of time 10 min. That sorption processes are described in a literature like anomalous [19, 20]. These anomalous processes of sulfur sorption to PE from its solutions in CS_2, can be explained by conformation changes of PE macromolecules and by the homogeneous transfers of cycle-octa sulfur molecules. When the crystals of rhombic sulfur, composed from S_8 molecules, solve in CS_2, the equilibrium between cycle S_8 molecules and the molecules with less and larger number of sulfur atoms [21] establishes, for example:

$$2\ \text{cycle-}S_8 \leftrightarrow \text{cycle-}S_6 + \text{cycle-}S_{10}\ . \qquad (1)$$

In the equilibrium system, the most part takes thermodynamically stable cycle-S_8 molecules, which sorbed by polymer from sulfur solution in CS_2 at the beginning of sorption process. However, after establishing of equilibrium, molecules of sulfur of less molecular weight, which are better soluble in the polymer, replace already sorbed cycle S_8 molecules, which are less soluble in polymer. I. e. some of them desorb from polymer, therefore the concentration of sulfur in PE decreases too. We have to point out, that such above described interpretation of sorption process can be applied only for the beginning of sulfur sorption into PE from its solutions in CS_2, up to 10 min. As it was mentioned, later on, by prolonging process of sulfurization, concentration of sulfur in PE increases again.

Together with sorption and desorption processes of sulfur molecules, conformational transformations, caused by effect of solvent CS_2 occurs in PE. Due to CS_2 action, some part of low molecular weight compounds scours out from amorphous areas of PE, macromolecules of PE rearrange and the density of PE increases. Sulfur homologous sorption and desorption processes and PE conformational transformations take place at the same time in first minutes of sulfurization process. Transformation of PE molecules in the amorphous areas induce the desorption of diffused into PE molecules of sulfur, therefore C_S decreases very rapidly after 5 min. Hereafter in a process gradually the equilibrium establishes and in a curves only negligible increases and decreases of C_S, are met, which can be caused by above mentioned homologous transformations.

By sulfuring PE in the solutions of elemental sulfur in CS_2, the saturated concentration of sulfur in PE is reached very rapidly – after few minutes, like by using solution of Na_2S_n as sulfurization agent. However, by using CS_2, reached C_S values are 2 – 4 times higher than by using Na_2S_n solution, though its temperature is higher (77 °C) [5]. By using solutions of polythionic acids, saturated concentration of sulfur in PE is reached only after 2 hours, and in $H_2S_nO_6$ solution (at temperature 80 °C) C_S is ~2.5 times lower than during sulfurization with sulfur solutions in CS_2 [6]. Maximal concentration of sulfur in PE even at fifth minute of sulfurization reached 38.4 mg/cm^3 at the temperature of 45 °C.

The results, obtained by sulfurization of PE in a saturated solutions of sulfur in CS_2 (large C_S values and quick saturation of PE by sulfur) enabled to shorten the duration of sulfurization and to use for sulfurization not saturated, but solutions of substantially lower concentration (0.59; 5.7; 7.12; 12.42 and 22.2 mol/dm^3) of sulfur in CS_2.

At the beginning the PE samples were sulfurized at the temperature 40 °C by decreasing concentration of sulfur solution – 22.2 mol/dm^3 by 2, 3 and 4 times, obtaining concentrations of 12.42; 7.12 and 5.7 mol/dm^3 correspondingly. Concentration of the last mentioned solution decreased by ten times - until 0.59 mol/dm^3. The obtained results (Fig. 1, 3 – 6 curves) shows, that saturated concentration of sulfur in PE is reached so quick (after 3 min – 5 min), like by sulfuring PE in saturated sulfur solutions in CS_2. Moreover, by sulfuring PE in the solutions of low concentration, earlier mentioned maxima and minima in the kinetic curves of sulfurization process reduce, but they remain by sulfuring in solutions of higher concentration (22.2, 12.42 and 7.12 mol/dm^3). Consequently, the concentration of sulfurization agent was decreased additionally (until 0.59 mol/dm^3) and the temperature of sulfurization process was decreased until 20 °C (Fig. 1, curves 1 and 2).

When the sample of PE removed from sulfurization solution, the equilibrium states in it became unbalanced: temperature decreases and volatile solvent removes from the sample. When the temperature decreases, together with evaporating solvent desorption of sulfur molecules occurs, which crystallizes on the surface of PE. This point is unhelpful on purpose to get layers of Cu_xS with good quality and adhesion with polymer. This defect can be eliminated by decreasing sulfurization temperature until 20 °C. Only negligible amount of sulfur crystallizes on a surface of PE after sample removing from sulfurization reactor at the temperature of 20 °C.

The results of research show that the solutions of sulfur in CS_2 are suitable for sulfurization of PE and are considerably more effective compared with earlier used agents of sulfurization – solutions of polysulfides and high polythionic acids. Hydrophobic PE [22] directly sorbs elemental sulfur; temperature of sulfurization process decreases. Very short time of polymer saturation by sulfur enables to shorten duration of sulfurization until 10 min, at the same time decreases unhelpful effect of solvent to polymer.

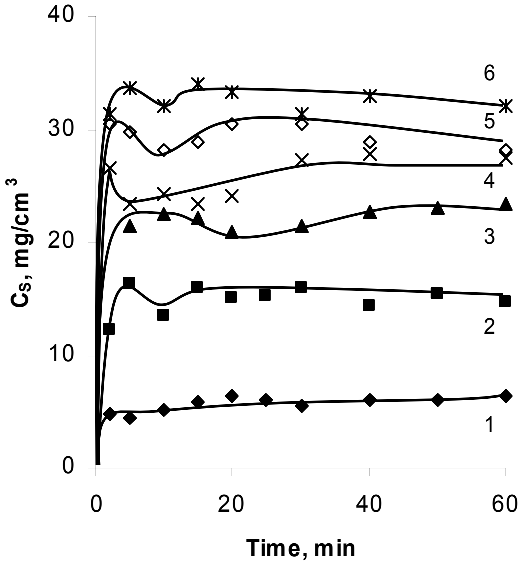

Fig. 1. Changes of sulfur concentration in PE with time during its treatment with sulfur solution in carbon disulfide of different concentration. Concentration of the solution, mol/dm^3 (temperature, °C): 1 – 0.59 (20); 2 – 5.7 (20); 3 – 5.7 (40); 4 – 7.12 (40); 5 – 12.42 (40); 6 – 22.2 (40)

PES fibre is very stable for the impact of various chemicals (acids, except the concentrated H_2SO_4, alkali, oxidisers, organic compounds). That may be explained by difficult diffusion of reagents to the bulk of polyethylentereftalate, because polyester is hydrophobic polymer. Organic solvents, such as acetone, benzene, chloroform, trichlorethane, toluene and other, effects PES fibre at the room temperature very slightly.

The samples of PES textile were sulfurized in the 0.59; 3 and 5.7 mol/dm^3 sulfur solutions in CS_2 at the temperature of 20 °C, extracted at several periods of time from 0.5 min to 10 min, then were dried. Crystallized sulfur from the surface of textile cleaned by filter paper. Concentration of sulfur in PES textile depends on concentration of sulfurization solution (Fig. 2): concentration of sulfur increases when the concentration of solution increases. As it was found in investigations of PE, the solution of cycle S_8 in CS_2 is perfect bearer of sulfur; it is perfectly suitable for the sulfurization of hydrophobic polymers.

Molecules of solvent from solution sorb into polymer jointly bearing molecules of sulfur. After removing the sample from sulfurization solution, the same phenomenon like in sulfurization process of PE film was observed: together with rapid evaporation of solvent molecules, jointly desorbs sulfur molecules from polymer. Part of desorbed sulfur crystallizes on a surface of samples, which can be cleaned by filter paper. Bigger amount of sulfur crystallizes on a surface of PES textile when the polymer has been sulfurized in the solution of higher concentration (5.7 mol/dm^3), while the surface of samples, sulfurized in the solution of 0.59 mol/dm^3 concentration becomes only slightly yellowish. In solutions of lower sulphur concentration (3 mol/l and 0.59 mol/l) PES textile saturates at first minutes of sulfurization and after 3 min C_S in samples practically do not vary. When PES is sulfurized in 3 mol/dm^3 sulfur solution in CS_2, maximal concentration of sulfur is 0.09 g/g of textile, and in 0.59 mol/dm^3 solution – 0.0244 g/g of textile. Somewhat another character has kinetic curve of sulfur diffusion to PES textile from 5.7 mol/dm^3 sulfur solution in CS_2: concentration of sulfur in textile increases very rapidly during 0.5 min, later on increases gradually and after 10 minutes of sulfurization reaches concentration 0.211 g/g (Fig. 2).

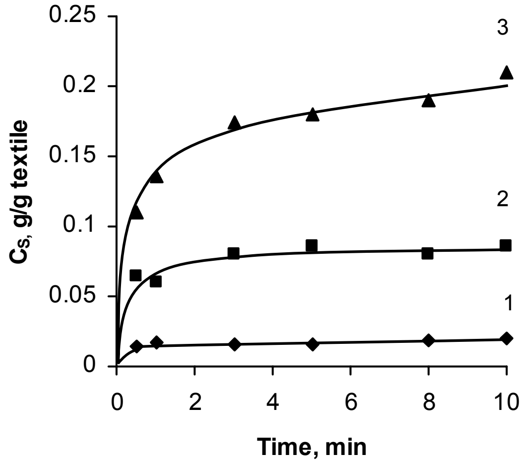

Fig. 2. Changes of sulfur concentration in PES with time during its treatment with sulfur solution in carbon disulfide at 20 °C. Concentration of the solution, mol/dm^3: 1 – 0.59; 2 – 3; 3 – 5.7

Using for sulfurization of PES textile sulfur solution in CS_2 allows decreasing of temperature of sulfurization to 20 °C, the duration of PES saturation by sulfur might be reduced to 10 min.

The sulfur amounts found in PES samples were several times higher, than those found in PE samples. That might be explained by the larger amount of adsorbed sulfur on the surface of PES fibre.

When the sulfurized hydrophobic polymers are treated with copper (I-II) salts solution, the layers of copper sulfides in a matrix of polymers are obtained. During the investigations of PE sulfurization by solutions of high polythionic acids, it was determined that when the C_S in a polymer is 7.2 mg/cm^3, the layers of Cu_xS with the best characteristics are obtained. Therefore, for the formation of Cu_xS layers at the first stage PE was sulfurized 10 min in sulfur solution in CS_2 of concentration 0.59 mol/dm^3 (at the temperature 20 °C), because the C_S in it is reached approximately 3.2 mol/dm^3 (closer to the earlier established optimal value). Sulfurized PE samples were treated with Cu (I-II) salt solution for period 0.25 min – 30 min. Depending on the conditions of PE treatment and reached C_S, bright brown or even black electrically conductive layers of Cu_xS were obtained. However, after treating the samples of PE, sulfurized in 0.59 mol/dm^3 sulfur solution in CS_2, with Cu (I-II) salt solution, the Cu_xS layers obtained cover the surface of PE very uneven and in some places were translucent. That happens, because the sulfur, sorbed by polymer from its solution of low concentration (0.59 mol/dm^3) are very uneven distributed on the surface of PE.

Whereas it was difficult to examine the properties of such thin layers, the Cu_xS were formed on a surface of PE samples with higher C_S (12.8 mg/cm^3), which were sulfurized in 5.7 mol/dm^3 sulfur solution in CS_2 at the temperature 20 °C.

Cu_xS forms during the heterogeneous reaction between elemental sulfur in PE and Cu (I) ions, present in copper salt solution:

$$2x\,Cu^+ + 1/8\,S_8 \rightarrow Cu_xS + xCu^{2+}. \qquad (2)$$

Later on, the layer of Cu_xS forms when the copper ions of diffuse into the depth of polymer. Mostly intensive the layer of Cu_xS forms at the zone of contact of two different phases: of sulfurized PE and Cu (I-II) salt solution.

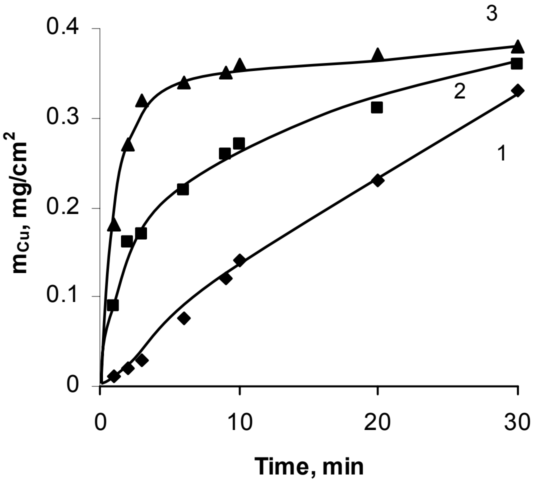

Fig. 3. Changes of copper amount in Cu_xS layer in the surface of PE with time. Sulfurized PE (C_S = 12.8 mg/cm^3) was treated with copper (I-II) salt solution at the different temperatures. Temperature, °C: 1 – 40; 2 – 60; 3 – 80

After measuring amount of copper in the layer of sulfide, it was stated, that the amount of copper depends on the initial concentration of sulfur in PE and increases (Fig. 3) when the temperature of copper (I-II) salt solution (from 40 °C till 80 °C) and the time of treatment in it (from 0.25 min till 30 min) is increased

Measurements of sheet resistance (*R*) showed (Fig. 4), that the curves of *R* dependence on the duration of treatment with Cu (I-II) salt solution have various minima. When C_S in PE is approximately 12.8 mg/cm^3, at the temperature 80 °C, the minimum of *R-t* curve is at the interval of time 1 min – 2 min, at the temperature 60 °C – 6 min – 8 min, at the temperature 40 °C – 8 min – 10 min. At the temperature 40 °C the Cu_xS layers with low sheet resistance (43.1 Ω/□ – 81.3 Ω/□) are obtained only after 7 min – 30 min. While at the higher temperature (80 °C) even after 1 min – 5 min resistance low (11.2 Ω/□ – 49.5 Ω/□) have been reached.

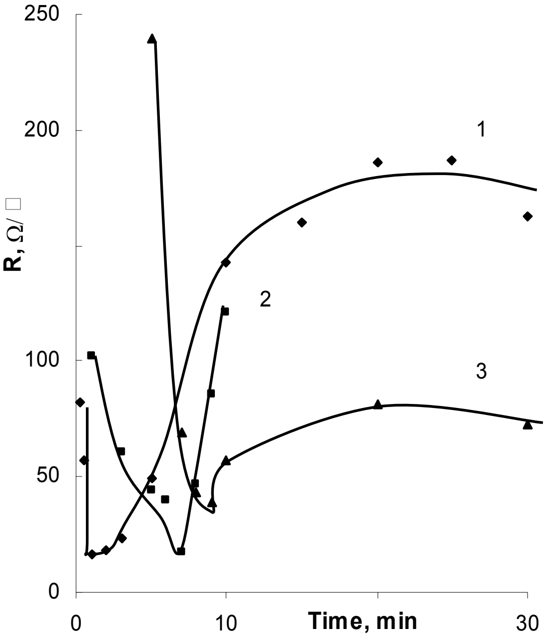

Fig. 4. Dependence of the sheet resistance (Ω/□) of Cu_xS layer on PE with time. Sulfurized PE (C_S = 12.8 mg/cm^3) was different time treated with copper (I-II) salt solution at the different temperatures. Temperature, °C: 1 – 80; 2 – 60; 3 – 40

The minima on the curves can be explained similarly like in previous studies [23]. When at the beginning on the surface of PE very thin Cu_xS layer have been formed, the value x in it equals 1.12. This sulfide is can be treated as abnormal, electroconductive semiconductor. Further, due to diffusion of copper ions thickness of the layer increases and the resistance decreases. In this process varies not only the thickness of the layer but the stoichiometric composition too. Therefore, the value of x increases. Then an “abnormality” of sulfide layer on the polymer decreases ant the resistance increases. When x > 1.98, conductivity of copper sulfide decreases and chemical composition approaches close to Cu_2S, *R* reaches the maximal value; the process of layer formation comes to the end.

In the study [16] it was pointed out, that the composition of copper sulfide layers approximately could be estimated according to its electrode potentials in the acidic solution of $CuSO_4$, where the reversible reaction takes place:

$$Cu_xS \leftrightarrow Cu_{x-y}S + yCu^{2+} + 2ye. \quad (3)$$

The electrode potential *E* of Cu_xS layer can vary from 290 mV, what corresponds to very electroconductive phase of *covellite* (CuS), to 0 mV, what corresponds almost not conductive phase of *chalcocite* (Cu_2S) [16]. There were measured the potentials of the layers with the different concentration of sulfur, which were formed by treating with Cu (I-II) salt solution at the various (40, 60 and 80 °C) temperatures. It was determined, that the values of potentials of Cu_xS layers decrease from 231.4 mV to 162.9 mV (for the sample with C_S – 12.8 mg/cm^3, and temperature 60 °C) when the duration of treatment in Cu (I-II) salt solution increases, because the value of x in the Cu_xS layer increases too. The electrode potentials of the same samples after few months increase (value of *E* 231.4 mV increases to 256.6 mV, when the period of treating of sulfurized PE sample with Cu (I-II) salt solution was 1 min; the value of 162.9 mV increases till 209.9 mV, when the period of treatment 20 min). That means, the x value in the Cu_xS layer decreases because of interaction of formed Cu_xS layer with not reacted sulfur:

$$(x-y)Cu_xS + y/8\, S_8 \rightarrow xCu_{x-y}S. \quad (4)$$

The largest values of electrode potentials measured for layers, formed at the temperatures 40 °C, the measured values almost not varied by prolonging the period of sulfurized PE treatment in Cu (I-II) salt solution.

The phase composition of Cu_xS layers on PE established by the method of X-ray diffraction analysis. The phase composition of the formed layer was established by comparing its X-ray diffraction patterns with those of known minerals [24, 25]. The chemical composition and crystal structures of number of Cu_xS minerals, such as *chalcocite*, Cu_2S, *djurleite*, $Cu_{1.95}S$, *digenite*, $Cu_{1.8}S$, *anilite*, $Cu_{1.75}S$, *geerite,* $Cu_{1.6}S$, *spioncopite*, $Cu_{1.4}S$, *yarrovite*, $Cu_{1.12}S$ and *covellite*, CuS has been investigated already [26].

Nevertheless, the investigation of the layers of Cu_xS, formed by sorption-diffusion method, is complicated due to the crystallinity of polymer itself and the presence of few different by composition and structure phases at the same time [25].

X-ray diffraction verified that the formation of Cu_xS layers goes according to the earlier described mechanism, when the layer is formed by increasing of index x. At the beginning very conductive phase of *yarrowite* $Cu_{1.12}S$ forms, later on, by diffusing of copper ions through the formed layer of *yarrowite*, the phase transfer from *yarrowite* to *spioncopite* takes place. *Spioncopite*, by prolonging the duration of PE treatment with Cu (I-II) salt solution transfers to *digenite* $Cu_{1.8}S$ and *djurleite* $Cu_{1.95}S$ (Fig. 5). The presence of these phases was confirmed by the measurements of electrode potentials. In the study [27] it was pointed out, that the values of electrode potential *E* = 230 mV – 235 mV are typical for *yarrowite*, *E* = = 280 mV – 290 mV – for *covellite*, *E* = 160 mV – 145 mV – for *anilite* and *djurleite*, *E* = 0 mV – 120 mV – for *chalcocite*. The X-ray diffraction patterns show (Fig. 5), that in the layer of Cu_xS the phases of *covellite* and *chalcocite* are not present. The absence of these phases was proved by the measurements of electrode potential that varied in the interval 227.7 mV – 139.1 mV, i.e. the values 290 mV and 0 mV, typical for *covellite* and *chalcocite*, never been obtained.

Sulfurized samples of PES textile treated for 15 min with the Cu (I-II) salt solution at temperatures 40, 60 and 80 °C. Depending on the initial concentration of sulfur in

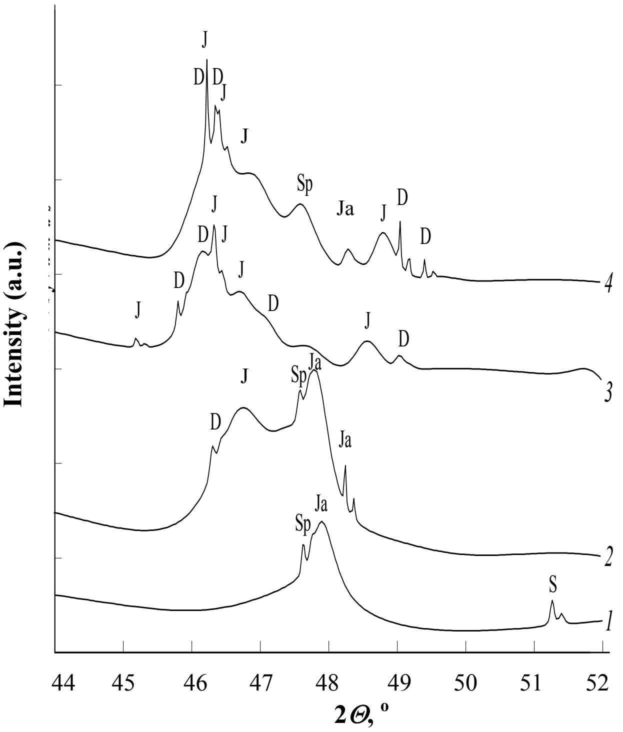

Fig. 5. X-ray diffraction patterns of the layers of Cu_xS on PE (peaks of *yarrowite* – Ja, *spionkopite* – Sp, *digenite* – D, *djurleite* – J, *sulfur* – S). The sulfur concentration in PE – 12.8 mg/cm^3. Period of treatment with the Cu(I-II) salt solution at 80 °C, min: 1 – 0.25; 2 – 3; 3 – 5; 4 – 10

PES textile, light or dark grey Cu_xS layers were obtained on the surface of PES. The spots of not reacted sulfur can be visible on the surface of textile samples with the higher concentration of sulfur in it. The data presented in Fig. 6 shows that the concentration of copper in the Cu_xS layer slightly increases by the increasing the concentration of sulfuring agent.

Moreover, by prolonging the duration of sulfurization, at the same by increasing concentration of sulfur in the samples, the concentration of copper do not increases, as it expected, but even decreases. After treating the samples, which were sulfurized in the sulfur solutions in CS_2 of different concentration, for 10 min with Cu (I-II) salt solution, the concentrations of copper become almost equal (Fig. 6).

Although the samples of PES after sulfurization could be cleaned by filter paper, during the treatment with Cu (I-II) salt solution part of formed copper sulphide gets off and falls down from the surface of PES textile. Moreover, by measuring the concentration of copper in the samples, dissolved in concentrated HNO_3, the non-reacted elemental sulfur obtained too (that detected in the samples, sulfurized in the 5.7 mol/dm^3 solution of sulfuring agent).

All described above allow to conclude, that the elemental sulfur, sorbed by PES textile as though occupies all vacant places in the fibre of textile and the sorption of copper ions occurs very difficult in sulfurized textile. After formation of thin layer of Cu_xS on the surface of PES, the copper ions even difficult pass the layer of sulfide.

The amounts of adsorbed elemental sulfur on the surface of PES textile were much higher than on the surface of PE film, therefore the amounts of copper in the formed Cu_xS layers on PES also were higher.

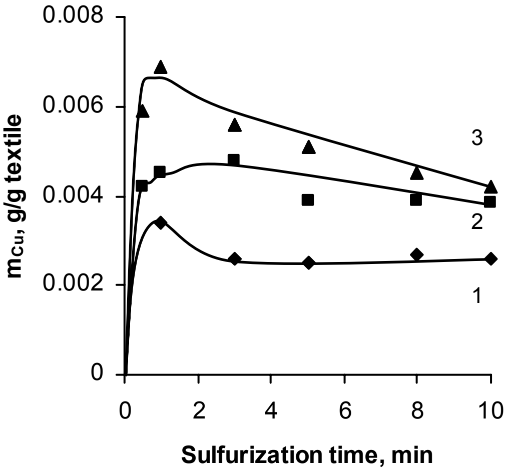

Fig. 6. Changes of the concentration of copper in Cu_xS layer on the surface of PES with time of PES treatment with sulfur solution in carbon disulfide at 20 °C. Concentration of sulfur solution in carbon disulfide, mol/dm^3: 1 – 0.59; 2 – 3; 3 – 5.7. Sulfurized PES was treated 15 min with Cu(I-II) salt solution at 80 °C

The described regularities concerning the variations of copper concentration in the layer of Cu_xS explain the changes of surface resistivity of the layers. The surface resistivity of the Cu_xS layers, formed at analogous conditions changes very narrowly in some series of samples. We consider that occurs because the concentration of sulfur by prolonging the duration of sulfurization increases very little (Fig. 2), and the concentration of copper in the samples of the same series is similar too (Fig. 6). By treating the samples, sulfurized in the 0.59 mol/dm^3 sulfur solution in CS_2, with Cu (I-II) salt solution (at the temperature 80 °C), nearly grey Cu_xS layers were obtained, the measuring of surface resistivity for these layers failed. That happens because the layer Cu_xS, obtained on the PES samples with low C_S, covered the surface of PES textile very uneven. By treating the samples, sulfurized in the 3 mol/dm^3 and 5.7 mol/dm^3 sulfur solution in CS_2, with Cu (I-II) salt solution (at the temperature 40 °C), surface resistivities of the obtained layers are the same – of the range ~10^{12} Ω. A little lower values of surface resistivity of the layers (~10^7 Ω) were measured by treating the samples, sulfurized in the 5.7 mol/dm^3 sulfur solution in CS_2, with copper salt solution at the temperature 60 °C. Whereas by treating in the samples sulfurized in the 3 mol/dm^3 sulfur solution in CS_2, with Cu (I-II) salt solution at the temperature 60 °C, the layers Cu_xS with the higher surface resistivities (of the range 10^{12} Ω – 10^{13} Ω) were obtained. The layers with the lower surface resistivity obtained by treating sulfurized PES samples with Cu (I-II) salt solution at the temperature 80 °C.

The electrode potentials measured for samples, obtained by treating the samples, sulfurized in 3 mol/dm^3 and 5.7 mol/dm^3 sulfur solution in CS_2, with Cu (I-II) salt solution at the temperature of 80 °C. The measured values are quite high: the potential of the sulfide layer of textile, sulfurized in 3 mol/dm^3 sulfur solution in CS_2, varies from 220 mV to 207 mV, and of layers, sulfurized in 5.7 mol/dm^3 sulfur solution in CS_2, varies from 212 mV to 205 mV. According the data of [16], quite conductive phase of Cu_xS, with the $1.36 < x < 1.65$ in such layers should prevail.

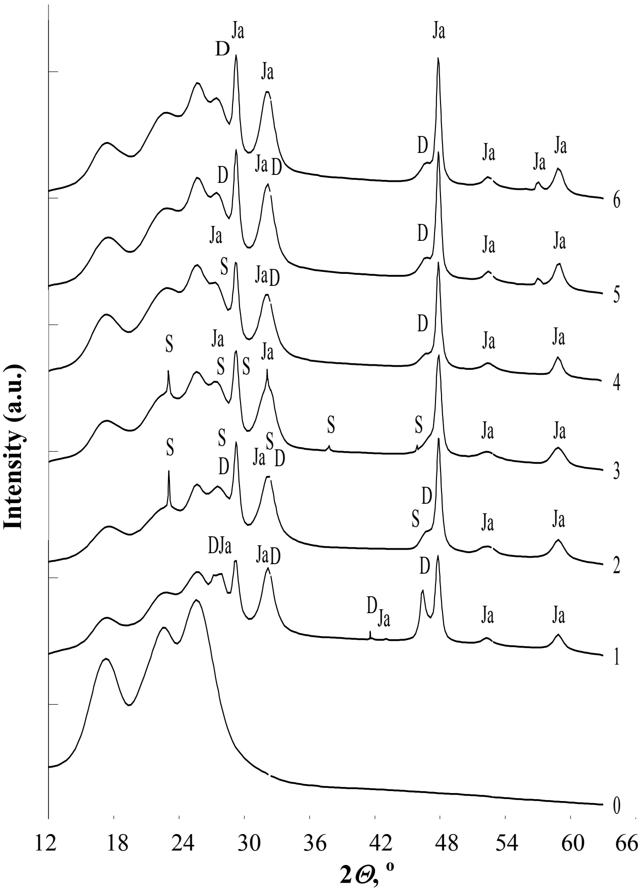

Fig. 7. X-ray diffraction patterns of the layers of Cu_xS on PES (peaks of *yarrowite* – Ja, *digenite* – D, *sulfur* – S). 0 – X-ray diffraction pattern of polyester textile. 1, 2 and 3 – PES was treated with 5.7 mol/dm^3 sulfur solution 1, 5 and 10 min; 4, 5 and 6 – PES was treated with 3 mol/dm^3 sulfur solution 0.5, 5 and 10 min. Sulfurized PES was treated 15 min with copper (I-II) salt solution at 80 °C

According to the data, presented in the Fig. 7, all X-ray diffractograms (curves 1 – 6) are very similar, despite the fact that the samples 1 – 3 were sulfurized in 5.7 mol/dm^3 sulfur solution in CS_2, the samples 4 – 6 – in 3 mol/dm^3 sulfur solution in CS_2. The difference is that in the diffractograms of Cu_xS layers on the samples of PES textile with the higher concentration of sulfur in it are visible the peaks of not reacted elemental sulfur. It is interesting that elemental sulfur, detected in the diffractograms of the textile samples, sulfurized in the 5.7 mol/dm^3 sulfur solution during 5 min and 10 min. While in the diffractogram of the sample, sulfurized in the same solution for 1 min, the peaks of sulfur were not detected or they were too small to be detectible together with the peaks of PES textile.

All residual peaks are referable to copper sulfides and they can be found in all diffractograms. Two phases of copper sulfide identified on the PES textile: *yarrowite* $Cu_{1.12}S$ and *digenite* $Cu_{1.8}S$. The large part of *digenite* and peaks that are more intensive identified in the diffractogram of the sample of PES textile, which was sulfurized in a 5.7 mol/dm^3 solution for 1 min (Fig. 7, curve 1). Curves 2 and 3 show, that by prolonging the time of sulfurization, at the same time by increasing the concentration of sulfur in textile, the intensity of the peaks of *digenite* decreases and the peaks of elemental sulfur and *yarrowite* increase. In the diffractograms of the Cu_xS layers on PES textile with the lower concentration of sulfur (i.e. samples sulfurized in 3 mol/dm^3 solution) the peaks of elemental sulfur were not detected, only the peaks of *yarrowite* and *digenite*. It was noticed the intensification of the peaks of *yarrowite* by prolonging the duration of initial sulfurization. That can be explained by the hypothesis, raised by discussing the concentration of copper in the samples with different C_S: when the PES sulfurized in the solution of higher (5.7 mol/dm^3) sulfur concentration, the solvent, evaporating from the sample together extracts diffused molecules of sulfur, which crystallizes very thick on a surface of PES. Thus they form compact layer, which is difficult pervious for copper ions. The penetration of copper ions becomes even more complicated after formation of copper sulfide layers on the surface. Even if the crystallized sulfur was cleaned up from the surface of sulfurized PES samples with filter paper, after treating of sulfurized samples with the Cu (I-II) salt solution, the part of formed copper sulfide crumbles away from the surface of PES textile. There can be drawn a conclusion that after formation of copper sulfide layer on the surface of PES, the further formation of sulfide goes when the particles of sulfur diffuses toward the surface of the layer. In the PES samples, sulfurized in the solution of lower concentration (3 mol/dm^3) or 1 min in 5.7 mol/dm^3 solution, sulfur present in the PES textile can more easily diffuse through at the beginning formed layer of *yarrowite* and to form the phase of *digenite*, where the value of x can be even 1.8.

The presence of copper sulfide phases confirms potentiometric investigations, when quite high values of electrode potentials were measured, which varied in narrow interval (207 mV – 220 mV, when the samples of PES were sulfurized in 3 mol/dm^3 sulfur solution, and 205 mV – 212 mV – in 5.7 mol/dm^3 solution).

Although the potentiometric investigations proved the formation of conductive *yarrowite*, the resistance of layers on textile samples was quite high. That can be explain that the *yarrovite* forms not on plain surface, but unequally distributes on the uneven surface of textile fibre, where the not reacted sulphur is visible. Therefore, the measurements of resistance of such samples were complicated.

In summary we can maintain, that the sulfurization agent – solution of elemental sulfur in CS_2 is suitable for the formation of electrically conductive layers of Cu_xS. This agent of sulfurization enables to simplify the process of sulfurization of hydrophobic polymers and at the same time to simplify the process of formation of complete Cu_xS layer. Using this solution for the sulfurization stage it is not necessary to use high temperature (it is enough 20 °C) and long duration (until 10 min). The layers of good physical properties (low resistance, good adhesion with polymer) were obtained when the PE samples were sulfurized 10 min in 5.7 mol/dm^3 sulfur solutions, and when the PES samples were sulfurized for period of 1 min – 3 min in 3 mol/dm^3 sulfur solution in CS_2. Low temperature and short duration of sulfurization process reduces the effect of solvent on the structure of polymer. Consequently, this agent of sulfurization surpasses earlier used agents, when the sulfurization process needs high temperatures and takes few hours; equally simplifies the process of formation of copper sulfide layers on PE surface.

CONCLUSIONS

1. The polyethylene film and polyester textile can be effectively sulfurized in the solutions of cycle-octa sulfur S_8 in carbon disulfide. The concentration of sulfur in PE and PES increases with the increase of temperature and concentration of sulfur solution. The sulphur amounts found in PES samples are several times higher, than those found in PE samples. The use of elemental sulfur solutions enable to decrease the temperature of polymeric material sulfurization stage to 20 °C and to shorten its duration to about 10 min.
2. The Cu_xS layers ($1 < x < 2$) in the surface matrix of PE and PES are formed when these sulfurized polymeric materials are treated with the solution of copper (I-II) salt. The amount of copper in the copper sulfide layer increases with the increase of temperature of copper (I-II) salt solution. The amount of copper in the copper sulfide layer in the surface of PE increases with the increase of sulfur concentration in the polymer and the time of treatment with copper salt solution, but the amount of copper in the copper sulfide layer on PES decreases. The amounts of copper in the formed Cu_xS layers on PES are higher.
3. The Cu_xS layers of the lowest electrical resistance are formed when the polyethylene film is sulfurized in the 5.7 mol/dm^3 and polyester textile – in 3 mol/dm^3 solution of sulfur at the temperature of 20 °C, and when the duration of sulfurization is 1 min – 3 min.
4. The values of electrode potentials of Cu_xS layers on the surface of PE and PES decrease with the prolongation of sulfurized polymeric material treatment time in the copper (I-II) salt solution at the temperature of 80 °C: from 230 mV to 145 mV – of Cu_xS layers on PE and from 212 mV to 205 mV – of Cu_xS layers on PES.
5. The Cu_xS layers on the surface of PE consist of three phases: hexagonal *yarrowite*, hexagonal *spioncopite* and cubic *digenite* at the beginning of the layer formation, and of *spioncopite*, *digenite* and orthorhombic *djurleite* – after 10 min treatment in the solution of copper (I-II) salt at the temperature of 80 °C. The Cu_xS layers on the surface of PES consist of two phases: *yarrowite* and *digenite*. Non-reacted elemental sulfur on PE and PES is present too.
6. The regularities determined enable formation by sorption-diffusion method of copper sulfide layers of desirable composition and electrical conductivity using the elemental sulfur solutions in carbon disulfide as sulfurization agent of polyethylene film or polyester textile. The use of elemental sulfur solutions in carbon disulfide for sulfurization significantly simplifies the sulfurization stage (decrease of the temperature and shortening of the duration).

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