Materials Science-Poland, Vol. 25, No. 4, 2007

Spectroscopic and diffraction studies of chemical deposition of copper sulfide films on polyamide surface using potassium pentathionate

V. KRYLOVA[*]

Departament of Inorganic Chemistry, Kaunas University of Technology,
Radvilėnų str. 19, LT-50254 Kaunas, Lithuania

Sulfur sorption–diffusion by polyamide PA 6 film exposed to potassium pentathionate $K_2S_5O_6$ solutions was investigated by the UV, IR absorption spectroscopy and chemical analysis methods. $S_5O_6^{2-}$ anions were found to sorb into the polymer. The study of sulfur sorption–diffusion kinetics showed that the concentration of sorbed pentathionate ions in polyamide film increased with increasing duration of treatment and the temperature of solution. Sulfur concentration in the polymer was found to depend on the conditions of sorption and varied between 0.94 and 7.64 mg/cm^3. The estimated apparent diffusion coefficients of $S_5O_6^{2-}$ ions in polyamide increased with increasing temperature of $K_2S_5O_6$ solution. On treating sulfured polyamide film with copper(I) salt solution, copper sulfide (Cu_xS) layers are formed in the surface matrix of the polymer. The content of Cu_xS depended on the concentration of $S_5O_6^{2-}$ ions in the polyamide matrix. Initially dielectric, polyamide films after formation of Cu_xS layers in their surface matrix become electrical conductors. Samples sulfured in $K_2S_5O_6$ solution at 293 K for 240 min were the most conductive. X-ray diffraction studies of Cu_xS layers revealed the presence of two phases: chalcosine and djurleite.

Key words: *polyamide; potassium pentathionate; sulfuration; copper sulfide layer*

1. Introduction

Polymers modified with various films on their surface represent a new class of materials – composites with a novel combination of properties. Polymers are often modified by thin electrically conductive or semi-conductive films of binary inorganic compounds, particularly copper sulfide [1–4]. Copper sulfide thin films on polymers are relevant in solar radiation absorbers, solar cells. These composites may be used as conductive substances for metal deposition or semiconductor coatings by electrolytic

---

[*] E-mail*:* Valentina.Krylova@ktu.lt

deposition and as a conductive base for optoelectronic device structures [1–4]. Recently, Cu_xS thin films on dielectrics have been used in resistive gas sensors [5].

Various methods, such as vacuum evaporation [7, 8], activated reactive evaporation, spray pyrolysis, electroless deposition, successive ionic layer adsorption and reaction and chemical bath deposition [9] were used for the formation of metal sulfide layers on various dielectrics and polymers. Simple and promising is the sorption –diffusion method [10]. Hydrophilic and semi-hydrophilic polymers, including polyamide (PA 6), are capable of absorbing ions of various sulfuration agents, e.g., sulfur solutions in organic solvents [11], sodium polysulfide (Na_2S_n, $n = 4.8$) aqueous solutions [12], polythionic acid ($H_2S_nO_6$, $n = 9–45$) aqueous solutions [13]. To prevent environmental pollution with vapours of toxic solvents and to avoid swelling of some polymers in organic solvents, the use of sulfide solutions is limited because of their high alkalinity. The synthesis of sulfurous polythionic acids appears to be fairly complicated and prolonged (up to 2 days), and it is based on the reaction of interaction of toxic hydrogen sulfide and thiosulfurous acid. Aqueous solutions of polythionic acids are unstable and are rapidly decomposed with isolation of elemental sulfur. Recently, the adsorption–diffusion method of formation of thin copper sulfide layers on PA 6 surface based on the initial treatment of a polymer with solutions containing polythionate anions, $S_nO_6^{2-}$ ($n \le 6$) has been under extensive investigation [14−16].

In the present study, binary compounds of copper sulfide in the surface layer of PA 6 were obtained by the sorption−diffusion method [10, 14]. In the first stage of the process, sulfur-containing particles from 0.15 mol/dm^3 potassium pentathionate ($K_2S_5O_6$) solution were adsorbed on PA 6 samples [15]. In the second stage, sulfurised PA 6 was treated with Cu(II) sulfate solution containing hydroxylamine sulfate as the reducing agent [10].

In the present study, the sulfuration of polyamide film in potassium pentathionate solutions and the generation of Cu_xS layers on the surface of sulfured PA 6 by treatment with copper(I) salt solution have been investigated. The usefulness of composites obtained by modifying polymers with copper sulfide layers was determined by their electrical properties which vary significantly even when the chemical composition is only slightly changed [10, 15]. Electrical resistance itself increases over six times when the value of x in Cu_xS is increased from 1 to 2 [9]. Therefore, electrical measurements provide preliminary information on the composition of the layer. The composition can be more precisely determined by X-ray diffraction studies.

2. Experimental

Copper sulfide layers were deposited on a PA 6 (specification TY 6-05-1775-76, grade PK-4, produced in Russia) film 70 μm thick. The diameters of the pores in the film do not exceed 1.5 nm. The porosity was measured by the BET method [18] using the Quantasorb sorption system (USA). Samples 15×70 mm^2 were used to remove the remainder of the monomer. Before sulfurisation, the samples were boiled in distilled water for 2 h, they were dried with filter paper and subsequently kept over $CaCl_2$ at least for 24 h [14].

$K_2S_5O_6 \cdot 1.5H_2O$, was prepared and chemically analyzed according to [19, 20]. PA 6 samples were exposed to potassium pentathionate solution. Previous experiments [14] have shown that sorption from 0.1 mol/dm^3 $K_2S_5O_6$ was too slow and insufficient. Therefore, 0.15 mol/dm^3 solutions were chosen for this work. At temperatures higher than 303 K, gradual spontaneous decomposition of polythionate occurs, with liberation of elemental sulfur [19]:

$$S_5O_6^{2-} \longrightarrow 3S + SO_2 + SO_4^{2-} \tag{1}$$

The sorption process was performed at temperatures ranging from 273 to 293 K. The samples were rinsed with distilled water, dried over $CaCl_2$, analyzed, and then used in further experiments. The content of sulfur in PA 6 samples in the form of sulfates was determined turbidimetrically [21]. Samples of sulfurised PA 6 were treated with the solution of 0.4 mol/dm^3 Cu(I) salt prepared from crystalline $CuSO_4 \cdot 5H_2O$ and hydroxylamine sulfate [10]. After treatment, the samples were rinsed with distilled water and dried over $CaCl_2$. The content of copper in PA 6 samples was determined by atomic absorption spectrometry (AAS) [22]. UV spectra (from 200 nm to 400 nm) were recorded on a Spectronic^R Genesys™ 8 UV/Visible spectrophotometer with compensation of PA 6 absorption. IR spectra (from 200 to 1300 cm^{-1}) were recorded on a Perkin-Elmer FT-IR Spectrum GX spectrophotometer by the compensation method. Phase compositions of copper sulfide layers were investigated by X-ray diffraction using a DRON-6 diffractometer (CuK$_\alpha$ radiation). In order to eliminate the maxima of PA 6, X-ray diffractograms were analyzed using the Search Match, ConvX, Xfit, and Microsoft Excel programs. The sheet resistance of Cu_xS layers was measured at a constant current using the E7–8 digital multimeter (Russia) with custom design electrodes. The measurements were carried out per 1 cm^2 square electrodes, therefore the resistance is given in Ω/cm^2.

3. Results and discussion

The nature of sulfur-containing particles sorbed by PA 6 film was studied employing UV and IR spectroscopy. A chain of three divalent sulfur atoms $^-O_3S{-}S{-}S{-}S{-}SO_3^-$ of a low oxidation state is present in the anion of potassium pentathionate. Optical absorption spectra of thin sulfide films on PA 6 revealed their high absorbance (10^4 cm^{-1}), indicating direct band gap transition. According to data of a study of UV absorption spectra of lower potassium polythionates [23, 24], the most intensive absorption peaks of polythionate ions appear at 256 nm and 295 nm. In addition, the UV absorption spectra of nanofilms formed using a single precursor $K_2S_5O_6$ are identical. UV absorption spectra of PA 6 samples sulfured for various periods of time in a solution of

$K_2S_5O_6$ at various temperatures (273–293 K) are presented in Fig. 1. Two absorption peaks are observed in the spectra: at λ = 250 nm, and as a less intense and shallower band at λ = 295 nm. Thus the UV absorption spectra recorded by us confirm that sulfur is sorbed by PA 6 films in the form of pentathionate ions. The intensity of absorption maxima in the spectra increases upon increasing exposure time and the temperature of polymer treatment with potassium pentathionate solution. With decreasing temperature of the solution, the absorption peak in the spectra is shifted towards λ = 240 nm.

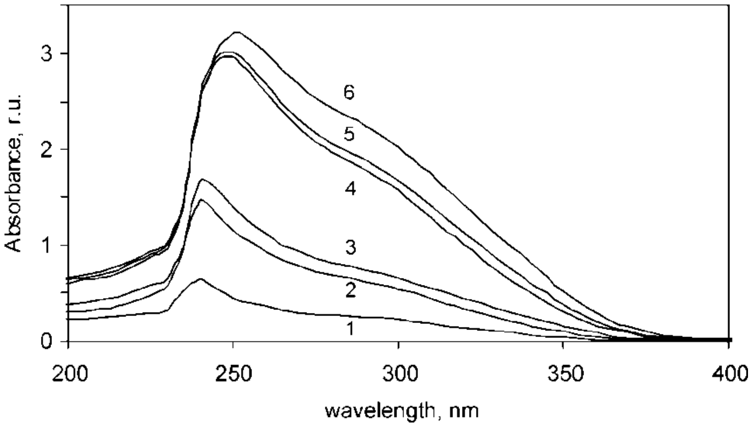

Fig. 1. UV absorption spectra of PA 6 films sulfured in 0.15 mol/dm^3 $K_2S_5O_6$ solution in 0.1 mol/dm^3 HCl, (pH = 1.5) at various times τ_s [min] and temperatures [K]: 1 – 273 (τ_s = 240), 2 – 283 (τ_s = 240), 3 – 293 (τ_s = 60), 4 – 293 (τ_s = 120), 5 – 293 (τ_s = 180), 6 – 293 (τ_s = 240)

The most intensive bands in the IR spectra of PA 6 samples sulfured in $K_2S_5O_6$ solutions, recorded by the compensation method (with PA 6 absorption eliminated), were located at 242–245, 337–385, 421–470, 523–536, 580–611, 1021–1022, 1202 –1268 cm^{-1}. For identification of characteristic vibration frequencies, the IR spectra were compared with the spectra of pure $K_2S_5O_6 \cdot 1.5H_2O$ [25] and spectra reported in literature [26–29]. Data on IR spectra are presented in Table 1.

Based on the literature data [25–28], the bands at 1000–1250 cm^{-1} correspond to vibration frequencies of the SO bond (Table 1). The band at 1022 cm^{-1}, corresponding to symmetrical valence vibrations of S–O entity, does not split, and this feature shows that the symmetry of the pentathionate ion is not disrupted. A comparison of the recorded spectra with the spectrum of pure $K_2S_5O_6 \cdot 1.5H_2O$ salt showed the tendency of displacement of their frequencies towards lower values. This might be explained by the formation of hydrogen bonds between SO_3^{2-} ions and the polymer chains. For this reason, the S−O bonds in $S_5O_6^{2-}$ ions become weaker and the absorption peaks shift towards lower frequencies.

Analysis of the IR spectra of sulfured PA 6 samples shows that the intensity of absorption peaks increases on increase $K_2S_5O_6$ solution temperature and exposure time.

These results confirm that the sorption of pentathionate ions by PA 6 occurs during polymer treatment with acidified $K_2S_5O_6$ solution.

Table 1. Characteristic IR absorption bands ν [cm^{-1}] from $K_2S_5O_6 \cdot 1.5H_2O$ and $S_5O_6^{2-}$/PA 6 at 293 K in the frequency range 200–1300 cm^{-1}

$K_2S_5O_6 \cdot 1.5H_2O$	$S_5O_6^{2-}$/PA 6	Assignment	Reference
244	242	δ(SSS)	[29]
342	340	$\gamma_r(SO_3)$	[29]
	379		
428	426	ν(S–S)	[27]
	464		
514	503	δ_{as}(O–S–O)	[25, 29]
	524		
542	536		
618	611	δ_s(O–S–O)	[25, 29]
650	absent		
1024	1022	ν_s(S–O)	[25–28]
1050			
1207	1203	ν_{as}(S–O)	[25–28]
1218	1222		
1234			
1250			
1263[*]	1263		

[*] Arm of the absorption band.

Chemical analysis of PA 6 samples sulfured in a $K_2S_5O_6$ solution showed that the concentration of sulfur sorbed by the polymer depends on the temperature of the sulfuration solution and exposure time.

Table 2. Dependence of sulfur concentration close to saturation $c_{s\infty}$, in polyamide treated in $K_2S_5O_6$ solution at various temperatures, apparent $S_5O_6^{2-}$ ion diffusion coefficient D and apparent adsorption heat $-\Delta H_{\mathrm{ads}}$

Temperature [K]	$c_{s\infty}$ [mg/cm^3]	D×10^{-11} [cm^2/s]	$-\Delta H_{\mathrm{ads}}$ [kJ/mol]
273	1.52	2.2	–
283	4.25	3.3	66.64
293	7.64	4.7	47.01

It was found that the sulfur concentration (c_s, mg/cm^3) in the samples kept in potassium pentathionate solutions at 273, 283 and 293 K increased with time. The sorption–diffusion process becomes faster on increasing temperature, resulting in a higher sulfur concentration in the film. The sulfur concentrations close to saturation ($c_{s\infty}$) of all films are given in Table 2. The highest values of $c_{s\infty}$ were obtained in samples treated with potassium pentathionate at 293 K. The sulfur concentrations in samples treated at 293 K were twice or fivefold higher than those in samples treated at 283 K and 273 K. The concentration of sulfur sorbed at 283 and 293 K increased significantly upon increasing temperature of potassium pentathionate solution (Fig. 2).

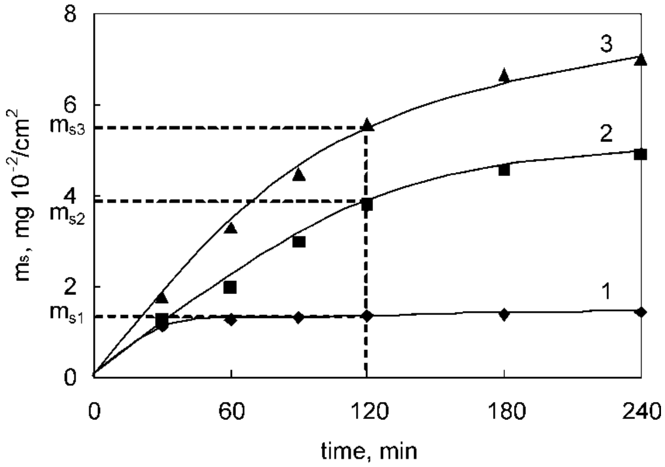

Fig. 2. Dependence of the adsorbed sulfur content in polyamide on the exposure time in solution of $K_2S_5O_6$ (c = 0.15 mol/dm^3). The temperature of PA 6 sulfuration [K]: 1 – 273, 2 – 283, 3 – 293

After lowering the temperature of the sulfuration solution, $c_{s\infty}$ in polyamide film samples clearly decreases: from 293 K to 283 K by a factor of 1.8 and from 283 K to 273 K 2.8 times. These values imply that sulfur sorption–diffusion in polyamide is less affected by the solution temperature. This is confirmed by the lowest value of the apparent adsorption heat $|\Delta H_{\mathrm{ads}}|$ obtained (Table 2). We calculated the apparent adsorption heat from the Langmuir equation [30]. Examples representing sulfur adsorption for the determination of $|\Delta H_{\mathrm{ads}}|$ are shown in Fig. 2. The apparent adsorption heat was negative, because molecule adsorption on the surface is an exothermic process [30]. We found that $|\Delta H_{\mathrm{ads}}|$ increased at lower temperatures: it was almost 1.4 times smaller at the temperature interval from 283 K to 273 K than at the temperature interval from 293 K to 273 K.

To characterize the process kinetically, the apparent diffusion coefficient (D, cm^2/s) of sulfur diffusion into polyamide has been calculated. Since the diffusing substance tends to get uniformly distributed, D becomes a measure of the rate at which the system manages to reduce the concentration gradient. This rate is related to certain system parameters characterizing the thermal mobility of a diffusing particle as a part of the diffusion environment [31, 32].

Calculations of diffusion process parameters are based on Fick's second law [30, 31]. Until the front of the diffusate has not reached the centre of the film, i.e. when $c_{s\tau}/c_{s\infty} > 0.5$, the apparent coefficients of sulfur diffusion in polyamide are calculated from the slopes [33] of the curves $1-c_{s\tau}/c_{s\infty} = f(\tau^{0.5})$ by means of the Boltzmann resolution for the semi-infinite environment expressed by

$$1-\frac{c_{s\tau}}{c_{s\infty}}=\frac{\pi}{l}\sqrt{\frac{D\tau}{8.2}} \tag{2}$$

where l is the thickness of the film, $c_{s\tau}$ is the concentration of sulfur in the sample at the time τ, and $c_{s\infty}$ is the sulfur concentration close to saturation in a sample. The calculated error in D is within ±10 %. The highest D value was obtained for the sample sulfured at 293 K: $D = 2.2\times10^{-11}$ cm^2/s. The values of D for films increased upon increasing temperature of solution (Table 2).

The dependence $\ln D = f(1/T)$ was found to be linear. Therefore, the apparent activation energy E calculated between 273–293 K by the Arrhenius equation was 25.5 kJ/mol. These values are nine to four times smaller than the energy needed for polythionate decomposition (~100 kJ/mol) [34].

Copper sulfide layers in the surface of polyamide samples were formed by the sorption–diffusion method in a heterogeneous reaction [13]:

$$S_5O_6^{2-} + 2Cu^+ + 2H_2O \longrightarrow Cu_2S + 2S + 2H_2SO_4 \tag{3}$$

Pentathionate anions diffusing into the polymer from $K_2S_5O_6$ solution interact with cuprous ions in the solution of copper(I) salt. Depending on the initial sulfur concentration in the polyamide and the duration of the treatment with the copper salt solution, light brown, brown or even black copper sulfide layers were obtained.

Since the mobility of Cu^+ ions is considerably higher than that of $S_5O_6^{2-}$ ions, the Cu_xS layer is formed by cuprous ions diffusing into sulfured polyamide. A thin sulfide layer formed on the surface of the polymer separates the reacting substances and hinders further diffusion of Cu^+ ions into the polymer. Diffusion of $S_5O_6^{2-}$ ions, as well as copper ions, is possible only in amorphous phase zones of the polyamide, however, due to the presence of structural defects, diffusion of small-molecular compounds continues, despite the presence of Cu_xS layers.

The properties of the obtained copper sulfide layers are not only dependent on the sulfur concentration but also on the content of reacted copper. Therefore, after formation of the sulfide layers, the content of copper per unit area of the layer has been determined. It was found that the content of copper is dependent on the conditions of sulfuration. The content of copper increases with increasing content of sulfur in the polyamide film. Thus, irrespective of sulfuration conditions, the highest values of m_{Cu} were obtained in PA 6 film samples treated at 293 K. Figure 3 shows the dependence of the content of copper in a sulfide layer on the duration of treatment with $K_2S_5O_6$ solutions at 293 K.

It has been found that the content of copper in a layer strongly depends on the concentration of sulfur diffused in polyamide, i.e. the content of copper varies in proportion to the sulfur concentration in PA 6. The data obtained show also that the content of copper in a sulfide layer increases uniformly and depends on the temperature of the sulfuration solution. The highest differences in copper contents were obtained in PA 6 samples sulfured in $K_2S_5O_6$ solutions at 303 K; m_{Cu} was six times higher than in the samples sulfured at 293 K. The highest values of copper content were obtained in samples treated in $K_2S_5O_6$ solution at 303 K. The content of copper in PA 6 samples sulfured at 303 K varies only slightly, i.e. m_{Cu} values in PA 6 samples are only about twice higher.

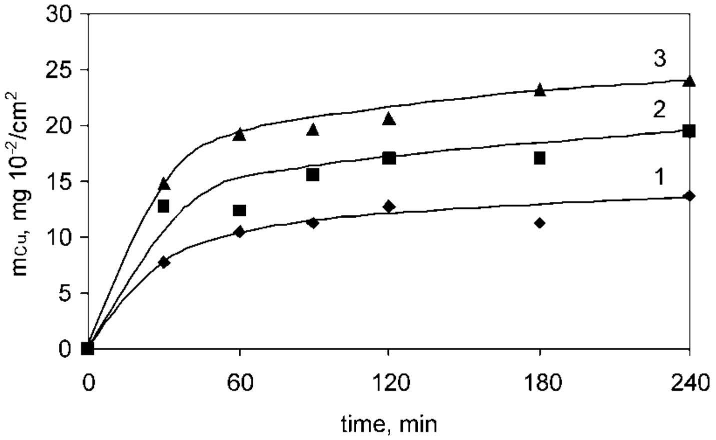

Fig. 3. Dependence of copper content (m_{Cu}) in the Cu_xS layer on polyamide on its exposure time in a 0.15 mol/dm^3 $K_2S_5O_6$ solution in 0.1 mol/dm^3 HCl at various temperatures. Sulfured PA 6 was treated with Cu(I) salt solution at 308 K for 30 min. Temperature [K]: 1 – 273, 2 – 283, 3 – 293

Copper content in PA 6 samples sulfured in $K_2S_5O_6$ solutions at 273 K was approximately 1.5 times smaller than that at 283 K and two times smaller than at 293 K. Since the Cu_xS layer is very thin in comparison with the whole thickness of the PA 6 film, and in the IR spectra not only vibrations corresponding to Cu_xS, but also to the reaction (3) products are observed, the ATR-FTIR spectrum was additionally recorded.

ATR-FTIR spectra of virgin polyamide and polyamide initially treated with $K_2S_5O_6$ solution at 293 K for 240 min and subsequently with a Cu(I) salt solution for 30 min are presented in Fig. 4. In ATR-FTIR spectra of modified polyamide, besides the polymer peaks, a broad absorption band in the range 1000–1100 cm^{-1} and narrow peak at 613 cm^{-1} appear. According to the published data [25–28], the peak at 1062 cm^{-1} is due to symmetrical valence vibrations and another one at 1107 cm^{-1} to asymetrical valence vibrations of S=O group. The peak at 613 cm^{-1} corresponds to δ_s(O–S–O) [25, 29]. Peaks of ν(S–S) and ν(Cu–S) are located in the range 200–500 cm^{-1} and have not been recorded in the presented spectrum. X-ray analysis was carried out for a further characterization of Cu_xS layers.

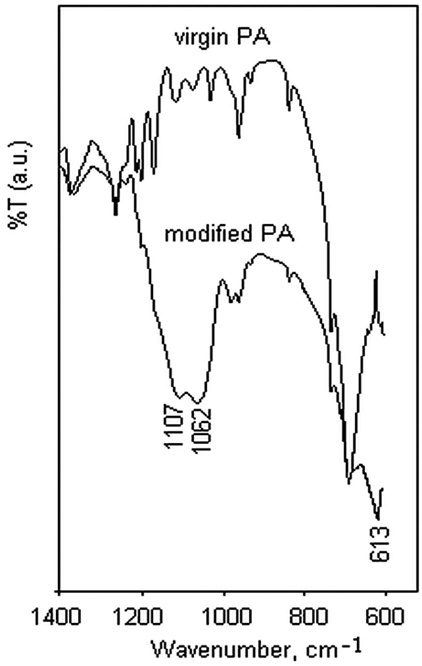

Fig. 4. ATR-FTIR spectra of virgin PA 6 and PA 6 initially treated with solution of $K_2S_5O_6$ at 293 K for 240 min and subsequently with a Cu(I) salt solution for 30 min; *T* – stands for transmittance

Cu/S molar ratios in copper sulfide layers on polyamide sulfured in solutions at various temperatures are presented in Table 3. At 273 K, the ratio is practically independent of the sulfuration time, whereas at higher temperatures it decreases with increasing time. Most probably, due to a high sulfur concentration in the film, the dense Cu_xS layer formed in the surface of PA 6 prevents the penetration of Cu^+ ions into the polymer and the interaction with the diffused pentathionate ions. These results imply that the composition of the copper sulfide layers obtained by the sorption–diffusion method is variable.

Table 3. Cu/S molar ratios in copper sulfide layers on polyamide first treated in $K_2S_5O_6$ solution at various temperatures and then in Cu(I) salt solution at 308 K for 30 min

Exposure time, min	Cu/S (S=1)		
	273 K	283 K	293 K
30	6.3	6.4	6
60	5.8	3.5	4.4
90	5.6	3.5	3.3
120	6.7	3.5	2.5
180	5.8	3.2	2.4
240	6.6	3.2	2.3

Initially, dielectric polyamide films after their modification with copper sulfide layers on their surface matrix become semiconductors (Table 4).

Table 4. Sheet resistance (R) of Cu_xS layers on polyamide first treated in $K_2S_5O_6$ solution at various temperatures and then in Cu(I) salt solution at 308 K for 30 min

Exposure time, min	R, kΩ/cm^2		
	273 K	283 K	293 K
30	7.8×10^3	6.3×10^3	222
60	6.4×10^3	5.3×10^3	224
90	2.7×10^3	3.8×10^3	162
120	0.8×10^3	1.1×10^3	34
180	0.4×10^3	366	28
240	380	498	6.3

Electrical resistance on the surface of a modified PA 6 film decreases upon increasing temperature of the sulfuration solution and its value depends on the sulfuration conditions. Samples sulfured at 273 K and then treated with copper(I) salt solution were not electrically conductive. The lowest resistances were obtained in PA 6 samples sulfured in $K_2S_5O_6$ solution at 283 K. PA 6 samples sulfured at 293 K were found to be most conductive, possibly because of the varying composition of copper sulfide layers formed in the surface of the PA 6 film (Table 3), since it is known [9] that the specific electrical resistance of Cu_xS decreases by six orders of magnitude with a decrease in x from 2 to 1. The lowest resistances were obtained for PA 6 samples when the Cu/S molar ratio in the layer was close to 2.3.

Cu_xS layers are formed both on the surface and in the bulk of the polymer. However, the electrical resistance depends only on the characteristics of the surface layer. Thus, the electrical properties of Cu_xS layers are related not only to the chemical composition but also to the homogeneity of the layer.

Polyamide consists of randomly distributed amorphous and crystalline zones. Copper sulfide isles are formed in amorphous zones, therefore, the coating can be nonuniformly distributed on the surface of the polymer. Due to smaller amorphous zones in polyamide films, thinner, discontinuous and less electrically conductive Cu_xS layers are formed [16].

The phase composition of the deposited film was established by comparing its X-ray images with those of known minerals [2, 4, 35]. The chemical composition and crystal structure of the majority of Cu_xS minerals such as chalcosine (Cu_2S), djurleite ($Cu_{1.95}S$), yarrowite ($Cu_{1.12}S$), and covellite (CuS) were investigated [36]. The crystal structure of Cu_xS depends on the chemical composition and synthesis conditions. The composition of Cu_xS deposited by chemical methods has been scarcely investigated. Structural studies of Cu_xS layers deposited by sorption−diffusion methods are limited by the polycrystallinity of the layers obtained, by the existence of Cu_xS phases of various compositions and structures, and by the crystallinity of the PA 6 film itself. The intensity of its maximum at $\Theta = 130^\circ$ exceeds a few times the intensity of copper sulfide maximum a few times. Therefore, the region of $2\Theta \geq 26.0^\circ$ was investigated in detail. When keeping PA 6 samples with the sorptive pentathionate anions (initially treated with $K_2S_5O_6$ solution at a temperature of 293 K for different time) in copper salt solution at 308 K, Cu_xS layers of various compositions were obtained. X-ray diffractograms of the layers showed the peaks of two various copper sulfide phases (Fig. 5).

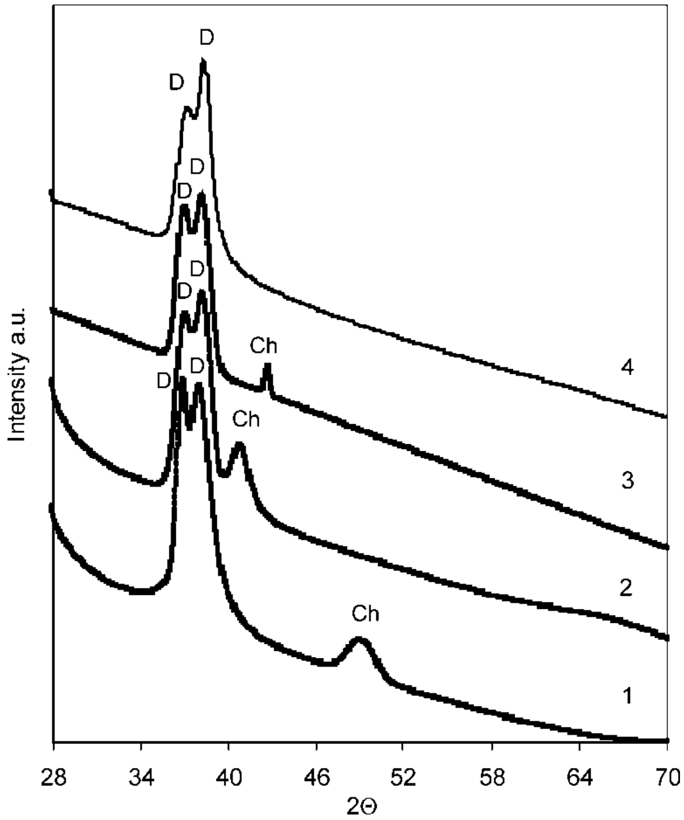

Fig. 5. X-ray diffraction patterns of layers of Cu_xS on PA 6 (D – djurleite, Ch – chalcosine). PA 6 initially treated with solution of $K_2S_5O_6$ at 293 K for various times τ_s and subsequently with a Cu(I) salt solution for 30 min. The concentration of sulfur in the polymer c_s [mol/dm^3]: 1 – 1.85 (τ_s = 30 min), 2 – 4.55 (τ_s = 90 min), 3 – 5.995 (τ_s = 120 min), 4 – 7.64 (τ_s = 240 min)

The monoclinic djurleite ($Cu_{1.9375}S$) prevails (PDF 42–564, maxima $2\Theta = 36.96^o$ and 38.2^o) in the composition of sulfide films on PA 6 initially sulfurised for 30–240 min (Fig. 5, curves 1–4) in $K_2S_5O_6$ solution at 293 K (the time of the sulfurised PA 6 treatment with Cu(I) salt solution was 35 min, the temperature of the Cu(I) salt solution was 308 K). When the time of treatment in the potassium pentathionate solution is lower than 240 min, changes in the film composition occur: the intensity increases for the peaks of monoclinic djurleite, and a new phase in the composition of the sulfide film on PA 6 – a phase of tetragonal chalkosine (Cu_2S) (PDF 84–209) maxima 2Θ

= 49.28° (Fig. 5, curve 1), maxima 2Θ = 40.96° (Fig. 5, curve 2) and maxima 2Θ = 42.7° (Fig. 5, curve 3) also appears.

The obtained results lead to the conclusion that potassium pentathionate solutions at 293 K are good sulfuring agents for polyamide films. By treating the sulfured PA 6 samples with copper(I) salt solutions, electroconductive or semi-conductive copper sulfide layers of various chemical compositions are obtained.

4. Conclusions

The analysis of UV and IR spectra confirm that sulfur is sorbed by PA 6 films in the form of pentathionate ions. Sulfur concentration in polyamide increases with increasing temperature of the potassium pentathionate solution and the exposure time of the polymer. The apparent diffusion coefficient of sulfur in polycaproamide increases from 2.2×10^{-11} cm^2/s to 4.7×10^{-11} cm^2/s with increasing temperature of the potassium pentathionate solution. The calculated apparent activation energy of pentathionate diffusion in polyamide is four times smaller than that needed for polythionate decomposition. By treating sulfured PA 6 films with Cu(I) salt solution, copper sulfide (Cu_xS) layers are formed on the surface matrix of a polymer. The content of copper in these layers depends on the content of sulfur in the PA 6 matrix. Copper sulfide layers with the Cu/S molar ratio close to 2.3 exhibit low electrical resistance (6.3 kΩ/cm^2). The phase composition of a Cu_xS layer depends on the Cu/S molar ratio. Monoclinic djurleite ($Cu_{1.9375}S$) prevails in the composition of all Cu_xS films obtained on PA 6 surface. When the Cu/S molar ratio is higher than 1 : 2.3, the phase of tetragonal chalkosine (Cu_2S) is also found in film layers.

References

[1] Korzhuev M. A., Phys. Sol. State, 40 (1998), 217.

[2] Cardoso J., Gomezdaza O., Ixtlilco L., Nair M. T. S., Nair P. K., Semicond. Sci. Technol., 16 (2001), 123.

[3] Nascu C., Pop I., Ionescu V., Indra I., Bratu I., Mater. Lett., 32 (1997), 73.

[4] Nomura R., Konayo K., Matsuda H., Ind. Eng. Chem. Res., 28 (1989), 877.

[5] Galdikas A., Mironas A., Strazdien□ V., Šetkus A., Ancutien□ I., Janickis V., Sensors Act. B, 67 (2000), 76.

[6] Yamamoto T., Tanaka K., Kubota E., Osakada K., Chem. Mater., 5 (1993), 1352.

[7] Hermann A.M., Fabick L., J. Cryst. Growth, 61 (1983), 658.

[8] Rezig B., Duchemin S., Gustavino F., Sol Energy Mat., 2 (1979), 53.

[9] Žebrauskas A., Chem. Techn., 3 (1996), 39 (in Lithuanian).

[10] Žebrauskas A., Chemistry, 2 (1992), 112 (in Russian).

[11] Janickis V., Ancutien□ I., Žukauskait□ J., Chem. Techn., 3 (2000), 28 (in Lithuanian).

[12] USSR Patent 895542, 1982.

[13] Ancutien□ I., Janickis V., Grevys S., Chemistry, (1997), No. 2, 3 (in Russian).

[14] Krylova V., Ivanauskas R., Janickis V., Chem. Techn., 4 (2002), 56 (in Lithuanian).

[15] Krylova V., Dukštien□ N., Chem. Techn., 2 (2005), 91 (in Lithuanian).

[16] Janickis V., Maciulevičius R., Ivanauskas R., Ancutien□I., Colloid. Polym. Sci., 281 (2003), 84.

[17] Foss O., *Structures of Compounds Containing Chains of Sulfur Atoms*, [in:] *Advances in Inorganic Chemistry and Radiochemistry*, H.J. Emeleus, A.G. Sharpe (Eds.), Academic Press, New York, 1960, p. 237.

[18] Gregg S.J., Sing K.S.W., *Adsorption Surface Area and Porosity*, Academic Press, New York, 1969.

[19] Brodskij A.I., Jeriomenko R.K., Rept. USSR Acad. Sci., 101 (1955), 487 (in Russian).

[20] *Handbook of Preparative Inorganic Chemistry 1*, G. Brauer, (Ed.), Ferdinand Enke, Stuttgart, 1975 (in German).

[21] Vogel A., *Textbook of Quantitative Chemical Analysis I*, Longman, London, 1989.

[22] *Analytical Methods for Atomic Absorption Spectrometry Perkin-Elmer 503*, Perkin-Elmer, 1973.

[23] Golding R.M., J. Chem. Phys., 23 (1960), 1666.

[24] Šukyt□ J., Ivanauskas R., Petrašauskien□ N., Janickis V., Žalenkien□ S., Chem. Techn., 2 (2005), 46 (in Lithuanian).

[25] Janickis V., Janickij I., Trans. Lithuanian Acad. Sci. B, 6 (1986), 43 (in Russian).

[26] Nickless G., *Inorganic Sulphur Chemistry*, Elsevier, Amsterdam, 1968, p. 199.

[27] Julien C., Barnier S., Ivanov I., Guittard M., Pardo M.P., Chilouet A., Mat. Sci. Eng. B, Solid, 57 (1999), 102.

[28] Nyquist R.A., Kagel R.O., *Infrared Spectra of Inorganic Compounds*, Academic Press, New York, 1971.

[29] Mickevičius D., *Methods of Chemical Analysis*, Žiburys, Vilnius, 1998 (in Lithuanian).

[30] Alberty R.A., Silbey R.J., *Physical Chemistry*, Wiley, New York, 1996.

[31] Malkin A.J., Tchalych A.E., *Diffusion and Viscosity of Polymers*, Khimya, Moscow, 1979 (in Russian).

[32] Tchalych A.E., *Diffusion in System of Polymers*, Khimiya, Moscow, 1987 (in Russian).

[33] Tchalych A.E., *Methods of Measuring Diffusion of Polymers*, Znaniie, Moscow, 1975 (in Russian).

[34] Janickis V., *Formation, structure and the physical chemistry properties of derived sulfane and selenane*, Thesis, Polytechnical Institute, Kaunas, 1983, p. 447 (in Russian).

[35] Žebrauskas A., Mikalauskien□ A., Latvys V., Chemistry, (1992), No. 2, 131 (in Russian).

[36] Goble R., Can. Mineral, 23 (1985), 61.

Received 7 September 2006
Revised 4 May 2007