

INVESTIGATION OF Cu_xS LAYERS ON POLYPROPYLENE FILM FORMED BY USING DIFFERENT SULFURING AGENTS

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Copper sulfides, Cu_xS , layers on the surface of polypropylene film were formed by sorption-diffusion method using two sulfurizing agents – thiourea solution and molten sulfur. The samples were studied by UV/VIS, X-ray diffraction (XRD), optical microscopy, and scanning electron microscopy (SEM) methods; electrical characteristics: electromotive force and sheet resistance were measured. All methods confirmed that a layer of nonstoichiometric copper sulfide was formed on the surface of the polypropylene film. The sheet resistance of the obtained layer varies from 1.0 to 3.7 $\text{k}\Omega\cdot\text{cm}^{-2}$ (sulfuring agent thiourea), and from 20 to 80 $\Omega\cdot\text{cm}^{-2}$ (sulfuring agent molten sulfur). After annealing electrical characteristics changed as confirmed by the composition change in the Cu_xS layers.

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1. Introduction

As important semiconductors, copper sulfides (Cu_xS) are widely used as p-type semiconductors in solar cells [1], gas sensors functioning at room temperature [2-5], chemical sensors [3, 6-9], lithium ion batteries [10], as optical filters [11-13], superconductors [14], superionic materials [15-19] and catalysts [20]. Due to their unique optical and electrical properties, they can also be applied in thin films and composite materials [21] formed on metals [21, 22], glass [4, 21, 22] or polymeric materials [22] by different physical [5, 21] and chemical [4, 22, 23] methods.

Electrically conductive Cu_xS layers on polymers can be prepared by the sorption-diffusion method, described earlier **Error! Reference source not found.** By this method, the surface of a polymer is initially treated by a different sulfurization agent [24-29] and, subsequently, aqueous Cu (I/II) salt solution.

Herein, we report the preparation of electroconductive Cu_xS layers on polypropylene (PP) films using thiourea solution and molten sulfur as the sulfurization agents.

The aim of this work was investigation and comparison of surface structure and morphology of isotactic polypropylene (PP) films coated with thin layers of electrically conductive copper sulfide with XRD, UV, and SEM analysis methods.

2. Methods

2.1. X-ray diffraction (XRD)

The X-ray diffraction analysis was performed on the D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) operating at the tube voltage of 40 kV and tube current of 40 mA. The X-ray beam was filtered with Ni 0.02 mm filter to select the Cu $K\alpha$ wavelength. Diffraction patterns were recorded in a Bragg-Brentano geometry using a fast counting detector Bruker

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LynxEye based on a silicon strip technology. The samples were scanned over the range $2\theta = 3\text{--}60^\circ$ at a scanning speed of 6° min^{-1} using a coupled two theta/theta scan type. The peaks obtained were identified on the basis of those available in PDF-2 data base [32].

2.2. 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.

2.3. Measurements of electrical resistivity

The constant current resistivity of the copper sulfide 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 870 g weight was used to press the electrodes to the sample surface. The concept of sheet resistance is used to characterize thin deposited layers.

2.4. Optical microscopy

Optical microscopy of PP samples was carried out by optical microscope Olympus CX31 (Olympus, Philippines), 400-fold increase, and photo camera Olympus C-5050 (Olympus, Japan).

2.5. UV spectroscopy

PP samples with sulfur and Cu_xS layers were characterized by UV spectroscopy (190–590 nm) using UV/VIS spectrometer *SPECTRONIC® GENESYS™8* (*Perkin Elmer*).

2.6. Measurements of electromotive force

Electromotive force of copper sulfide layer and copper was measured using pH-meter – potentiometer *HI 9321* (*Portugal*). The samples were staked up to copper holder and immersed into aqueous 0.01 mol/l CuSO_4 solution acidified with 0.1 mol/l sulfuric acid. Copper wire of 1.4 mm diameter electrochemically coated with copper was used as a reference electrode.

2.7. Turbidimetric method

Amount of sulfur ($\lambda = 400 \text{ nm}$) and copper ($\lambda = 670 \text{ nm}$) were measured by photo colorimeter *KΦK-2* (*Russia*). A sample of a sulfurized PP film was treated for 48–60 h in acetone for dissolving sulfur. The samples of PP/ Cu_xS were treated at 80–90°C by 1:1 solution of HNO_3 , and rinsed with distilled water. The solution obtained was neutralized with 2 mol/l $\text{NH}_3 \cdot \text{H}_2\text{O}$, the excess of 2 mol/l $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution was added and the solution was diluted to a final volume of 100 ml.

3. Experimental

15 mm × 45 mm size samples of non-oriented isotactic PP film of 150 μm thickness (*Proline X998, KWH Plast, Finland*) 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 formation of Cu_xS layers on PP was carried out in the glass reactor using a sorption–diffusion method [24, 29].

The hydrophobic PP requires an initial surface pre-treatment and weight losses after chemical treatment are recommended to be 2 g m^{-2} [30]. This result was reached when PP film was etched for 25 min at 90 °C with oxidizing solution ($\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (1:1), saturated with CrO_3) [29].

Oxidized PP samples were sulfurized in two ways: in thiourea solution (TU) and in molten sulfur. Sulfurization in the first way was done at 70–90 °C in acidic (pH ~ 0.8) 3 mol/l TU with

0.005 mol/l oxidizing additive $(\text{NH}_4)_2\text{S}_2\text{O}_8$ for 1–7 h. Sulfurization in molten sulfur was done at 135 °C for 0.5–7 min.

Afterwards, sulfurized PP samples were treated at 30–90 °C with 0.4 mol/l aqueous solution of CuSO_4 containing hydroquinone $\text{C}_6\text{H}_4(\text{OH})_2$ 0.1 mol/l as reducing agent (Cu(I/II)) for 0.5–12 min.

The $\text{PP/Cu}_x\text{S}$ samples were annealed at 80 °C for 30 min in thermostat and investigated further.

4. Results and discussion

4.1. Cu_xS layer deposition

Results of chemical analysis showed that amount of sulfur sorbed in the PP film from TU increased with increasing temperature (Fig. 1). When treatment temperature was 70 °C, amount of sorbed sulfur was $0.01 \text{ mg}\cdot\text{cm}^{-2}$, at 80 °C it was $0.06 \text{ mg}\cdot\text{cm}^{-2}$ and at 90 °C – $0.067 \text{ mg}\cdot\text{cm}^{-2}$. It was found that at 70 °C a very low amount of sulfur was sorbed (Fig. 1a, curve 1), sheet resistance of the formed Cu_xS layers was high and the measurement failed. Therefore, further experiments were carried out at 90 °C.

During sulfurization process in molten sulfur the amount of sorbed sulfur on PP film surface increased with increasing treatment duration (Fig. 1b) until the 3-rd min of sulfurization, and then it decreased practically negligibly. Probably, the decrease of sulfur amount on the PP was caused by the starting desorption process.

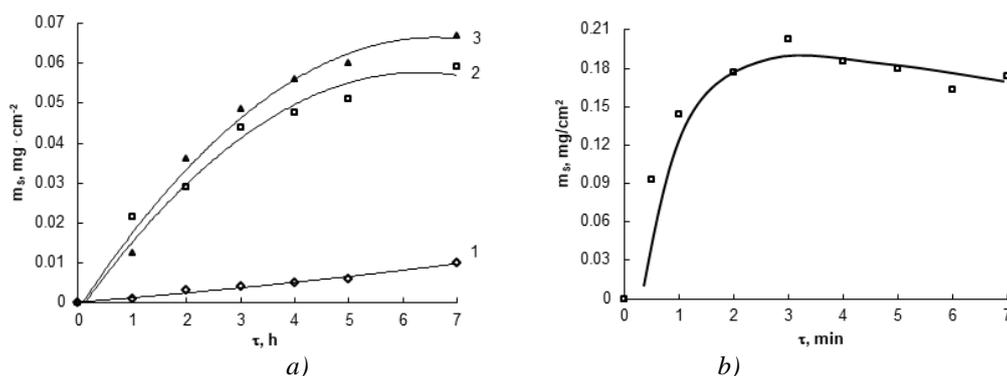


Fig. 1. Changes of sulfur amount in the PP films sulfurized: a – in TU at 70 °C (1), at 80 °C (2), and at 90 °C (3); b – in molten sulfur at 135 °C

Maximal amount of sulfur ($0.2 \text{ mg}\cdot\text{cm}^{-2}$) (Fig. 1b) in PP sulfurized by molten sulfur for 3 min was significantly bigger in comparison with the one treated in thiourea solution at 90 °C for 7 h ($0.067 \text{ mg}\cdot\text{cm}^{-2}$) (Fig. 1a).

The PP films sulfurized by different methods were treated with Cu(I/II) solution for 0.5 min–12 min.

The results obtained by turbidimetric analysis of Cu amount in the $\text{PP/TU/Cu}_x\text{S}$ (Fig. 2, curves 1–4) showed that the quantity of copper sulfide in Cu_xS layers increased with the increasing temperature of sulfurization solution and prolonging of treatment duration in Cu(I/II) solution. Quantity of copper stabilized or increased very slightly from the 12th min of treating samples with Cu(I/II) solution.

Amount of copper sulfide in $\text{PP/S/Cu}_x\text{S}$ increased till the 6-th min (Fig. 2, curve 5) and then stayed constant.

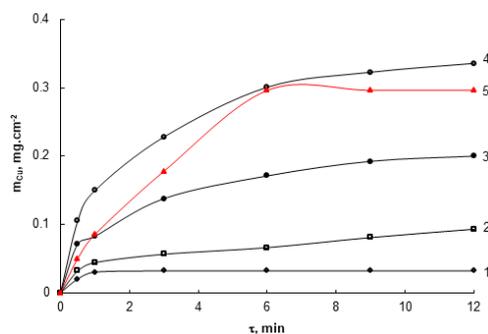


Fig. 2. Dependence of copper amount on the duration of treatment in Cu(I/II) solution at different temperature in the PP/TU/Cu_xS: 1 – at 30°C, 2 – at 50°C, 3 – at 80°C, 4 – at 90°C; 5 – in the PP/S at 80°C

4.2. Measurements of electrical resistivity

The specific electrical resistivity of polypropylene is approx. $10^{19} \Omega \cdot \text{m}$. One of the aims of this work was to obtain electrically conductive Cu_xS layers on a polymer.

The values of the surface sheet resistance of the PP/TU/Cu_xS were in 1.0–3.7 k $\Omega \cdot \text{cm}^{-2}$ interval (Fig. 3a, curve 1), and the one for PP/S/Cu_xS – in 20–80 $\Omega \cdot \text{cm}^{-2}$ interval (Fig. 3b, curve 1) of the formed Cu_xS layers. After annealing, the sheet resistances of the layers decreased to approx. 140 $\Omega \cdot \text{cm}^{-2}$ (Fig. 3a, curve 2) and 10–60 $\Omega \cdot \text{cm}^{-2}$ (Fig. 3b, curve 2), respectively. Surface sheet resistance of the samples with Cu_xS layers was lower for the samples treated in molten sulfur. Surface sheet resistance after annealing decreased by approximately 20 $\Omega \cdot \text{cm}^{-2}$ (Fig. 3b, curve 2), but the one for the PP/TU/Cu_xS decreased and remained constant. Their values did not depend on duration of treatment in Cu(I/II) solution (Fig. 3a, curve 2).

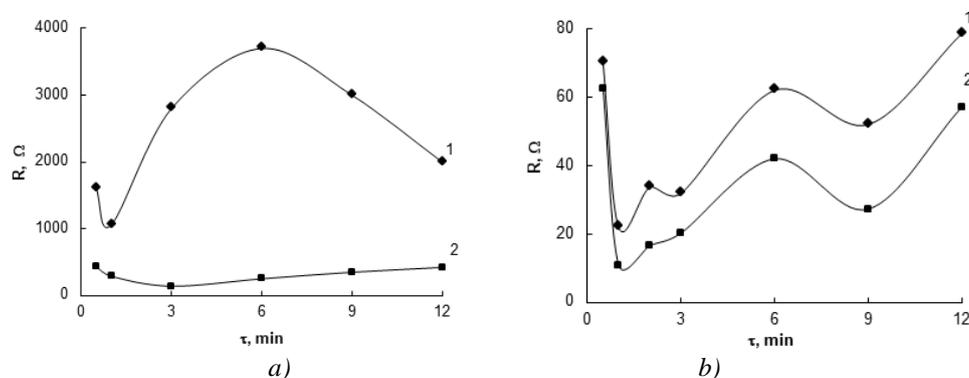


Fig. 3. Dependence of surface sheet resistances of the Cu_xS layers on the duration of treatment in Cu(I/II) solution of PP/TU/Cu_xS (a) and PP/S/Cu_xS (b): 1 – formed; 2 – annealed

The square sheet resistance measurements of Cu_xS layers on PP matrix showed that the best results were obtained by treating PP/TU sulfurized at 90°C for 7 h (Fig. 1a, curve 3), and treated in Cu(I/II) solution for 3 min (Fig. 2, curve 3) and PP/S sulfurized at 135°C for 3 min and treated in Cu(I/II) solution for 1 min (Fig. 2, curve 5). These samples were chosen for further investigation.

4.3. Measurements of electromotive force

Depending to the different reaction rates, the composition of the formed Cu_xS layers can vary, i. e., x value can vary in the interval of $1 < x < 2$. Electromotive force of copper sulfide phases varies in the interval of 0 mV–290 mV [31].

The results of electromotive force measurement showed that when duration of the interaction of PP/TU with Cu(I/II) solution was increasing, the electromotive force values of Cu_xS layers decreased from 186 mV, and after 12 min they stabilized at ~140 mV (Fig. 4a, curve 1). Cu_xS layers corresponded predominantly to djurleite, digenite and chalcocite ($1.8 < x < 2$). It was found that the electromotive force of the annealed samples increased and reached 226 mV (corresponded to spioncopite and geerite, ($1.4 < x < 1.65$)). When the treatment duration in Cu(I/II) solution was increased, the electromotive force became almost constant ~183 mV (corresponded to geerite ($1.36 < x < 1.4$)) (Fig. 4a, curve 2).

The electromotive force values of Cu_xS layers on PP/S increased from 170 mV (after treatment for 0.5 min) to 175 mV (after treatment for 1 min) and then decreased to 150 mV, and after 3 min they became almost constant and were ~155–165 mV (Fig. 4b, curve 1). After annealing, the electromotive force of the samples increased (Fig. 4b, curve 2) and reached 234 mV (after treatment in Cu(I/II) solution for 0.5 min) and 244 mV (after treatment in Cu(I/II) solution for 1 min) (corresponded to spioncopite and geerite, ($1.4 < x < 1.65$)). When the treatment duration in Cu(I/II) solution increased, the electromotive force became almost constant at 225 mV (corresponded to geerite ($1.36 < x < 1.4$)) (Fig. 4, curve 2).

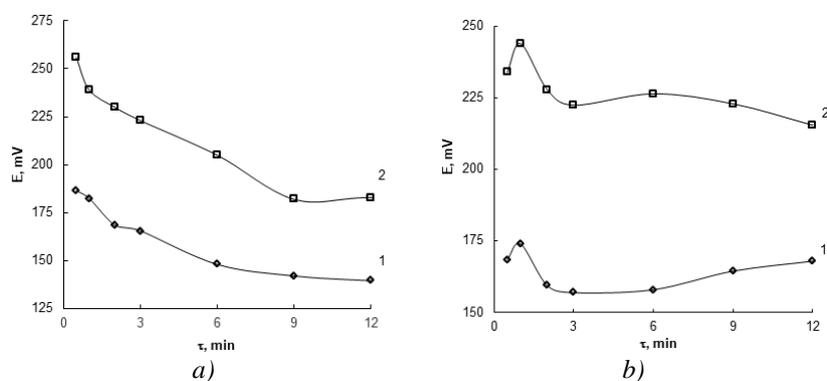


Fig. 4. Electromotive forces of the Cu_xS layers: of formed PP/TU/ Cu_xS (a1) and PP/S/ Cu_xS (b1) and annealed samples (a2; b2)

4.4. X-ray diffraction analysis

As seen from the data of XRD analysis of modified PP (Table 1), α -sulfur dominates in PP/TU, sulfur S_{18} in PP/S, roxbyite, Cu_7S_4 ; covellite, CuS ; djurleite, $\text{Cu}_{31}\text{S}_{16}$ in PP/TU/ Cu_xS , and α -chalcocite, Cu_2S in PP/S/ Cu_xS [32]. In the annealed samples dominate as follow: copper sulfide, $\text{Cu}_{1.8}\text{S}$, in PP/TU/ Cu_xS , and covellite, CuS in PP/S/ Cu_xS .

Table 1. *d*-Spacing, angle values, and their respective planes for Cu_xS layers after different PP treatment stages

| Standard d-spacing (Å) | Observed | | h k l Planes |
|---|-----------|---------------------|-----------------|
| | d-spacing | Angle (2θ) | |
| Polypropylene [00-050-2397] | | | |
| 6.32 | 6.32 | 14.00 | 110 |
| 5.25 | 5.26 | 16.85 | 040 |
| 4.78 | 4.80 | 18.47 | 130 |
| 4.20 | 4.22 | 21.01 | 111 |
| 4.07 | 4.07 | 21.81 | -131 |
| α Sulfur [8-247] | | | |
| 4.80 | 4.79 | 18.51 | 202 |
| 3.85 | 3.86 | 23.04 | 222 |
| 2.57 | 2.57 | 34.85 | 333 |
| Sulfur S_{18} [71-569] | | | |
| 3.87 | 3.86 | 23.58 | -103 |
| 3.13 | 3.13 | 28.32 | -311 |
| 2.57 | 2.57 | 34.76 | -313 |
| Roxbyite Cu_7S_4 [23-958] | | | |
| 4.24 | 4.23 | 20.99 | 1002 |
| 3.15 | 3.16 | 28.25 | 604 |
| Covellite CuS [78-876], [6-464] | | | |
| 3.05 | 3.05 | 29.25 | 102 |
| 2.81 | 2.81 | 31.76 | 103 |
| 2.10 | 2.10 | 42.93 | 106 |
| 1.90 | 1.89 | 47.88 | 107 |
| Djurleite $Cu_{31}S_{16}$ [42-564] | | | |
| 3.63 | 3.65 | 24.38 | -413 |
| 3.52 | 3.49 | 25.49 | 341 |
| 2.34 | 2.36 | 38.18 | 1120 |
| α Chalcocite Cu_2S [2-1294] | | | |
| 3.37 | 3.35 | 25.6 | 341 |
| 1.94 | 1.95 | 46.57 | 573 |
| Copper sulfide $Cu_{1.8}S$ [75-2241] | | | |
| 4.10 | 4.06 | 21.8 | 101 |
| 1.93 | 1.94 | 46.8 | 212 |
| 1.93 | 1.89 | 47.8 | 221 |

4.5. UV/VIS investigation

The UV/VIS absorption maxima in the spectrum of PP/TU were as follows: peak at 240 nm, and shoulder at 270 nm (Fig. 5, curve 1). Comparison of this spectrum with the spectrum of the PP/S (Fig. 5, curve 2), has revealed that the curves shifted towards shorter wavelengths and peaks were observed at 245 nm and 295 nm. An additional shoulder at 325 nm and peak at 330 nm there appeared as well indicating that the PP film in TU solution sorbed compounds with the following functional groups: $-NH_2$, $-S-$, and $-S-S-$.

The UV/VIS spectrum of PP/TU/ Cu_xS (Fig. 5, curve 3) had absorption maxima at 245 nm, peaks of low intensity at 250, 265, 295, 305, 320, 340, 390, and 395 nm, and a shoulder at 325 nm. The UV/VIS spectrum of annealed sample had the same peaks and shoulders, but with higher intensity (Fig. 5, curve 4).

The UV/VIS spectrum of PP/S/ Cu_xS (Fig. 5, curve 5) had absorption maxima at 250 nm, and many negligible peaks of higher intensity comparison with the 3-rd spectrum, indicating that annealing decreased intensity of the peaks (Fig. 5, curve 6). This can be explained by the fact that during annealing of the samples, Cu_xS reaction with sulfur proceeded, and amount of the elemental S in the sample decreased.

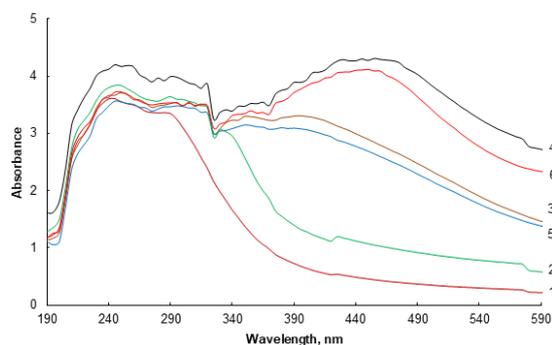


Fig. 5. UV/VIS spectra of films: 1 – PP/TU, 2 – PP/S, 3 – PP/TU/Cu_xS, 4 – PP/S/Cu_xS, 5 – annealed PP/TU/Cu_xS, 6 – annealed PP/S/Cu_xS

4.6. Investigation by optical microscopy

Photo of the PP sample surface has shown that the structure of the untreated PP surface is not homogeneous. PP consists of spherulites – PP macromolecules of helical shape (Fig. 6a). Oxidized PP surface revealed concentric internal structure of microfibrils (Fig. 6b). PP/TU and PP/TU/Cu_xS had clear spherulitic structure (Fig. 6c, 6e) because sulfur and Cu_xS layers were thin, unlike PP/S (Fig. 6d) and PP/S/Cu_xS (Fig. 6f) where layers were thicker.

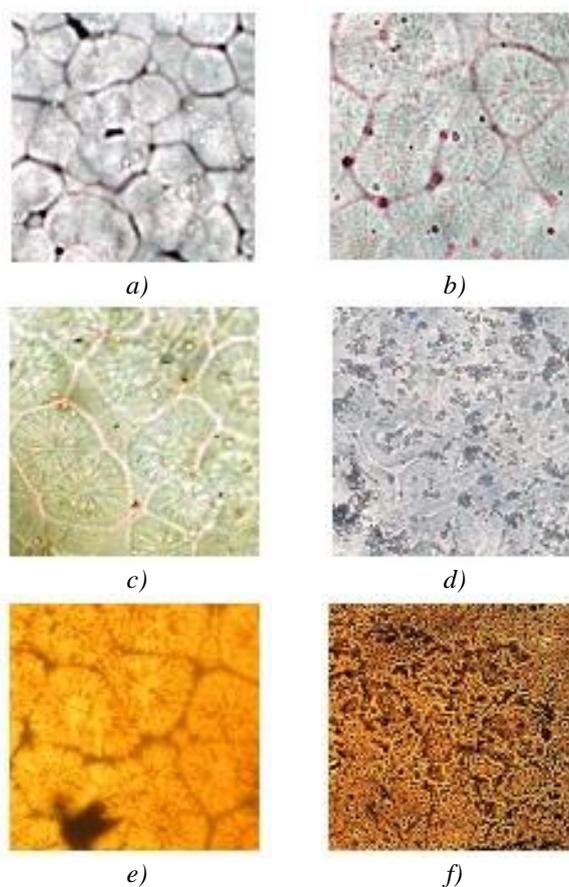


Fig. 6. Photos of PP samples (400-fold increase): a – untreated; b – oxidized; c – PP/TU; d – PP/S, e – PP/TU/Cu_xS; f – PP/S/Cu_xS

4.7. SEM analysis

The cross-section SEM images reveal the surface character of the samples. PP/TU image shows the uniformity of the diffused layer (Fig. 7a), however on PP/S sulfurized layer is adsorbed on the matrix surface (Fig. 7c) and has grain surface structure (Fig. 7d). SEM image of PP/TU surface show nonuniform and spotty layer (Fig. 7c).

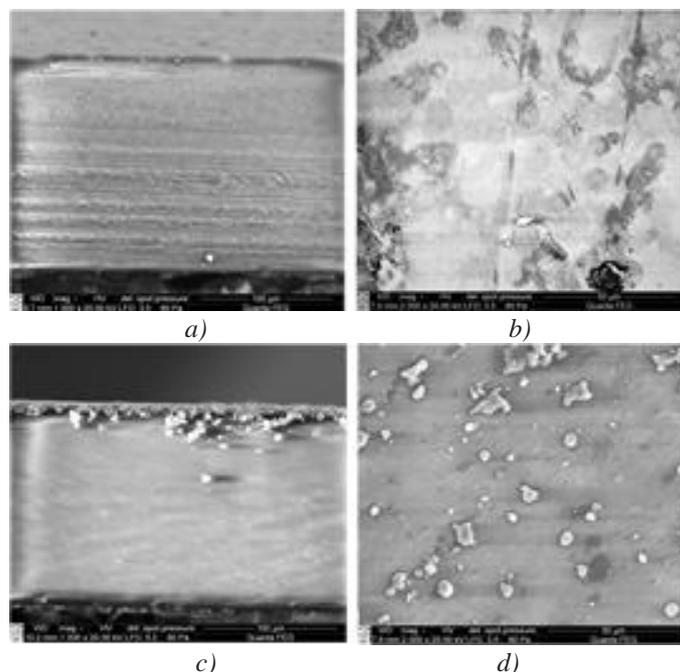


Fig. 7. Cross-sectional SEM images: a – PP/TU, c – PP/S; and surface images: b - PP/TU, d - PP/S

SEM investigation of samples' surface with Cu_xS layers (Fig. 8b, 8d) has shown that compact layers of grain structure containing the remaining sulfur conglomerates formed on PP film in both cases. Conglomerates of sulfur were larger and structure of Cu_xS layers was denser on PP/S/ Cu_xS (Fig. 8d) than the ones on PP/TU/ Cu_xS (Fig. 8b).

The thickness of the formed Cu_xS layers on the polymer was approximately 25 μm on PP/TU/ Cu_xS (Fig. 8a), and almost all it was diffused into matrix. On PP/S/ Cu_xS (Fig. 8c) outside layer thickness was 5 μm and ~ 12 μm was diffused into PP.

During annealing process, solid state reactions took place in the Cu_xS layer and Cu_xS combined with elemental sulfur. At the same time, Cu_xS diffused into polymer matrix. In the PP/TU/ Cu_xS , the layer thickness in the polymer increased to 30 μm (Fig. 9a), whereas, in the PP/S/ Cu_xS elements diffused from the outside layer and thickness of the composite reduced to 15 μm (Fig. 9c).

Surface images of the annealed samples show that structure of Cu_xS became grain (Fig. 9b, 9d) and some sulfur was removed from the polymer.

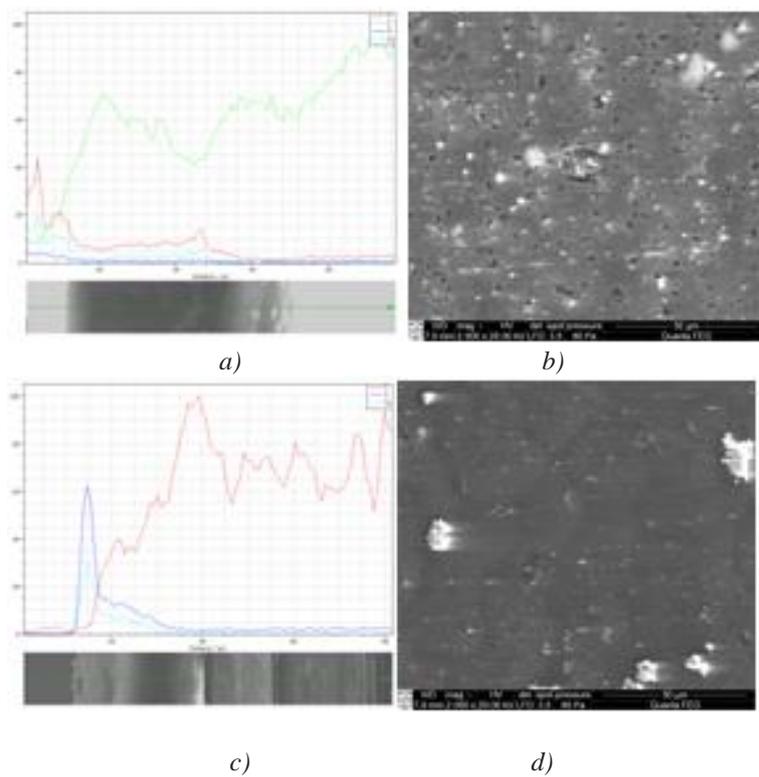


Fig. 8. Cross-sectional SEM images and elemental distribution: a – PP/TU/Cu_xS, c – PP/S/Cu_xS; and surface images: b - PP/TU/Cu_xS, d - PP/S/Cu_xS

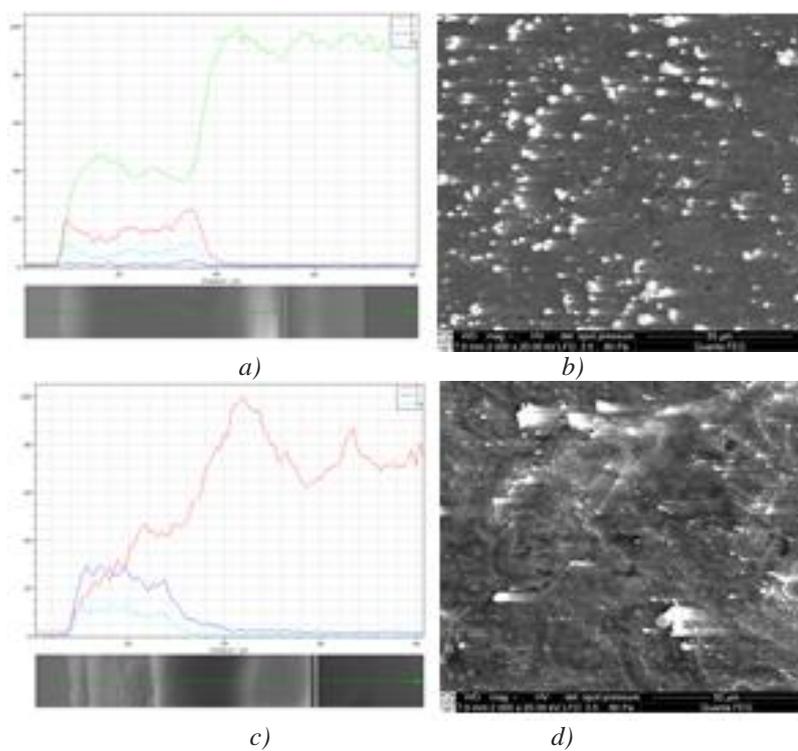


Fig. 9. Cross-sectional SEM images and elemental distribution of annealed samples: a – PP/TU/Cu_xS, c – PP/S/Cu_xS; and surface images: b - PP/TU/Cu_xS, d - PP/S/Cu_xS

5. Conclusions

Amount of sulfur and copper on PP increased with increasing temperature and treatment duration. Surface sheet resistance of the samples PP/TU/Cu_xS was in 1.0–3.7 kΩ·cm⁻² interval and the one for PP/S/Cu_xS was in the range of 20–80 Ω·cm⁻². Electromotive force measurement results confirmed the composition of the formed Cu_xS layers: djurleite – on PP/TU, anilite and djurleite – on PP/S.

The data of XRD analysis have shown that on the sample PP/TU α- sulfur dominates, on the PP/S – sulfur S₁₈, in the PP/TU/Cu_xS – roxbyite, Cu₇S₄; covellite CuS; djurleite Cu₃₁S₁₆, in the PP/S/Cu_xS – α-chalcocite, Cu₂S. After annealing resistance of Cu_xS layers decreased, electromotive forces increased what confirmed the composition change in the Cu_xS layer. XRD analysis has shown that in the annealed samples dominate: PP/TU/Cu_xS – copper sulfide, Cu_{1.8}S, PP/S/Cu_xS – covellite, CuS.

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