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COMPARISON OF THE SURFACE CHARACTERISTICS OF POLYETHYLENE AND POLYPROPYLENE FILMS AND POLYESTER TEXTILE COATED WITH ELECTROCONDUCTIVE COPPER SULPHIDE THIN FILMS

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Formation of copper sulphide layers on polyethylene and polypropylene films, and polyester textile was investigated. Cu_xS layers were prepared by the sorption-diffusion method using thiourea solution as a sulphuring agent on various polymers. Samples with sheet resistance till 1 $k\Omega\cdot cm^{-2}$ were chosen for investigation. XRD analysis has confirmed the formation of different form of sulphur on various polymers. In Cu_xS layers were found: on PE – anilite, on PP – roxbyite, covellite, and djurleite, on PES – anilite and djurleite. SEM investigation of samples surface with Cu_xS layers showed that compact layer formed on PE film, and grain structure – on PP film and PES fibre, but grain structure was larger on fibre. On the surface of all polymers Cu_xS layer containing the remaining sulphur conglomerates can also be observed. The cross-section analysis of the sulphurized polymer samples provides information about the thickness of the sulphurized layer, which was approximately 7 µm for PE, 10-15 µm for PP, and for PES sorption of sulphur was in the whole volume. Cu_xS layer thickness is about 20 µm for PE, 25 µm PP, and for PES – in whole volume, but most amount of Cu_xS is on the surface.

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1. Introduction

Copper sulphides have the ability to form various stoichiometries, at least five phases of which are stable at room temperature: i.e., covellite (CuS), anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurlite ($Cu_{1.95}S$), and chalcocite (Cu_2S). Their complex structures and valence states result in some unique properties and promising applications in numerous fields, such as solar control coatings and photovoltaic devices, optical filters [1–3], chemical sensors [4–8], superconductors [9], as superionic materials [10–14], and catalysts [15]. Due to their unique optical and electrical properties, they can also be applied in thin films and composite materials [16].

Polymers modified by thin metallic sulphide layers have considerable importance in various fields of advanced technology. Nowadays, usage of flexible polymeric matrix with electroconductive layers has notably increased because such polymers have resistance against corrosion, are elastic, have very low density, and low toxicity [17–20].

Electroconductive layers on polymers can be prepared chemically by deposition from solutions and by sorption-diffusion methods. In the last method, the surface of a polymer film is initially treated by the solution containing sulphurization agent and then by the aqueous solution of Cu (I-II) salt. Sodium polysulphides [21], polythionic acids and polythionates [22, 23], sulphur in carbon disulphide solution [24], thiourea solutions [25], and sulphur [26] have already been used for sulphurization of polymer films by this method.

The aim of this work was investigation and comparison of surface structure and morphology of polyethylene (PE), isotactic polypropylene (PP) films, and polyester (PES) textile coated with thin layers of electrically conductive copper sulphide with XRD, FTIR, and SEM analysis methods. Firstly, polymers were pre-treated for surface activation, and subsequently Cu_xS

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layers were prepared by the sorption-diffusion method using thiourea solution as a sulphuring agent on different polymers.

2. Experimental

2.1. Cu_xS layers deposition on PP, PE and PES

15 mm × 40 mm size samples of low density PE film of 150 μm thicknesses (TS 8125744-01-96, "Maldis", Lithuania), 15 mm × 70 mm size samples non-oriented isotactic PP film of 150 μm thicknesses (Proline X998, KWH Plast, Finland), and raw PES textile ("Marsas", surface density 124.65 $g \cdot m^{-2}$, JSC "Kauno audiniai", Lithuania) were used for the experiments.

Distilled water and analytically pure reagents were used to prepare reaction solutions. Only freshly prepared solutions were used for experiments and were not de-aerated during the experiments.

The initial electrical resistivity of polymers was approx. $10^9 - 10^{16}$ Ω m. The first task of our work was to form polymers with electroconductive layers of Cu_xS. Square sheet resistance of Cu_xS layers on polymeric matrixes was measured and samples with sheet resistance till 1 kΩ cm^{-2} were chosen for further investigation.

The hydrophobic polymer samples require an initial surface pre-treatment process in order to facilitate its adhesion properties. PE film was treated in 1 M NaOH solution for 1 h and then in acetone for 1 h. After treatment samples were dried at 60 °C [25]. PP film was etched for 25 min at 90 °C with oxidizing solution (H_2SO_4/H_3PO_4 (1:1), saturated with CrO_3) [27]. PP weight losses after chemical treatment are recommended to be 2 $g \cdot m^{-2}$ [28]. PES textile was degreased in 0.025 M Na_2CO_3 solution at 80°C for 30 min. Afterwards, the PES surface was treated with 0.75 M NaOH solution containing polydimethyldiallylammonium chloride as a polymeric catalyst at 90°C for 60 min [29]. After alkaline treatment tissue mass losses are recommended to be 6-7% weight of the textile [28]. Thus obtained polymer samples were removed from the reaction solution, rinsed with distilled water, and dried at room temperature.

All polymers were sulphurized in acidic solutions of thiourea and optimal conditions of sulphurizing for each polymer matrix were chosen: PE was sulphurized in 2.5 M thiourea with 3.5 M HCl and 0.005 M $K_2S_2O_8$ additive at 80 °C for 3 h; PP was sulphurized in 3.0 M thiourea with 3.5 mol/l M HCl and 0.005 M $(NH_4)_2S_2O_8$ additive at 90 °C for 7 h, and PES was sulphurized in 3.6 M thiourea with 3.5 M HCl additive at 80 °C for 1 min.

After sulphurization samples were treated at 80 °C with 0.4 M aqueous solution of $CuSO_4$ containing different reducing agents. 0.03 M hydroxyl amine sulphate $(NH_2OH)_2 \cdot H_2SO_4$ reducing agent was used for PES, whereas hydroquinone $C_6H_4(OH)_2$ 0.1 M was used for PP and PE.

The lowest resistance has been obtained by treating sulphured polymer with Cu (I-II) solution for 6 min (PE), PP – 3 min, and PES – 10 minutes.

2.2. X-ray diffraction (XRD)

The XRD patterns of samples were recorded with a conventional Bragg-Brentano geometry on a DRON-6 automated diffractometer equipped with a secondary graphite monochromator. Cu Kα radiation (λ = 0.1541838 nm) was used as a primary beam. The patterns were recorded from 10 to 60° 2θ in steps of 0.02° 2θ, with the measuring time of 0.5 s per step. The diffraction patterns were recorded automatically by a data acquisition system. The peaks obtained were identified on the basis of those available in PDF-2 data base [30].

2.3. FTIR spectroscopy

The changes in chemical structure and binding configuration were analysed by attenuated total reflectance (ATR) spectroscopy, since ATR spectroscopy is an often chosen technique as it may be used to obtain the spectra of the surfaces of the adhesive sides of a sample. ATR-FTIR spectra were recorded in the wavenumber range of 4000–600 cm^{-1} on a Perkin Elmer FT-IR Spectrum GX spectrophotometer by averaging 64 scans with a wave number resolution of 1 cm^{-1} at room temperature.

2.4. Scanning electron microscope (SEM)

The scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDS) Quantax 200 with a detector X Flash 4030 (Bruker AXS Microanalysis GmbH, Germany) was applied for analysis surface of the obtained Cu_xS layers.

2.5. Measurements of electrical resistivity

The constant current resistivity of the copper sulphide films was measured using a multimeter *MS8205F* (*Mastech, China*) with special electrodes. The electrodes were produced from two nickel–plated copper plates. The plates were fixed with 1 cm spacing and the dielectric material (organic glass) was placed between them. The concept of sheet resistance is used to characterize thin deposited layers. The 870 g weight was used to press the electrodes to the sample surface.

The fabric surface resistivity was measured with tera-ohm-meter E6-13 (Russia) using two- electrodes method. The 870 g weight was used to press the measured samples.

2.6. Measurements of electromotive force

Electromotive force of copper sulphide layer and copper was measured using pH-meter – potentiometer *HI 9321 (Portugal)*. The samples were fixed in a copper holder and immersed into aqueous 0.01 M $CuSO_4$ solution acidified with 0.1 M sulphuric acid. Copper wire of 1.4 mm diameter electrochemically coated with copper was used as reference electrode. Electromotive force is proportional to the difference between the redox potentials of copper ions and metal in the voltaic cell [31]:

$$Cu_xS \mid 0.01\ M\ CuSO_4 + 0.1\ M\ H_2SO_4 \mid Cu.$$

3. Results and discussion

3.1. X-ray diffraction and FTIR analysis

The surface structure of initial polyethylene film used in experiments was investigated by XRD analysis. Figure 1 presents the X-ray diffraction pattern of the initial PE film samples. The peaks of high crystalline PE with a very small amount of amorphous phase between 10 to 50° (in 2θ) are observed (Fig. 1, a). These peaks, in accordance with JCPDS 00-040-1995, appear at 21.56°, 23.87°, 30.18°, and 36.29° that correspond to the (110), (200), (210) and (020) planes, respectively [27]. Polyethylene (FTIR) spectrum do not show any change, because the polymer was only cleaned and the surface was not oxidized.

The peaks of sulphurized PE (Fig. 1, b) found at 17.03° and 36.30° correspond to the (111) and (–414) planes, respectively, and they are attributed to sulphur S_7 [72-1001]; the peaks at 21.56° and 23.89° correspond to (110) and (111) planes and belong to polyethylene urea complex $C_{14,76}H_{41,52}N_{12}O_6$ [34-1766].

The peaks of PE with Cu_xS layers (Fig. 1, c) found at 27.72° and 46.19°, correspond to the (202) and (224) planes, respectively, and belong to anilite Cu_7S_4 [33-484].

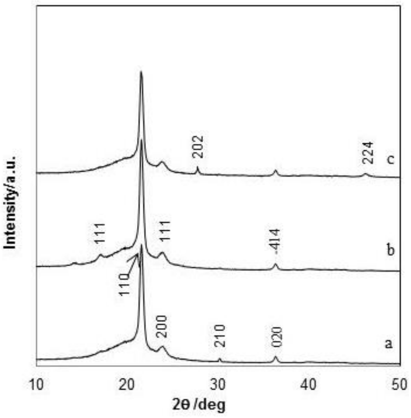

Fig. 1. XRD patterns of surfaces: a – initial PE, b – sulphurized PE; c – PE with Cu_xS *layers*

The peaks of semicrystalline PP (Fig. 2, a), in accordance with JCPDS 00-050-2397, appear at 14.00° (110), 16.85° (040), 18.47° (130), 21.01° (111), and 21.80° (–131). The X-ray diffraction of initial PP represent the typical α-form PP samples [27]. Analysis of sulphurized PP (Fig. 2, b) shows S [8-247] with peaks at 18.51° (202), 23.04° (222), and 34.85° (333).

XRD analysis of the PP samples with Cu_xS layers (Fig. 2, c) has shown the presence of roxbyite Cu_7S_4 [23-958], 20.99° (1002) and 28.25°(604); covellite CuS [78-876], 29.25° (102) and 42.93° (106); djurleite $Cu_{31}S_{16}$ [42-564], 24.38°(-413), 25.49° (341) and 38.18° (1120).

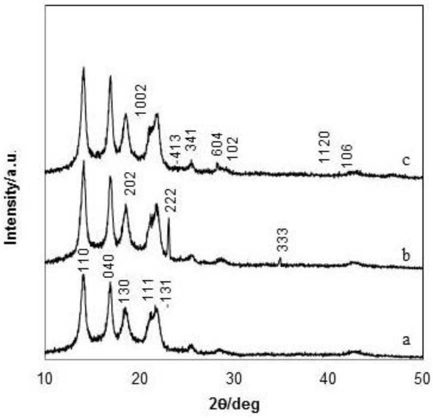

Fig. 2. XRD patterns of surfaces: a – initial PP, b – sulphurized PP; c – PP with Cu_xS *layers*

Fig. 3 shows the FTIR-ATR spectra of initial (a) and oxidized (b) polypropylene film. Some changes are observed in the spectrum of oxidized PP sample. The characteristic peaks diminish sharply in intensity and a new signal appears at 1719 cm^{-1}. This signal is attributed to the carbonyl group (C=O) stretching [32]. The spectrum of oxidized PP confirms that the oxidative treatment of polypropylene increases the surface hydrophilicity by introducing oxygen containing polar groups.

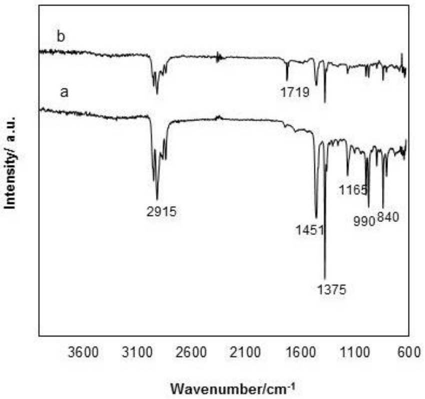

Fig. 3. FTIR spectra: a – initial PP, b – PP pre-treated with oxidation solution

The peaks of raw PES textile show semicrystalline structure of polymer (Fig. 4, a). In accordance with JCPDS 00-035-1876, peaks appear at 16.32° (010), 25.40° (100), and 28.90° (1–11). The XRD spectra of PES treated in thiourea solution show peaks at 14.15° (011) and 16.99° (111) (Fig. 4, b). These peaks confirm existence of S_{18} [71-569]. The peaks at 16.16° and 26.05° correspond to the (001) and (210) planes, respectively, and belong to thiourea [76-1129].

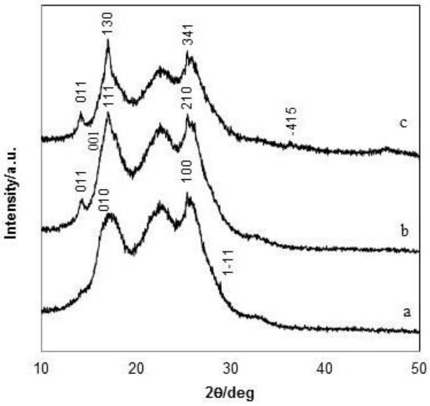

Fig. 4. XRD patterns of surfaces: a – initial PES, b – sulphurized PES; c – PES with Cu_xS layer

Existence of thiourea on PES textile has been confirmed by the presence of a peak at 3300 cm^{-1} in the FTIR spectrum (Fig. 5).

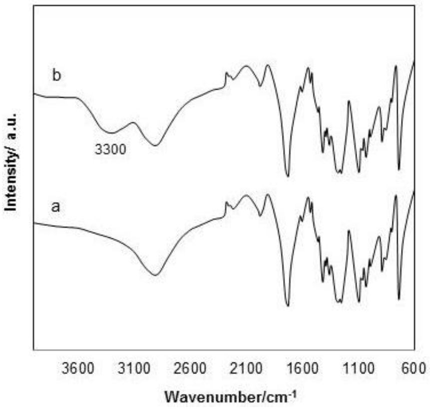

Fig. 5. FTIR spectra: a – initial PES, b – sulphurized PES

The spectrum of PES fibre with Cu_xS layers (Fig. 4, c) shows existence of anilite Cu_7S_4 [72-617], 14.12° (011) and 60.20° (334); and djurleite $Cu_{31}S_{16}$ [42-564], 16.99° (130), 25.43° (341), and 36.27° (–415).

3.2 Measurements of electromotive force

Due to the different reaction rates, the composition of the formed Cu_xS layers in different depths can vary, i.e., x value can vary in the interval of $1<x<2$ [28].

The results of electromotive force measurement showed that Cu_xS layers of different stoichiometry were formed on various polymers. Electromotive force values of Cu_xS layers on PE were approximately 190 mV and corresponded predominantly to anilite, the ones on PP were approximately 168 mV and corresponded predominantly to djurleite, and the ones on PES corresponded to anilite and djurleite (approximately 154 mV).

3.3. SEM analysis

SEM is a promising technique for the study of morphology of thin films. It gives an important information regarding growth, shape, and size of the particles.

SEM micrographs of sulphurized polymers (Fig. 6, a) show nonuniform layer on PE, however all surfaces were coated of PP and PES fibre.

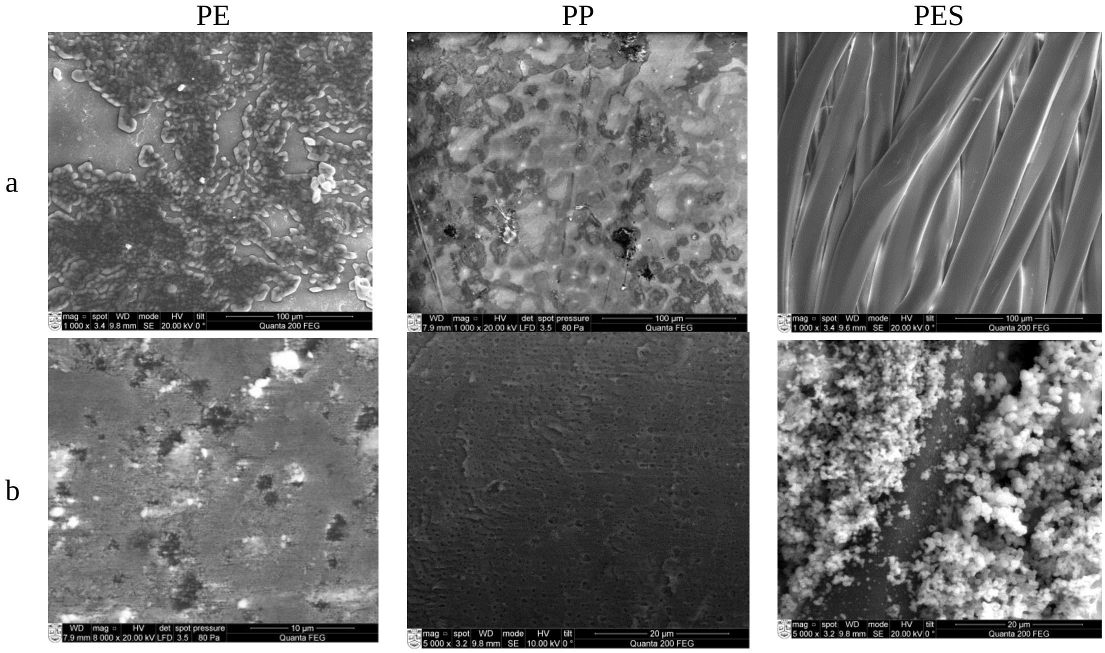

Fig. 6. SEM images of polymer surface: a – sulphurized, and b – with Cu_xS layers

SEM investigation of samples surface with Cu_xS layers (Fig. 6, b) has shown that compact layer formed on PE film, whereas grain structure was formed on PP film and PES fibre. However, grain structure was larger on fibre. Cu_xS layer containing the remaining sulphur conglomerates can also be observed on the surface of all polymers.

The cross-section analysis of the sulphurized polymers samples (Fig. 7, a) provides information about the thickness of the sulphurized layer, which was found to be approximately 7 µm for PE, 10–15 µm for PP, and for PES sorption of sulphur was in the whole volume.

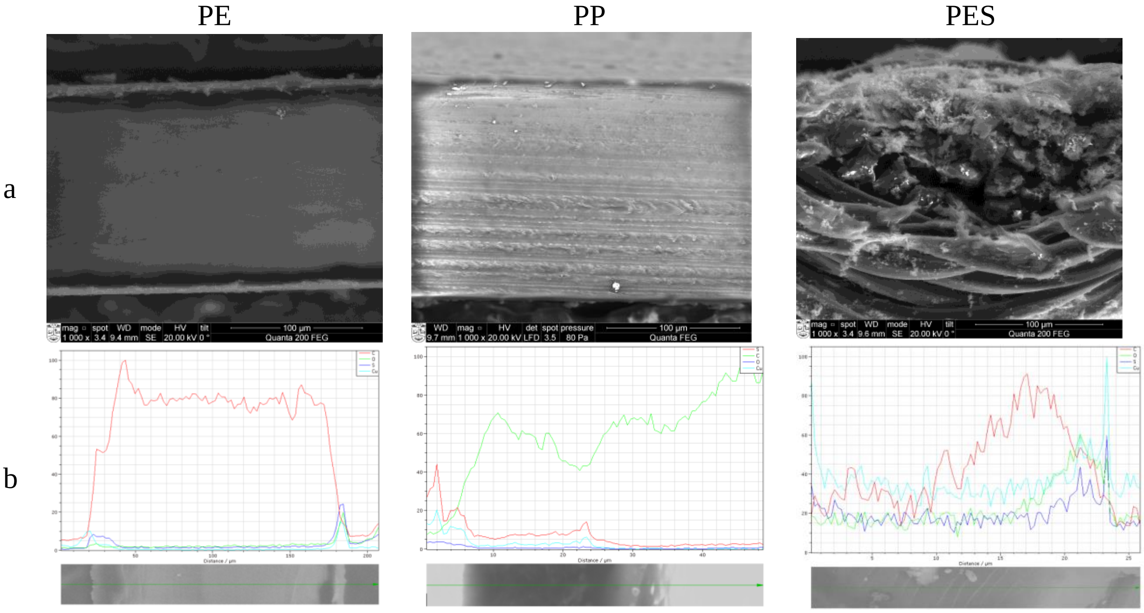

Fig. 7. Cross section images of polymers: a – sulphurized, and b – EDS with Cu_xS layers

The thickness of the formed Cu_xS layers on the polymers was approximately 20 µm for PE, 25 µm PP, and for PES – in the whole volume, but the largest amount of Cu_xS was on the fibre surface (Fig. 7, b).

4. Conclusions

Different polymers require different preparation of surface. PE and PES surfaces were cleaned, and this was enough for formation of Cu_xS layers. PP surface is inert, and needs thermo-oxidative chemical pre-treatment. It's led to changes in the physicochemical properties of the polymer due to chain scission and presence of carbonyl group as confirmed by FTIR.

The XRD analysis has clearly confirmed that the different forms of sulphur exist on different polymers although the same sulphuring agent was used: on PE – S_7 and polyethylene urea complex, on PP – S, on PES – S_{18} and thiourea molecules. In Cu_xS layers were found: on PE – anilite, on PP – roxbyite, covellite, and djurleite, on PES – anilite and djurleite.

Electromotive force measurement results confirmed the composition of the formed Cu_xS layers: anilite was formed on PE, djurleite – on PP, and anilite and djurleite – on PES.

SEM images of polymer surface show nonuniform sulphur layer on PE, uniform layer on PP and PES which sulphur diffused into polymer matrix. EDS show thickness of layers 20–25 µm on PE and PP, whereas sorption of Cu_xS in all PES volume.

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