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Modification of polyester textile by conductive copper sulfide layers

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A copper sulfide layer has been prepared on the surface of polyester textile by using a solution of elemental rhombic (α) sulfur in carbon disulfide and copper (II / I) salt solution. The influence of sulfur concentration in carbon disulfide, the temperature of the solutions and the time of treatment on sulfur and copper concentrations in samples was studied. Conducting copper sulfide layers were obtained when the polyester textile was sulfurized in a 3 mol/dm^3 solution of sulfur in carbon disulfide at a temperature of 20 °C and when the duration of sulfurization was 1–3 min. Cu_xS layers of the minimal surface resistance 10^2–10^4 Ω on polyester textile were formed when this sulfurized polymeric material was treated with copper(II / I) salt solution at a temperature of 80 °C. By X-ray diffraction studies it has been shown that copper sulfide layers on the surface of polyester textile consist of two phases: yarrowite and digenite. Non-reacted elemental sulfur is present on polyester textile, too. A simple way of obtaining copper sulfides on polyester textile is reported.

Key words: polyester textile, sulfurization, conductive layer

INTRODUCTION

Polyester is one of the most popular principal synthetic textile materials nowadays. Polyesters are versatile in properties and applications and have been a popular thermoset used as the polymer matrix in composites. They are widely produced industrially and possess many advantages compared to other thermosetting resins, including room temperature cure capability, good mechanical properties and transparency [1].

Modification of organic polymer films by metal chalcogenide layers is a promising approach to obtain electrically conductive films. Semiconductor transition metal chalcogenides have caused much interest due to their excellent properties and potencial applications. Among these chalcogenides, copper sulfide is widely used as thermoelectric cooling material, optical filter, optical recording material, solar cell and superionic material [2]. Also, copper sulfides can be used in photothermal conversion, electrodes, electronic devices and catalysis [3].

Copper sulfide is an important material for coating. Copper sulfides can form various stoichiometries with a complex structure and valence state [4]. Cu_xS is found to exist at room temperature in two forms as "copper-rich" and "copper-poor". Copper-rich phases are chalcocite, Cu_2S, djurleite, $Cu_{1.9375}S$, digenite, $Cu_{1.8}S$, and anilite, $Cu_{1.75}S$. A copper-poor phase is covellite, CuS. Covellite has one-third of its metal ions surrounded by three neighbouring S atoms at the corners of a triangle, and the remainders have four S neighbours arranged tetrahedrally [5]. Covellite, green copper sulfide, shows a metal-like electrical conductivity [6]. Cu_xS composition and properties depend on the precursor solutions' composition and deposition parameters.

Copper sulfide layers have been prepared by various methods including solid-state reactions [7], sonochemical routes [8], microwave irradiation techniques [9], pyrolysis of single source precursors [10], etc.

In this paper, we report a simple route of obtaining copper sulfide layers on the surface of polyester textile (PES) by using octa sulfur solutions in non-aqueous solvent – carbon disulfide, CS_2, as a precursor of sulfur. The characterization and electrical properties of the obtained layers are also described. The chemical and phase composition of Cu_xS layers, their electrical conductance were studied by the methods of spectrophotometry, atomic absorption spectroscopy, X-ray diffraction and by measuring surface resistance.

EXPERIMENTAL

Cu_xS layers were deposited on unimproved polyester textile "Marsas" made by the joint-stock company "Kauno audiniai". The surface density of PES was 0.125 kg/m^2. Samples 30 × 30 mm^2 in size were used. Before sulfurization they had

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been processed as described in the previous work [11]. Then PES samples were sulfurized in a 0.59–5.7 mol/dm^3 solution of elemental rhombic sulfur in CS_2 at 20 °C for 0.5 to 10 min. Then they were dried over $CaCl_2$ for 24 h. The concentration of sulfur in PES (C_s) was determined as described in [11]. The sulfur present in the samples was extracted with acetone, and the content in the extract was determined by a spectrometric cyanide method [12] using a КФК-3 photometer ($\lambda = 450$ nm).

For the formation of Cu_xS layers, samples of sulfurized PES were treated with unstirred 0.4 mol/dm^3 water solution of $CuSO_4$ with a 0.1 mol/dm^3 addition of a reducing agent (hydroquinone, $C_6H_4(OH)_2$). The composition of this solution as a mixture of univalent and divalent copper salts has been established earlier [13]: 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, PES samples were treated with a solution of copper(II / I) salt at a temperatures of 40, 60 and 80 °C for 0.25 to 30 min. Then samples with Cu_xS layers were washed with distilled water, dried over $CaCl_2$ and used in subsequent experiments.

A Cu_xS layer in the surface of PES was dissolved in concentrated nitric acid, and copper content was determined with an atomic absorption Perkin–Elmer 503 spectrometer ($\lambda = 325$ nm) [14].

The surface resistance of a PES sample with Cu_xS layer was measured on a teraohmeter E6-13 by a described technique [15].

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

RESULTS AND DISCUSSION

PES fibres are resistant to the action of various chemicals (acids, except concentrated H_2SO_4, alkali, oxidisers, organic compounds). This resistance may be explained by a difficult diffusion of reagents into the bulk of polyethylenetereftalate, since polyester is a hydrophobic polymer. Organic solvents, such as acetone, benzene, chloroform, trichlorethane, toluene and other, affect PES fibre at room temperature very slightly.

Samples of PES textile were sulfurized in the 0.59, 3.0 and 5.7 mol/dm^3 sulfur solutions in CS_2 at 20 °C, extracted at several periods of time lasting 0.5 to 10 min and then dried. Crystallized sulfur from the surface of textile was removed with filter paper. The concentration of sulfur in PES textile depends on the concentration of sulfurization solution (Fig. 1): the concentration of sulfur in PES increases with increasing the concentration of solution. As was found in investigations of PE sulfurization [14], the solution of cycle S_8 in CS_2 is a perfect bearer of sulfur; it is perfectly suitable for the sulfurization of hydrophobic polymers.

Molecules of the solvent sorb from solution into the 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: the rapid evaporation of solvent molecules is accompanied by the desorption of sulfur molecules from the polymer. Part of desorbed sulfur crystallizes on the surface of samples and may be removed with filter paper. Larger amounts of sulfur crystallize on the surface of PES textile when the polymer has been sulfurized in a solution of a higher concentration (5.7 mol/dm^3), while the surface of samples sulfurized in the 0.59 mol/dm^3 solution becomes only slightly yellowish. In solutions of a lower sulfur concentration (3.0 and 0.59 mol/dm^3), PES textile becomes saturated in the first minutes of sulfurization, and after 3 min the C_S in samples practically does not vary. Somewhat different is the kinetic curve of sulfur diffusion into PES textile from the 5.7 mol/dm^3 sulfur solution in CS_2: the concentration of sulfur in textile increases very rapidly during 0.5 min, later on it increases gradually and after 10 minutes of sulfurization reaches ~0.2 g/g (Fig. 1).

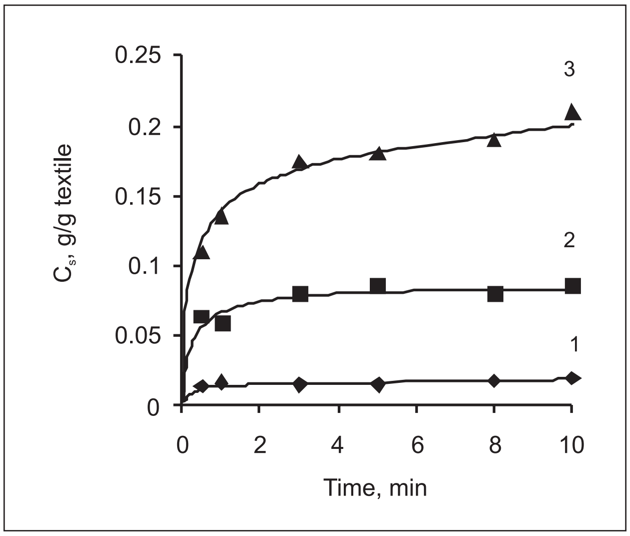

Fig. 1. Changes of sulfur concentration in PES with time during its treatment with sulfur solution in carbon disulfide at 20 °C. Concentration of the solution, mol/dm^3: *1* – 0.59; *2* – 3.0; *3* – 5.7

When sulfurized hydrophobic polymers are treated with copper(II / I) salt solution, layers of copper sulfides in a matrix of polymers are obtained [13]. Cu_xS forms during the heterogeneous reaction between elemental sulfur in PES and Cu(I) ions present in copper salt solution:

$$2x\mathrm{Cu}^+ + 1/8\mathrm{S}_8 \rightarrow \mathrm{Cu}_x\mathrm{S} + x\mathrm{Cu}^{2+}.$$

Later on, the layer of Cu_xS forms when the copper ions diffuse into the depth of the polymer. Most intensively the layer of Cu_xS is formed at the zone of contact of two different phases – sulfurized PES and Cu(II / I) salt solution.

Sulfurized samples of PES textile were treated for 15 min with a Cu(II / I) salt solution at 40, 60 and 80 °C. The concentration of copper in the copper sulfide layer increased with increasing the temperature of copper(II / I) salt solution (Fig. 2). The concentrations of copper found in the samples treated with a copper salt solution at 80 °C were twofold higher than those found in samples treated at 60 °C. Depending on the initial concentration of sulfur in PES textile, light or dark grey Cu$_x$S layers were obtained on the surface of PES. Spots of non-reacted sulfur may be visible on the surface of textile samples with a higher concentration of sulfur in it. The data presented in Fig. 3 show that the concentration of copper in the Cu$_x$S layer slightly increases with increasing the concentration of the sulfurization agent.

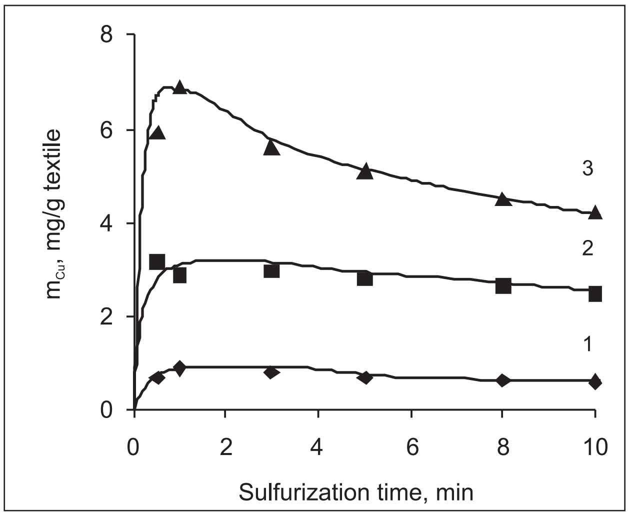

Fig. 2. Changes of copper concentration in Cu$_x$S layer on the surface of PES with time of PES treatment with 5.7 mol/dm^3 sulfur solution in carbon disulfide at 20 °C. Temperature of Cu(II / I) salt solution, °C: *1* – 40; *2* – 60; *3* – 80. Sulfurized PES was treated for 15 min with Cu(II / I) salt solution

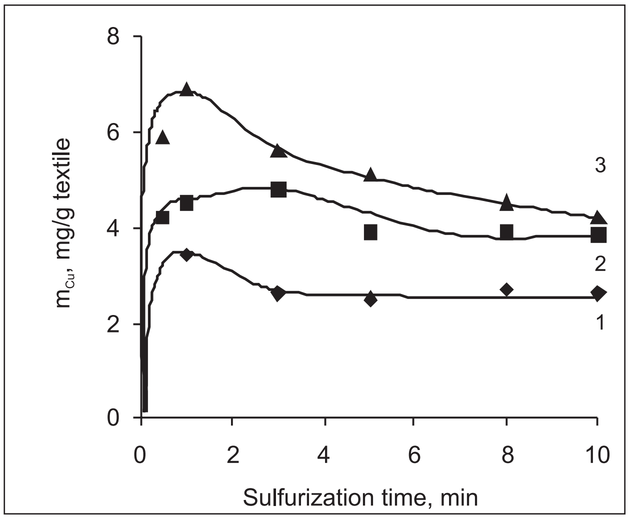

Fig. 3. Changes of copper concentration in Cu$_x$S layer on the surface of PES with time of PES treatment with sulfur solution in carbon disulfide at 20 °C. Concentration of sulfur solution in carbon disulfide, mol/dm^3: *1* – 0.59; *2* – 3.0; *3* – 5.7. Sulfurized PES was treated for 15 min with Cu(II / I) salt solution at 80 °C

Moreover, with prolonging the duration of sulfurization and thus increasing the concentration of sulfur in the samples, the concentration of copper does not increase as was expected, but even decreases. After treating the samples sulfurized in sulfur solutions in CS$_2$ of different concentration for 10 min with Cu(II / I) salt solution, the concentrations of copper became almost equal (Fig. 3).

Although samples of PES after sulfurization could be cleaned with filter paper, during the treatment with Cu(II / I) salt solution part of the formed copper sulfide 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$_3$, non-reacted elemental sulfur was obtained, too (detected in samples sulfurized in the 5.7 mol/dm^3 solution of sulfurization agent).

All the above facts allow to conclude that the elemental sulfur sorbed by PES textile seems to occupy all vacant places of the amorphous phase and the interphase in PES fibres, and the sorption of copper ions is very difficult in sulfurized textile. After formation of a thin layer of Cu$_x$S on the surface of PES, for the copper ions it is even difficult to pass the layer of sulfide.

The described regularities concerning the variations of copper concentration in Cu$_x$S layer explain the changes of surface resistance of the layers. The surface resistance of Cu$_x$S layers formed in analogous conditions changes very slightly in some series of samples. We consider this to occur because the concentration of sulfur with prolonging the duration of sulfurization increases very little (Fig. 1), and the concentration of copper in samples of the same series is similar, too (Fig. 3). By treating samples sulfurized in the 0.59 mol/dm^3 sulfur solution in CS$_2$ with Cu(II / I) salt solution (at 80 °C), nearly grey Cu$_x$S layers were obtained, and the measuring of surface resistance for these layers failed because the layer of Cu$_x$S, obtained on PES samples with low C_S, covered the surface of PES textile very unevenly. When treating samples sulfurized in the 3.0 and 5.7 mol/dm^3 sulfur solution in CS$_2$ with Cu(II / I) salt solution (at 40 °C), the surface resistance of the obtained layers is the same – $\sim 10^{12}\,\Omega$. Somewhat lower values of surface resistance of the layers ($\sim 10^{7}\,\Omega$) were measured by treating samples sulfurized in the 5.7 mol/dm^3 sulfur solution in CS$_2$ with copper salt solution at 60 °C, whereas by treating samples sulfurized in the 3.0 mol/dm^3 sulfur solution in CS$_2$ with Cu(II / I) salt solution at 60 °C, layers of Cu$_x$S with a higher surface resistance (10^{12}–$10^{13}\,\Omega$) were obtained. Layers with a lower surface resistance were obtained by treating sulfurized PES samples with Cu(II / I) salt solution at 80 °C.

The phase composition of Cu$_x$S layers on PES was determined by the method of X-ray diffraction analysis. The phase composition of the formed layers was established by comparing their X-ray diffraction patterns with those of known minerals [16, 17]. The chemical composition and crystal structures of a number of Cu$_x$S minerals, such as chalcocite, Cu$_2$S, djurleite, Cu$_{1.95}$S, digenite, Cu$_{1.8}$S, anilite, Cu$_{1.75}$S, geerite,

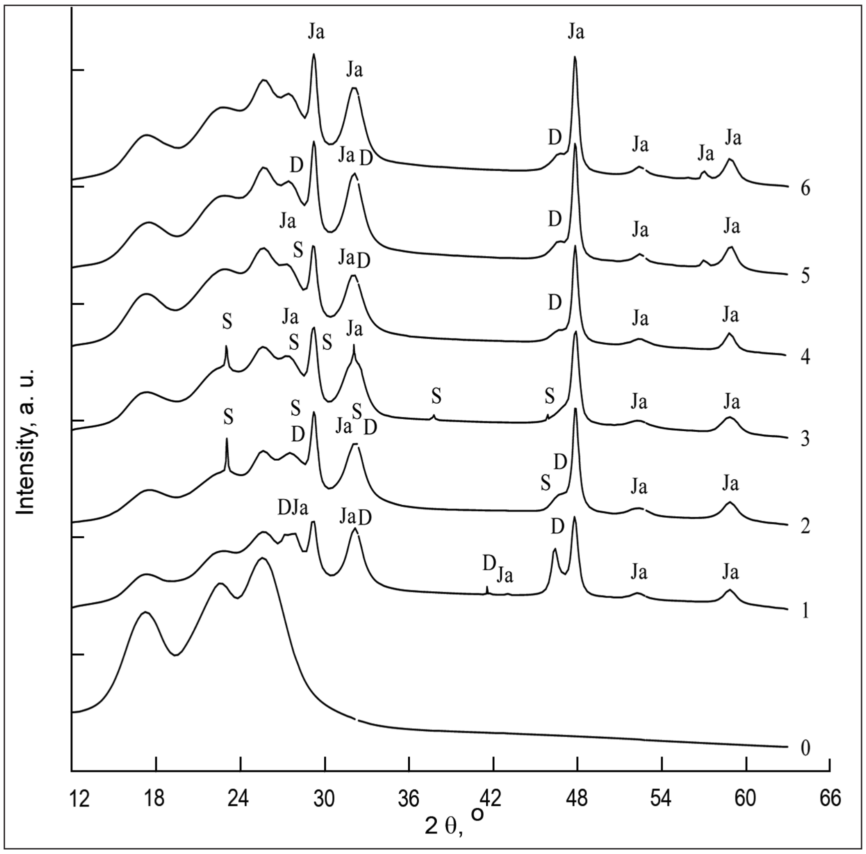

Fig. 4. X-ray diffraction patterns of Cu$_x$S layers on PES (peaks of *yarrowite* – Ja, *digenite* – D, *sulfur* – S). 0 – X-ray diffraction pattern of polyester textile. *1, 2* and *3* – PES was treated with 5.7 mol/dm^3 sulfur solution for 1, 5 and 10 min; *4, 5* and *6* – PES was treated with 3.0 mol/dm^3 sulfur solution for 0.5, 5 and 10 min. Sulfurized PES was treated for 15 min with copper(II / I) salt solution at 80 °C

Cu$_{1.6}$S, spioncopite, Cu$_{1.4}$S, yarrovite, Cu$_{1.12}$S and covellite, CuS have been already investigated [18]. Nevertheless, investigation of Cu$_x$S layers formed by the sorption–diffusion method is complicated due to the crystallinity of the polymer itself and the presence of a few phases differing in both composition and structure [17].

According to data presented in Fig. 4, all X-ray diffractograms (curves 1–6) are very similar, despite the fact that samples 1–3 were sulfurized in the 5.7 mol/dm^3 sulfur solution in CS$_2$ and samples 4–6 in the 3.0 mol/dm^3 sulfur solution in CS$_2$. The difference is that in the diffractograms of Cu$_x$S layers on samples of PES textile with a higher concentration of sulfur in it the peaks of non-reacted elemental sulfur are visible. Interestingly elemental sulfur was detected in diffractograms of textile samples sulfurized in the 5.7 mol/dm^3 sulfur solution for 5 and 10 min, while in the diffractogram of a sample sulfurized in the same solution for 1 min no peaks of sulfur were detected, or they were too small to be detectible together with the peaks of PES textile.

All residual peaks are referrable to copper sulfides, and they can be found in all diffractograms. Two phases of copper sulfide – yarrowite, Cu$_{1.12}$S, and digenite, Cu$_{1.8}$S – were identified on the PES textile. Most of digenite and more intensive peaks were identified in the diffractogram of the sample of PES textile sulfurized in a 5.7 mol/dm^3 solution for 1 min (Fig. 4, curve 1). Curves 2 and 3 show that by prolonging the time of sulfurization and thus increasing the concentration of sulfur in the textile, the intensity of the peaks of digenite decreases and that of the peaks of elemental sulfur and yarrowite increases. In the diffractograms of Cu$_x$S layers on PES textile with a lower concentration of sulfur (i. e. of samples sulfurized in the 3.0 mol/dm^3 solution), peaks of elemental sulfur were absent, and only peaks of yarrowite and digenite were detected. An intensification of yarrowite peaks by prolonging the duration of initial sulfurization was noted. It can be explained by the hypothesis raised while discussing the concentration of copper in samples with different C_S when PES sulfurized in a solution of a higher (5.7 mol/dm^3) sulfur concentration that the solvent, while evaporating from a sample, extracts diffused molecules of sulfur, which crystallize very densely on the surface of PES. Thus, they form a compact layer which is hardly 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 sulfurized samples with Cu(II / I) salt solution, part of the formed copper sulfide crumbles fell away from the surface of PES textile. It is possible to conclude that after formation of a copper sulfide layer on the surface of PES, the further formation of sulfide proceeds when the particles of sulfur diffuse toward the surface of the layer. In the PES samples sulfurized in the solution of a lower concentration (3.0 mol/dm^3) or for 1 min in the 5.7 mol/dm^3 solution, sulfur present in the PES textile can more easily diffuse through the initially formed layer of yarrowite and to form the phase of digenite in which the value of x can be even 1.8.

Although potentiometric investigations proved the formation of conductive yarrowite, the resistance of layers on textile samples was quite high. The possible explaination is that yarrovite forms not on a plain surface, but is unequally distributed on the uneven surface of a textile fibre where the non-reacted sulfur is visible. Therefore, measurements of the 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 Cu_xS layers. This agent enables to simplify the process of sulfurization of hydrophobic polymer and at the same time to simplify the process of formation of a continuous Cu_xS layer. Using this solution for sulfurization, high temperature (20 °C is enough) and long duration (below 10 min) are not necessary. Layers with good physical properties were obtained when PES samples had been sulfurized for 1–3 min in a 3.0 mol/dm^3 sulfur solution in CS_2. The low temperature and short duration of the sulfurization process reduce the effect of the solvent on the structure of the polymer. Consequently, this agent of sulfurization surpasses the earlier used agents when the sulfurization process needed high temperatures and took a few hours; equally simplified is the process of formation of copper sulfide layers on PES surface.

CONCLUSIONS

The polyester textile can be effectively sulfurized in solutions of cycle-octa sulfur S_8 in carbon disulfide. The concentration of sulfur in PES increases with increasing the temperature and concentration of sulfur solution. Cu_xS layers in the surface matrix of PES are formed when sulfurized polymeric material is treated with a solution of copper(II / I) salt. The content of copper in the copper sulfide layer increases with increasing the temperature of copper(II / I) salt solution and slightly increases with increasing the concentration of the sulfurization agent. Cu_xS layers of the lowest surface resistance are formed when the polyester textile is sulfurized in a 3.0 mol/dm^3 solution of sulfur at 20 °C and when the duration of sulfurization is 1–3 min. The Cu_xS layers on the surface of PES consist of two phases: yarrowite and digenite. Non-reacted elemental sulfur on PES is present, too.

The determined regularities enable formation by the sorption–diffusion method of copper sulfide layers of a desirable composition and surface resistance using the elemental sulfur solutions in carbon disulfide as a sulfurization agent of polyester textile.

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POLIESTERINIO AUDINIO MODIFIKAVIMAS ELEKTRAI LAIDŽIAIS VARIO SULFIDŲ SLUOKSNIAIS

Santrauka

Vario sulfidų sluoksniai gauti poliesterinio audinio paviršiuje, naudojant elementinės sieros tirpalus anglies disulfide ir vario druskų tirpalus. Darbe tirta sieros tirpalo anglies disulfide koncentracijos, tirpalų temperatūros ir apdorojimo tirpaluose trukmės įtaka sieros ir vario kiekiams bandiniuose. Ištyrus gautų sluoksnių laidumą elektrai nustatyta, jog laidžiausi sluoksniai gaunami poliesterinį audinį įsierinus 3 mol/dm^3 koncentracijos minėtame tirpale, kai sierinimo trukmė yra 1–3 min. Mažiausių paviršiaus specifinių varžų (10^2–10^4 Ω) sluoksniai poliesterinio audinio paviršiuje buvo gauti sierintus polimerus veikiant vario (II / I) druskų tirpalu 80 °C temperatūroje. Rentgeno difrakciniai tyrimai parodė, kad poliesterinio audinio paviršiuje Cu_xS sluoksnį sudaro dvi fazės: jarovitas ir digenitas. Sluoksniuose yra nesureagavusios elementinės sieros. Nustatyti dėsningumai leidžia, naudojant elementinės sieros tirpalus anglies disulfide kaip sierinimo agentą, sorbciniu–difuziniu metodu poliesterinio audinio paviršiuje sudaryti norimos sudėties ir laidumo elektrai vario sulfidų sluoksnius.