

Formation of copper sulfides on polypropylene matrix using various reducing agents

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Layers of copper sulfides, Cu_xS , on the surface of a polypropylene film were formed by the sorption–diffusion method using two reducing agents – hydroquinone and hydroxylamine sulfate. The formed copper sulfide layers were investigated by UV/VIS, X-ray diffraction (XRD) and water contact angle measurements (WCA). The investigations confirmed that a layer of nonstoichiometric copper sulfide was formed on the surface of the polypropylene film. The water contact angle measurements revealed the change in adhesive properties of the samples after each treatment stage.

Keywords: polypropylene, copper sulfide layer, water contact angle, X-ray diffraction, UV–VIS

INTRODUCTION

Copper sulfides have the ability to form various stoichiometries, at least five phases of which are stable at room temperature: covellite (CuS), anilite ($\text{Cu}_{1.75}\text{S}$), digenite ($\text{Cu}_{1.8}\text{S}$), djurleite ($\text{Cu}_{1.95}\text{S}$) and chalcocite (Cu_2S). Depending on the stoichiometric composition, these copper sulfides can be insulators, semiconductors, conductors and superconductors [1, 2]. Their unique properties determine promising applications in numerous fields, such as solar control coatings and photovoltaic devices, polarizers of infrared radiation [3], chemical sensors [4–8], optical filters [9–11], superionic materials [12–16], superconductors [17] and catalysts [18]. Due to their unique optical and electrical properties, they can also be applied in thin films and composite materials [19].

Usage of polymer films, coated with electroconductive layers, has been increasing in the past years due to their elasticity, resistance against corrosion and low toxicity. Electrically conductive Cu_xS layers on polymers can be prepared by methods of vacuum evaporation, activated reactive evaporation [20], electroless deposition [21], suc-

cessive ionic layer adsorption and reaction (SILAR) [22], chemical bath deposition [17, 23] and sorption–diffusion methods [24]. By the last method, the surface of a polymer is initially treated by a sulfurization agent: sodium polysulfides [25], polythionic acids and polythionates [26–35], sulfur in a carbon disulfide solution [36], thiourea solutions [37] and sulfur [38]. In the second stage sulfurized polymer films are treated with an aqueous Cu (I/II) salt solution [25, 29, 39].

Polypropylene (PP) is resistant toward many organic and inorganic solvents and is a chemically constructive plastic, which is characterized by good dielectric properties [40, 41]. PP, out of all other plastics, has very low density (about 900 kg/m^3) and an excellent resistance to high temperatures. Also, the global consumption of polypropylene means that the plastic has diverse applications.

The aim of this study was to form copper sulfide layers on polypropylene films using different reducing agents, investigate and compare their properties by UV/VIS, X-ray diffraction (XRD) and water contact angle measurements. Firstly, polymers were pre-treated for surface activation in a KMnO_4/HCl solution, and subsequently Cu_xS layers on PP were prepared by the sorption–diffusion method using a thiourea solution as a sulfuring agent.

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EXPERIMENTAL

Copper sulfide layers were formed on 15×70 mm, $150 \mu\text{m}$ thickness samples of polypropylene (PP). Only fresh reaction solutions, prepared using distilled water and analytically pure reagents, were used. The formation of Cu_xS layers on PP was carried out in a glass reactor using the sorption–diffusion method in atmospheric pressure conditions.

The hydrophobic PP requires an initial surface pre-treatment. First, the PP samples were cleaned ultrasonically for 10 min at 20°C in acetone and then in ethanol to remove organic material, and dried in an oven for 1 h at 50°C . The average weight loss was 0.19 g/m^2 . Then the PP samples were held in an oxidizing solution ($0.05 \text{ M KMnO}_4/2 \text{ M HCl}$) at 60°C temperature for 2 to 5 h to enhance their adhesive properties [42].

After the pre-treatment stage, the PP samples were sulfurized for 1–5 h in an acidic (HCl 1:1 H_2O) solution of 3 M thiourea ($(\text{NH}_2)_2\text{CS}$) with a 0.005 M ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) additive at 60°C .

Cu_xS layers were formed with 0.4 M CuSO_4 , using 0.1 M hydroquinone ($\text{C}_6\text{H}_4(\text{OH})_2$) or hydroxylamine sulfate 0.03 M ($(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$) with ammonia 3.2 M ($\text{NH}_3\text{-H}_2\text{O}$) as reducing agents for 1–20 min at 80°C . Afterwards, the PP films were thermally treated in an oven for 1 h at 80°C .

The X-ray diffraction analysis of the samples was performed on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) operating at 40 kV tube voltage and 40 mA tube current. The X-ray beam was filtered with a Ni 0.02 mm filter to select the Cu K α wavelength. The diffraction patterns were recorded in the Bragg–Brentano geometry using a fast counting detector Bruker LynxEye based on the 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 the PDF-2 database [43].

The PP samples with sulfur and Cu_xS layers were characterized by UV spectroscopy (190–500 nm) using a UV/VIS spectrometer SPECTRONIC® GENESYS8 (Perkin Elmer, USA).

Water contact angle (WCA) measurements were carried out at room temperature and atmospheric pressure using an optical measuring equipment – Theta Lite Optical Tensiometer TL100 (Biolin Scientific, Finland). A distilled water drop was released onto the test substrate surface using a syringe. The drop geometry was acquired by a numerical camera and transmitted to a computer workstation to calculate the WCA value. All WCA data were averaged from two measurements. Instrument specifications were the following: measuring range varied from 0° , mN/m to 180° , mN/m with an accuracy of $\pm 0.1^\circ$, mN/m. A USB3 digital camera was used. A light source was created with the LED based background lighting.

RESULTS AND DISCUSSION

Visual inspection. Colour intensity of the PP films with Cu_xS layers is directly proportional to the treating time (Fig. 1). Dark brown Cu_xS layers were formed using hydroquinone, whereas dark brown layers with a reddish tint were created using hydroxylamine sulfate as a reducing agent.

XRD analysis was applied to determine the structure, composition and physical properties of materials. The data of XRD analysis of the modified PP (Table 1) have shown that beta-sulfur and sulfur S_{18} dominate in sulfurized PP, chalcocite, Cu_2S ; djurleite, $\text{Cu}_{1.9375}\text{S}$ and $\text{Cu}_{31}\text{S}_{16}$ in the samples using hydroquinone and hydroxylamine sulfate as a reducing agent [43].

UV/VIS absorption maxima in the spectrum of PP sulfurized for 5 h were as follows: peak at 240 nm, and shoulders at 250 and 275 nm (Fig. 2, Curve 2). The spectra of PP films with copper sulfides were formed using hydroquinone display shoulders at 305, 320 and 325 nm (Fig. 2, Curve 3), and in the ones formed using hydroxylamine sulfate there are additional peaks at 360 and 405 nm (Fig. 2, Curve 4).

The UV/VIS analysis has shown that absorbance of the PP films increases after sulfurizing and coating with copper sulfides. The PP films treated using hydroquinone have a lower absorbance value (Fig. 2, Curve 3) than those treated with hydroxylamine sulfate as a reducing agent (Fig. 2, Curve 4).

The purpose of the contact angle investigation was to study the wetting when a solid and a liquid interact. Small contact angles (lower than 90°) correspond to high wettability, while large contact angles (greater than 90°) correspond to low wettability.

The investigation has shown that the PP films have gone through significant surface processing, because water contact angle values increased from 90° of the non-treated PP films to 130° of the treated PP films (Table 2).

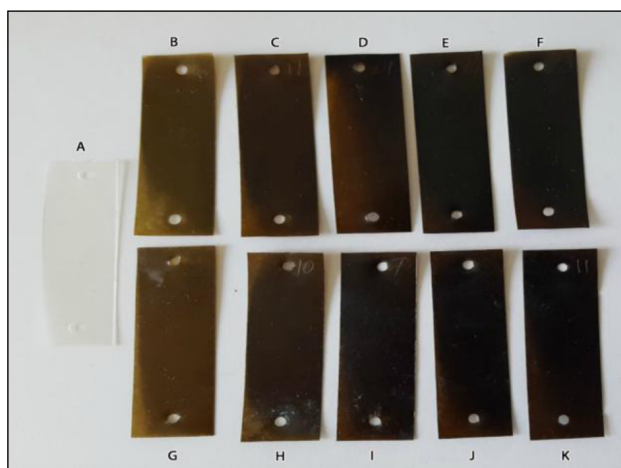


Fig. 1. Photos of the samples treated in Cu(I/II) solution for different duration: non-treated (A); using hydroquinone as a reducing agent: treated for 1 min (B), 3 min (C), 6 min (D), 9 min (E), 12 min (F); using hydroxylamine sulfate as a reducing agent: 1 min (G), 3 min (H), 6 min (I), 9 min (J), 12 min (K)

Table 1. d-Spacing, angle values and their respective planes for Cu_xS layers

Standard d-spacing (Å)	Observed		hkl planes
	d-spacing	Angle (2 θ)	
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
beta-sulfur S [34-941]			
4.06	4.07	21.84	-202
Sulfur S₁₈ [72-409]			
6.32	6.34	13.96	011
5.29	5.27	16.81	400
4.80	4.81	18.43	410
Chalcosine low Cu₂S [83-1462]			
6.37	6.35	13.93	-211/111
4.80	4.79	18.50	-302/102
Djurleite Cu_{1.9375}S [71-1383]			
4.77	4.79	18.50	-402/402
4.08	4.07	21.84	422/-512
Djurleite Cu₃₁S₁₆ [42-564]			
4.07	4.09	21.72	-512

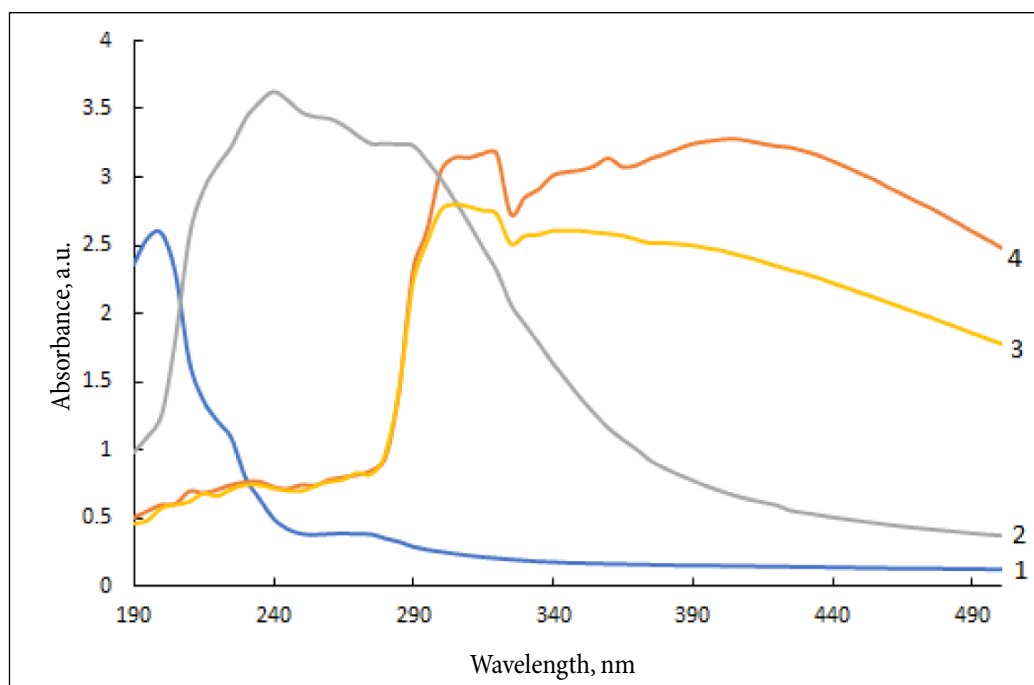


Fig. 2. UV/VIS spectra of the PP films: non-treated (1), oxidized for 5 h and sulfurized for 5 h (2), Cu_xS formed with hydroquinone as a reducing agent for 12 min (3), Cu_xS formed with hydroxylamine sulfate as a reducing agent for 12 min (4)

Table 2. Water contact angle

Name	Non-treated	Pre-treated	Oxidized	Sulfurized	Cu _x S formed with hydroquinone	Cu _x S formed with hydroxylamine sulfate
WCA (average)	90.00°	83.02°	92.00°	103.52°	131.11°	130.82°

The results showed that the pre-treated films had the lowest water contact angle. During all other treatment stages, starting from oxidation, the wettability increases (Fig. 3). The comparison of the samples with Cu_xS layers formed using different reducing agents has revealed that the highest contact angle was achieved in the case of treatment with hydroquinone.

sulfur S, sulfur S₁₈, chalcosine low Cu₂S, djurleite Cu_{1.9375}S and Cu₃₁S₁₆. The UV/IVS results showed that the absorption values were lower when hydroquinone was used as a reducing agent. Absorption increased with increasing the time of treating with CuSO₄. The results of the water contact angle measurement showed a significant change in the PP film wettability from the non-treated films to the films

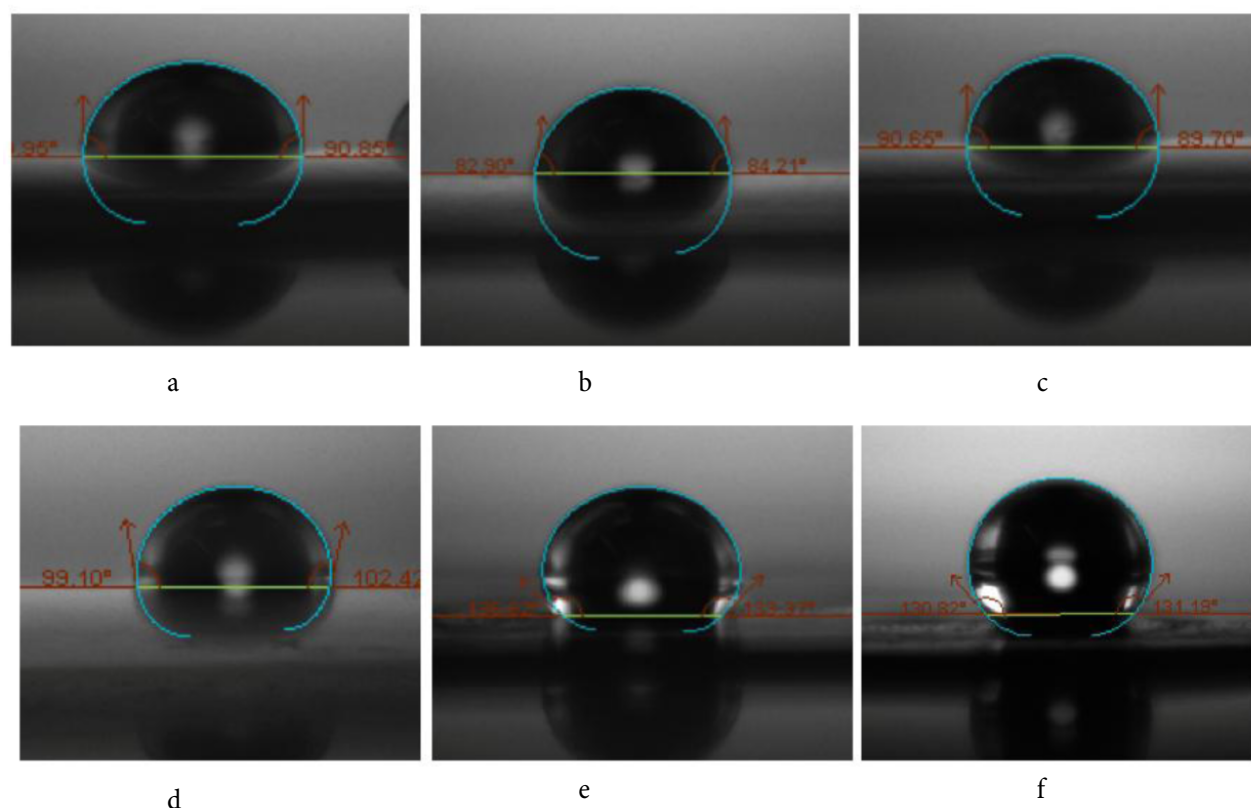


Fig. 3. Photos of the contact angle measurements of the PP films: non-treated (a), pre-treated (b), oxidized (c), sulfurized (d), Cu_xS formed with hydroquinone as a reducing agent for 12 min (e), Cu_xS formed with hydroxylamine sulfate as a reducing agent for 12 min (f)

CONCLUSIONS

The colour intensity of PP increased with increasing the treatment duration in the Cu(I/II) solution and depended on the used reducing agent. Dark brown and black Cu_xS layers were formed using hydroquinone, whereas dark brown layers with a reddish tint were created using hydroxylamine sulfate as a reducing agent. The XRD analysis has shown what phases were formed on the PP film. The main ones that dominated throughout all of the samples, treated with CuSO₄ and reducing agents, were beta-

which had copper sulfide layers on them. The PP films with Cu_xS showed lower wettability than the non-treated samples.

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VARIO SULFIDŲ SLUOKSNIŲ SUDARYMAS ANT POLIPROPILENO MATRICOS NAUDOJANT SKIRTINGUS REDUKTORIUS

S a n t r a u k a

Cu_xS sluoksniai ant polipropileno plėvelės buvo sudaromi sorb-cijos-difuzijos būdu, naudojant du reduktorius – hidrochinoną ir hidroksilamino sulfatą. Atlikta sudarytų sluoksnių rentgeno difrakcinė analizė (XRD), vandens kontaktinio kampo (vilgumo) matavimai (WCA) ir užrašyti UV / VIS spektrai. Proceso metu po kiekvienos operacijos vandens kontaktinis kampas kito. Tyrimai patvirtino, kad ant polipropileno matricos buvo gauti nestechiometriniai vario sulfido sluoksniai.

