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Formation of Copper Sulfide Layers on the Surface of Polyethylene Films of Various Density by the Use of Polythionic Acids

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The kinetic study of sulfur adsorption-diffusion processes from higher polythionic acid, $H_2S_{33}O_6$, solution into polyethylene films of high, medium and low density showed that the sulfur concentration in polyethylene of various density and thickness increases with increasing temperature of the solution and the duration of treatment. Sulfur concentration in the film is related to the film density and thickness. An increase in the negative apparent adsorption heat of sulfur adsorption was observed with an increase of polyethylene films density. The estimated apparent sulfur diffusion coefficients in polyethylene increase with increasing temperature of the polythionic acid solution but decrease with growing crystallinity in the films. The concentration of sulfur in the film is limited by the stage of the acid decomposition, because the apparent activation energy of sulfur diffusion in polyethylene is nine to seventeen times lower than the energy needed for the polythionic acid decomposition. By treating polyethylene film sulfured in $H_2S_{33}O_6$ solution with copper(I–II) salt solution, copper sulfide (Cu_xS) layers are formed in the surface matrix of a polymer. The amount of copper in these layers is related to the density and thickness of the polyethylene film and the sulfuration conditions. The amount of copper increases with a decrease in the density of the polyethylene film and with an increase in the temperature of $H_2S_{33}O_6$ solution used and the duration of the treatment. Initially, dielectric polyethylene films after formation of copper sulfide layers in their surface matrix become electrical conductors. Samples of low density polyethylene with the layers of Cu_xS were the most conductive.

Key words: polyethylene, high polythionic acid, sulfuration, diffusion, copper sulfide layer

Composites – substances known for the optimal combination of the properties of their components are frequently applied in contemporary engineering. Dielectrics, coated with electroconductive or semi-electroconductive layers, such as polymer films with copper sulfide layers, can be attributed to this class of materials. Practical application of copper sulfide coatings in various fields of engineering stimulates the interest in developing of new technologies. Electroconductive and highly adhesive copper sulfide coatings are used as sublayers for polymer metallization [1–4]. These

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coatings are also applied for glass decoration, as they increase its reflection in the infrared part of the spectrum [5,6]. Thin layers and coatings of copper sulfide are used to control solar radiation [3,7,8] in solar absorbers [9,10] and in the production of solar batteries [11]. Cu_xS layers on polyethylene or porous silicon are sensitive to ammonia, hence, they are applicable as gas sensors operating at room temperature [12–14].

An adsorption-diffusion method of obtaining copper sulfide layers is a new technology in which, after adsorption of the sulfuration agent, the polymer substance is treated with copper salt aqueous solution. Various solutions can serve as polyethylene sulfuration agents, *e.g.*, sulfur solutions in organic solvents [15], sodium polysulfide (Na_2S_n, $n = 4.8$) aqueous solutions [16], polythionic acid ($H_2S_nO_6$, $n = 9–45$) aqueous solutions [17]. Higher polythionic acids with n > 6 are compounds containing divalent sulfur atoms chains [18]. To prevent environmental pollution with vapours of toxic solvents and to avoid swelling of some polymers in organic solvents, sodium polysulfide and polythionic acid [19,20] solutions are preferable as sulfuration agents of polymeric materials such as polyethylene. Hydrophobic polymers adsorb elementary sulfur from Na_2S_n [21,22] or $H_2S_nO_6$ [23] solutions, while hydrophilic and semi-hydrophilic polymers adsorb polysulfide [24] and polythionate [25] ions from the above solutions. However, the use of Na_2S_n solutions is limited due to their high alkalinity.

The topics of the presented work is the investigation of the sulfuration of polyethylene films of various densities in high polythionic acid solutions and the generation of layers of copper sulfide on the surface of the polyethylene films.

EXPERIMENTAL

Films of high (HDPE 1, HDPE 2, HDPE 3), middle (MDPE 4) and low (LDPE 5) density polyethylene were used for the investigations. Films of HDPE 1 and HDPE 2 (Aldrich, MFI 36) were produced in the Laboratory of Polymer Processing at the University of Bayreuth by compression moulding at 180°C, HDPE 3 and MDPE 4 were obtained from Kirschneck GmbH, Selb (Germany), LDPE 5 (GOST 10354–82) from Plastic Plant "Plasta", Vilnius (Lithuania). Their thicknesses were measured with a Peacock micrometer to: HDPE 1: 110 ± 10 μm, HDPE 2: 155 ± 10 μm, HDPE 3: 18 ± 2 μm, MDPE 4: 26 ± 1 μm and LDPE 5: 140 ± 5 μm. Rectangular samples of 15×75 mm were used. Before sulfuration the surface of polyethylene films was cleaned in a 4% solution of a non-ionic surfactant (Prewocell WOF-100), degreased in toluene and washed in distilled water. For the inclusion of sulfur into the polyethylene a 2 mmol dm^{-3} solution of polythionic acid was used. It was prepared according to equation (1) [20]:

$$m(2H_2S + H_2SO_3) + 2H_2S_2O_3 \rightarrow H_2S_nO_6 + H_2S + 3mH_2O \qquad (1)$$

where $n = 3m + 3$. Then, on the basis of data of sulfite and cyanic [26] decomposition of polythionates, the average number of sulfur atoms (n) in a molecule of polythionic acid was calculated. PE was treated in a thermostatic vessel, using a continually stirred polythionic acid solution. At certain time intervals, samples were removed, rinsed with distilled water, dried with filter paper, left over $CaCl_2$ for 24 h, and then used in analysis and further experiments. The sulfur diffused into the polyethylene samples was extracted with acetone, and the content in the extract was determined by a spectrometric cyanide method [27] using a Specord UV/VIS spectrophotometer ($\lambda = 450$ nm). The density of polyethylenes was measured by a flotation method, using a series of water/acetone mixtures at 293 K. Fifty samples of PE 1–5 were immersed in liquids of different density (0.915–0.970 g cm^{-3}) seeking one in which they neither sink nor float. The percentage of crystalline and amorphous phases in the polyethylene films of various densities [28] was determined using a DRON-6 diffractometer (Cu-K_α radiation). X-ray diffractograms of PE 1–5 samples were treated using programs "Search Match", "ConvX", "Xfit", "Dplot95" and "Photo Styler".

After being immersed in the $H_2S_{33}O_6$ solution, the sample was treated with a Cu(I–II) solution, then rinsed with distilled water, dried over $CaCl_2$, and used for analysis and consequent experiments. A Cu(I–II) salt solution was made from crystalline $CuSO_4 \cdot 5H_2O$ and a reducing agent, hydroquinone, as described in [29]. In this mixture a ratio of univalent and divalent copper salts, independently on temperature, at 0.34 mol dm^{-3} Cu(II) salt and 0.06 mol dm^{-3} Cu(I) salt is present. The amount of copper in a PE sample was determined using an atomic absorption spectrometer Perkin-Elmer 503 ($\lambda = 325$ nm). The conductivity of the copper sulfide layers at constant current was measured using an E7-8 numerical measuring instrument with special electrodes.

RESULTS AND DISCUSSION

Sulfuration of polyethylene films. Sulfuration of polyethylene with polythionic acids proceeds according to (2) [19,30]:

$$H_2S_nO_6 \rightarrow H_2S_{n-x}O_6 + x \cdot S \qquad (2)$$

Elemental sulfur formed is adsorbed by the polyethylene. It has previously been found, that polyethylene treated in the solutions of higher $H_2S_nO_6$ contains rhombic-S_8 [23]. At higher solution temperatures (313–353 K), the polythionic acid decomposes much faster than at room temperature.

Previous experiments [23] have shown that sulfur adsorption-diffusion from $H_2S_nO_6$ solutions into low density polyethylene films is observed only when the number of divalent sulfur atoms (n-2) in a molecule of polythionic acid $HO_3S–S_{n-2}–SO_3H$ is higher than four. Sulfur concentration in polyethylene increases with an increasing average number of S atoms (n) in a polythionic acid molecule and the temperature of the $H_2S_nO_6$ solution, latter being more important for the sulfur concentration in the film.

The kinetics of sulfur adsorption-diffusion process from polythionic acid ($H_2S_{33}O_6$) solution of 2 mmol dm^{-3} into high, medium and low density PE films (Table 1) was investigated. Figure 1 shows the sulfur concentration in the five PE-films investigated as a function of immersion time.

It was found, that the sulfur concentration (c_s, mg cm^{-3}) in the samples, kept in high polythionic acid solution at 298, 313, 333 and 353 K, increases with time. Moreover, the adsorption-diffusion process becomes faster with increasing temperature, resulting in higher sulfur concentration in the film. The sulfur concentrations close to saturation ($c_{s\infty}$, mg cm^{-3}) of all films are shown in Figure 2.

Table 1. Characterization of the polyethylene films PE 1–5.

Sample	Film thickness [μm]	Density [g cm^{-3}]	Degree of crystallinity [%]	$-\Delta H_{ads}$$^{a)}$ [kJ mol^{-1}]
HDPE 1	110±10	0.961	60±2	64
HDPE 2	155±10	0.962	68±2	62
HDPE 3	18±2	0.960	65±2	51
MDPE 4	26±1	0.940	45±1	45
LDPE 5	140±5	0.919	41±1	36

$^{a)}$Apparent adsorption heat in the temperature interval of 313–353 K.

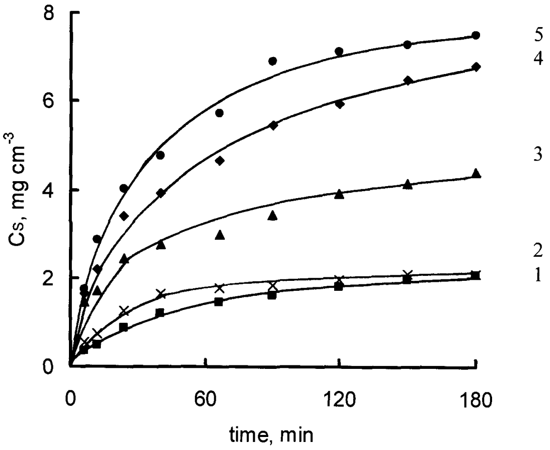

Figure 1. Dependence of sulfur concentration (c_s) in polyethylene on its immersion time in a 2 mmol dm^{-3} solution of $H_2S_{33}O_6$ at 333 K. Polyethylene films: 1 – HDPE 1, 2 – HDPE 2, 3 – HDPE 3, 4 – MDPE 4, 5 – LDPE 5.

The concentrations obtained for high density HDPE 1 and HDPE 2 films are lower than those in LDPE 5 film of similar thickness but lower density. The crystallinity in the high density polyethylenes exceeds 60%, while for low density PE 5 a crystallinity of ~40% was determined (Table 1). Thus, the influence on the sulfur concentration close to saturation might be the consequence of the crystallinity in the PE.

It is known [22], that polyolefines can adsorb sulfur well only in their amorphous phase zones and in the state of high elasticity. With increasing temperature of the sulfuration solution, the volume part of the amorphous phase zones increases, thus, large S_8 molecules (4.73 Å in diameter) [31] can easily penetrate into the polymer. The sulfur concentrations $c_{s\infty}$ determined in polyethylenes of various densities (Fig. 2) prove this point. The highest values of $c_{s\infty}$ were obtained in samples treated in polythionic acid solution at 353 K.

The sulfur concentrations found in samples of very thin HDPE 3 and MDPE 4 films are higher, and those treated at 353 K are twofold, threefold or even fourfold higher, than those found in HDPE 1 and HDPE 2 film samples. The amount of sulfur fo-

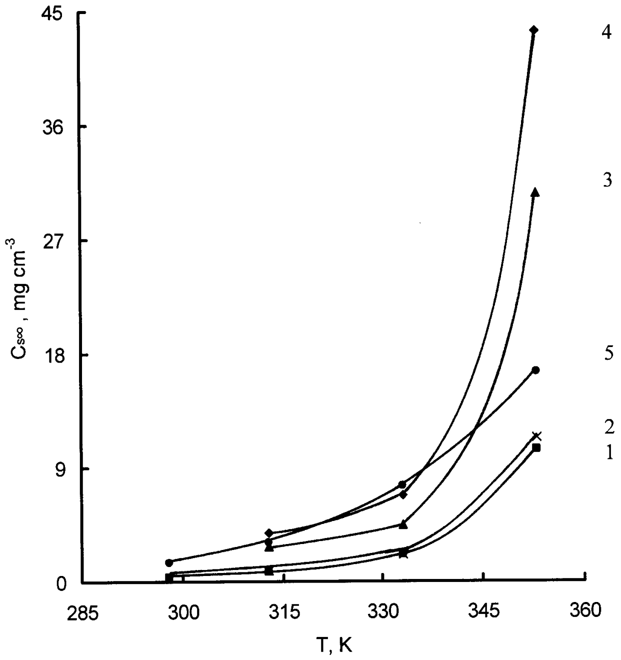

Figure 2. Dependence of sulfur concentration close to saturation ($c_{S\infty}$) in polyethylene treated in $H_2S_{33}O_6$ solution at four different temperatures of 298, 313, 333 and 353 K. Polyethylene films: 1 – HDPE 1, 2 – HDPE 2, 3 – HDPE 3, 4 – MDPE 4, 5 – LDPE 5.

und in the samples of HDPE 3 and MDPE 4 is two to four times smaller, compared to HDPE 1 and HDPE 2. The sulfur concentrations close to saturation determined in samples of the medium density MDPE 4 films treated at 313 and 333 K are close to those obtained in more than five times thicker, low density LDPE 5 film samples. After lowering the temperature of the sulfuration solution from 353 K to 313 K, $c_{S\infty}$ in polyethylene film samples decreases clearly: HDPE 1 by a factor of 15, HDPE 2 – 14, HDPE 3 and MDPE 4 – 11, LDPE 5 – 5 times. As it is evident from the values presented, sulfur adsorption-diffusion in low density polyethylene is less affected by the solution temperature. This is shown by the lowest value of the apparent adsorption heat $|\Delta H_{ads}|$ (Table 1) obtained for the LDPE 5 film. We calculated the apparent adsorption heat by the Langmuir equation [32]. Examples representing the sulfur adsorption for the determination $|\Delta H_{ads}|$ are shown in Figure 3. The apparent adsorption heat was negative, because the adsorption of a molecule on a surface was an exothermic process [32]. We found that $|\Delta H_{ads}|$ is almost twice smaller for low density polyethylenes as for high density PE of similar thickness within the same temperature interval. Thus, $|\Delta H_{ads}|$ increases with decreasing content of the amorphous phase in polyethylene films and with increasing of films density, because the bulky S_8 molecules cannot penetrate into the amorphous phase channels of more highly crystallized polymers. When the polymer is less crystalline, between its macromolecules are more cavities varied in size, therefore, LDPE 5 is more elastic and flexible. Highly crystallized PE becomes flexible thermoplastic only at higher solution temperatures. Then, due to a

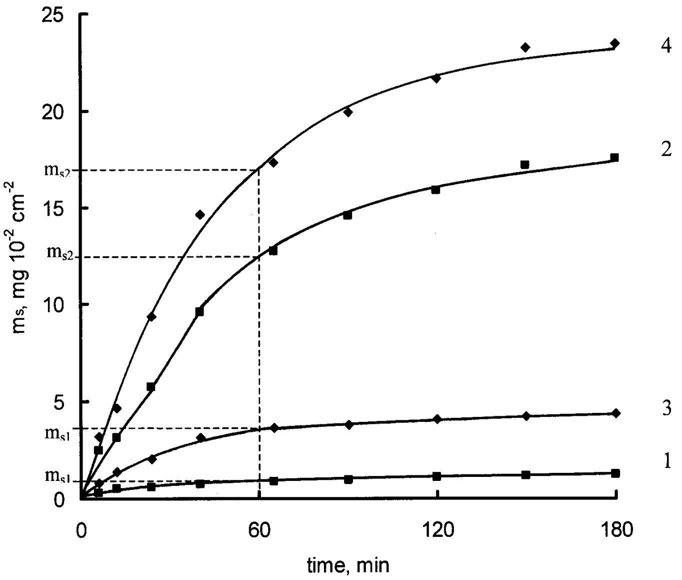

Figure 3. Dependence of adsorbed sulfur amount in polyethylene on immersion time in a 2 mmol dm^{-3} solution of $H_2S_{33}O_6$ at two temperatures. Polyethylene films (temperature): 1 – HDPE 2 (313 K), 2 – HDPE 2 (353 K), 3 – LDPE 5 (313 K), 4 – LDPE 5 (353 K).

considerable volumetric-thermal expansion coefficient of the amorphous phase in solutions of a sulfuration agent at higher temperature, S_8 can access the previously inaccessible narrow amorphous phase channels [22]. This is proved by increased values of $c_{s\infty}$ with increasing solution temperature (Fig. 2).

To characterize the process kinetically, an apparent diffusion coefficient (D, $cm^2\ s^{-1}$) of sulfur diffusion into polyethylene was introduced. Since the diffusible substance seeks to get uniformly distributed, D becomes a measure of the rate at which the system manages to reduce the difference in concentrations. This rate is related to certain system parameters, characterizing the thermal mobility of both, the diffusible particles and the macromolecules and their fragments, as part of the diffusion environment [33,34].

Calculations of diffusion process parameters are based on Fick's second law [32,33]. Until the front of the diffusate has not reached the center of the film, thus, when $c_{s\tau}/c_{s\infty} \leq 0.6$, the apparent coefficients of sulfur diffusion in polyethylene are calculated according to the inclination angle [33,34] of the curves $c_{s\tau}/c_{s\infty} = f(\tau^{0.5})$ by means of Boltzmann resolution for semi-infinite environment as expressed by

$$c_{s\tau}/c_{s\infty} = \frac{4}{l} \cdot \sqrt{\frac{D\tau}{\pi}} \tag{3}$$

where: l means the thickness of the film, $c_{S\tau}$ – the concentration of sulfur in the sample in period τ, and $c_{S\infty}$ the sulfur concentration close to saturation in the sample. The calculated error in D is in the range of ± 15%. Since the films of HDPE 3 and MDPE 4 were too thin, a calculation for these samples was not possible.

The value of D increases, when the temperature of $H_2S_{33}O_6$ solution is increased from 298 to 353 K, approximately twofold: for HDPE 1 $D = (1.6–3.0)\times10^{-9}$ cm^2 s^{-1}; for HDPE 2 $D = (3.3–5.9)\times10^{-9}$ cm^2 s^{-1}; for LDPE 5 $D = (6.0–12.7)\times10^{-9}$ cm^2 s^{-1}. The highest D value was obtained for the low density sample LDPE 5. Values of D for high density films HDPE 1 and HDPE 2 increase not only with increasing temperature of the $H_2S_{33}O_6$ solution, but also with increasing thickness of the film. At comparable film thicknesses the apparent diffusion coefficients increase with decreasing polyethylene density and its degree of crystallinity. Hence, the diffusate (elementary sulfur) in low density polyethylene spreads faster.

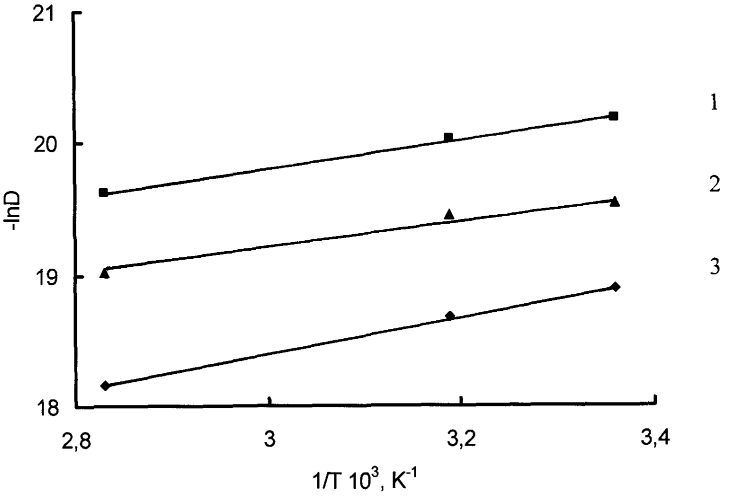

Figure 4. Dependence of apparent coefficient (D) of sulfur diffusion into polyethylene on the temperature of $H_2S_{33}O_6$ solution. Polyethylene films: 1 – HDPE 1, 2 – HDPE 2, 3 – LDPE 5.

The data in Figure 4 show, that the dependence $\ln D = f(1/T)$ on the temperature was found to be linear. Therefore, the apparent activation energy E was calculated between 313–353 K by the Arrhenius equation: for HDPE 1 a value of 9 kJ mol^{-1}, for HDPE 2 – 11 kJ mol^{-1} and for LDPE 5 – 6 kJ mol^{-1}. Values of E for high density films HDPE 1 and HDPE 2 were even twofold larger than that calculated for low density film LDPE 5 of similar thickness. Thus, elemental sulfur penetrates more easily into LDPE 5. These values are nine to seventeen times smaller than the energy needed for decomposition of polythionic acids (~100 kJ mol^{-1}) [30], thus, the amount of sulfur in polyethylene films is limited by the stage of acid decomposition and not by the amount of sulfur diffused in the polyethylene. Faster decomposition of polythionic acid at higher temperatures results in higher sulfur concentrations in the polyethylene films, *i.e.* the sulfur concentration $c_{S\infty}$ in PE 1–5 samples at 353 K is five to fifteen times higher than values obtained at 313 K (Fig. 2). Hence, polythionic acid solutions at higher temperature (333–353 K) are good sulfuring agents for polyethylene of any thickness and density.

Formation of copper sulfide layers. In this study the interaction of PE 1–5 sulfured in solutions of $H_2S_{33}O_6$ with a solution of Cu(I–II) salt was studied. Copper sulfide layers in the surface of polyethylene samples of various density were formed by a sorption-diffusion method, when the heterogeneous redox reaction (4) takes place [29]:

$$2xCu^+ + 1/8S_8 \rightarrow Cu_xS + xCu^{2+} \tag{4}$$

Elemental sulfur diffused into the polymer from a solution of $H_2S_{33}O_6$, interacts with cuprous ions present in the solution of copper(I–II) salt. Depending on the initial sulfur concentration in the PE 1–5 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_8 molecules, the Cu_xS layer is formed by cuprous ions diffusing into sulfured polyethylene. A thin sulfide layer, formed on the surface of the polymer (4), separates the reacting substances and hinders the diffusion of further Cu^+ ions into the polymer. Diffusion of sulfur, as well as copper ions, is possible only in amorphous phase zones of the polyethylene, however, due to the structural defects present, diffusion of small-molecular compounds continues, despite the presence of formed Cu_xS layers.

The properties of the obtained copper sulfide layers are not only related to the density of the polyethylene film and the sulfur concentration in it, but also on the amount of reacted copper. Therefore, having formed the sulfide layers, the amount of copper per unit of the layer area (m_{Cu}, mg 10^{-2} cm^{-2}) was determined. It was found that the amount of copper is related to the density and thickness of the polyethylene film and the conditions of sulfuration.

The amount of copper increases with decreasing density of the polyethylene film. Thus, irrespectively of sulfuration conditions, the highest values of m_{Cu} were obtained in low density LDPE 5 film samples. Figure 5 shows the dependence of the amount of copper in a sulfide layer on the duration of PE 1–5 treatment with $H_2S_{33}O_6$ solutions at 333 K.

It was found that the amount of copper in a layer depends strongly on the concentration of sulfur diffused in PE 1–5, *i.e.* the amount of copper varies in proportion to the sulfur concentration in PE. The data obtained show also that the amount of copper in a sulfide layer increases uniformly and depends on the temperature of the sulfuration solution. The greatest differences in copper amounts were obtained in PE 1-5 samples, sulfured in $H_2S_{33}O_6$ solutions at 313 K, *i.e.* m_{Cu} was 6–9 times higher in LDPE 5 than in high density HDPE 1 and HDPE 2 samples of the same thickness and even 11 times higher than that in the thin HDPE 3 film samples. The highest values of

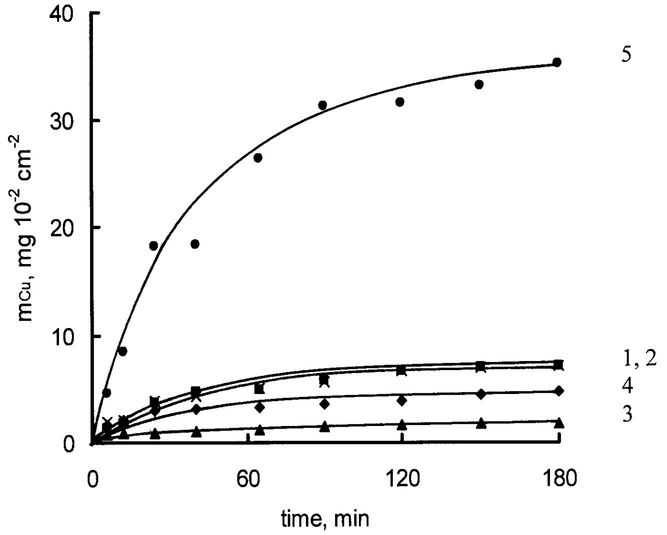

Figure 5. Dependence of copper amount (m_{Cu}) in the Cu_xS layer on polyethylene on its immersion time in a 2 mmol dm^{-3} solution of $H_2S_{33}O_6$ at 333 K. Sulfured PE was treated with Cu(I–II) salt solution at 353 K for 10 min. Polyethylene films: 1 – HDPE 1, 2 – HDPE 2, 3 – HDPE 3, 4 – MDPE 4, 5 – LDPE 5.

copper amount were obtained in samples treated in $H_2S_{33}O_6$ solution at 353 K. The amount of copper in PE 1–5 samples sulfured in 353 K solutions varies only slightly, *i.e.* m_{Cu} values in LDPE 5 samples are only about 1.5 times higher.

Copper amounts are related to the thickness of the film as well. The lowest m_{Cu} values were obtained in very thin high density HDPE 3 film samples, irrespectively of the sulfuration temperature. The copper amount obtained in thin medium density MDPE 4 film samples sulfured in $H_2S_{33}O_6$ solutions at 333–353 K was approximately 1.5 times smaller than those determined in thicker high density HDPE 1 and HDPE 2 film samples.

Cu and S molar ratios in copper sulfide layers on polyethylene of various densities are presented in Table 2. It is evident that these ratios in PE 1–5 samples vary insignificantly with increased sulfuration time in $H_2S_{33}O_6$ solutions. However, they are related to the temperature of the sulfuration solution, *i.e.* the above ratio raises in most high density polyethylene samples with an increase in the temperature of $H_2S_{33}O_6$ solution. This holds true except for LDPE 5 sulfured at 353 K, where Cu/S ratio is significantly smaller than those obtained in low density PE samples, sulfured at 333 and 313 K. The Cu/S ratio is close to 1 in LDPE 5 samples sulfured at 353 K. In our opinion, due to high sulfur concentration in the film, the dense Cu_xS layer formed in the surface of PE prevents the penetration of Cu^+ ions into the polymer and the interaction with the diffused sulfur. Our results lead to the conclusion, that the composition of the copper sulfide layers, obtained by the sorption-diffusion method, is variable.

Table 2. Cu/S molar ratios in copper sulfide layers on polyethylene first treated in $H_2S_{33}O_6$ solution at three different temperatures for 40 and 120 min, and then – in Cu(I–II) salt solution at 353 K for 10 min.

Sample	Cu/S (S = 1)					
	313 K		333 K		353 K	
	40 min	120 min	40 min	120 min	40 min	120 min
HDPE 1	1.0	1.2	1.8	1.7	1.6	1.5
HDPE 2	0.9	1.0	1.0	1.1	1.0	1.0
HDPE 3	1.2	1.2	1.0	1.0	1.6	1.7
MDPE 4	1.4	1.3	1.5	1.2	1.4	1.3
LDPE 5	1.3	1.7	1.6	1.7	1.0	1.1

Initially, dielectric polyethylene films after their modification with copper sulfide layers in their surface matrix become electrical conductors (Table 3).

Table 3. Sheet resistance (R) of Cu_xS layers on polyethylene first treated in $H_2S_{33}O_6$ solution at 333 K and 353 K for 60 and 120 min, and then – in Cu(I–II) salt solution at 353 K for 10 min.

Sample	R, Ω/□			
	333 K		353 K	
	60 min	120 min	60 min	120 min
HDPE 1	$3.6\cdot10^6$	$3.2\cdot10^6$	$9.3\cdot10^3$	$4.5\cdot10^3$
HDPE 2	$2.8\cdot10^6$	$2.3\cdot10^6$	$8.0\cdot10^3$	$3.2\cdot10^3$
HDPE 3	$3.5\cdot10^6$	$3.3\cdot10^6$	$7.4\cdot10^3$	915
MDPE 4	$3.0\cdot10^6$	$2.7\cdot10^6$	$2.2\cdot10^3$	830
LDPE 5	$1.2\cdot10^3$	399	726	273

On measuring the electrical resistance on the surface of modified PE 1–5 films, it was established that it decreases with an increase in the temperature of the sulfuration solution and its numerical value is related to the sulfuration conditions. Irrespective of the density and thickness of the PE film, the samples sulfured at 313 K and then treated with copper(I–II) salt solution were not electrically conductive. The lowest values of resistance were obtained in PE 1–5 samples, sulfured in $H_2S_{33}O_6$ solution at 353 K; LDPE 5 samples were found to be the most conductive. That can be explained by the variability of composition of copper sulfide layers, formed in the surface of the PE film (Table 2), since it is known [35] that the specific electrical resistance of Cu_xS decreases by six orders of magnitudes with a decrease in x value from 2 to 1. The lowest resistance values were obtained for the LDPE 5 samples, when the Cu/S molar ratio in the layer was close to one.

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

Polyethylene consists of variously distributed amorphous and crystalline zones. Copper sulfide isles are formed in the amorphous zones; therefore, the coating can be non-uniformly distributed on the surface of the polymer. Due to the smaller amorphous zones in higher density polyethylene films, thinner, discontinuous and less electrically conductive Cu_xS layers are formed.

The obtained results lead to the conclusion that solutions of high polythionic acids are good agents for sulfuration of polyethylene films of various density and thickness. By treating the sulfured PE with copper(I–II) salt solutions, electroconductive or semi-conductive copper sulfide layers of various chemical composition are obtained.

CONCLUSIONS

1. The sulfur concentration in polyethylene of various density and thickness increases with increasing temperature of a higher polythionic acid, $H_2S_{33}O_6$, solution and the duration of treatment.
2. The sulfur concentration, close to saturation in polyethylene films of comparable thickness, increases with decreasing of polyethylene density and the degree of its crystallinity.
3. The negative apparent adsorption heat of sulfur adsorption increases with increasing of polyethylene samples density.
4. Apparent coefficients of sulfur diffusion in polyethylene increase with decreasing degree of polyethylene crystallinity and increasing temperature of the polythionic acid solution.
5. The concentration of sulfur in a polymer film is limited by the stage of acid decomposition, since the apparent activation energy of sulfur diffusion in polyethylene is nine to seventeen times smaller than that needed for the polythionic acid decomposition.
6. By treating PE film sulfured in $H_2S_{33}O_6$ solution with Cu(I–II) salt solution, copper sulfide (Cu_xS) layers are formed in the surface matrix of a polymer. The amount of copper in these layers is related to the density and the thickness of the PE film and the sulfuration conditions. The amount of copper increases with decreasing density of the polyethylene film, with the increase in temperature of $H_2S_{33}O_6$ solution used and the duration of the sulfuration stage. The highest copper amounts were found in samples sulfured at 353 K.
7. Cu_xS layers of the lowest electrical resistance were obtained in the surface of polyethylene initially sulfured in $H_2S_{33}O_6$ solutions at 353 K for 120 min. Low resistance (273 Ω/□) exibit copper sulfide layers on low density polyethylene film samples with the Cu/S molar ratios close to 1.
8. The regularities established enable a proper choice of various density polyethylene sulfuration with high polythionic acid solution conditions and formation in the polymer surface of electrically conductive and semi conductive copper sulfide layers.

REFERENCES

1. ebrauskas A., Spirikavičienė R. and Baranauskas M., *J. Adhesion Sci. Technol.*, **4**, 25 (1990).
2. Suchentrunk R., Metallising of Plastics – A Handbook of Theory and Practice, Finishing Publications, Hertfordshire (1993).
3. Hu H. and Nair P.K., *Surface and Coatings Techn.*, **81**, 183 (1996).
4. Cardoso J., GomezDaza O., Ixtlilco L., Nair M.T.S. and Nair P.K., *Semicond. Sci. Technol.*, **16**, 123 (2001).
5. Nair M.T.S. and Nair P.K., *Semicond. Sci. Technol.*, **4**, 191 (1989).
6. Nair P.K., Garsia V.M., Fernandez A.M., Ruiz H.S. and Nair M.T.S., *J. Phys. D: Appl. Phys.*, **24**, 441 (1991).
7. Nascu C., Ionescu V. and Pop I., *Revista de Chimie*, **49**, 535 (1998).
8. Nair M.T.S. and Nair P.K., *Semicond. Sci. Technol.*, **4**, 599 (1989).
9. Agnihotri O.P. and Gupta B.K., Solar Selective Surfaces, Wiley, NY (1981).
10. Hu H., Campos J. and Nair P.K., *J. Mater. Res.*, **11**, 739 (1996).
11. Chopra K.L. and Das S.R., Thin Film Solar Cells, Plenum, NY (1983).
12. Galdikas A., Mironas A., Strazdienė V., Šetkus A., Ancutienė I. and Janickis V., *Sensors and Actuators B*, **67**, 76 (2000).
13. Šetkus A., Galdikas A., Mironas A., Šimkienė I., Ancutienė I., Janickis V., Kačiulis S., Mattogno G. and Ingo G.M., *Thin Solid Films*, **391**, 275 (2001).
14. Šetkus A., Galdikas A., Mironas A., Strazdienė V., Šimkienė I., Ancutienė I., Janickis V., Kačiulis S., Mattogno G. and Ingo G.M., *Sensors and Actuators B*, **78**, 208 (2001).
15. Janickis V., Ancutienė I. and ukauskaitė J., *Chem. Techn. (Lithuania)*, **3**, 28 (2000) (in Lithuanian).
16. Baranauskas M., ebrauskas A. and Šalkauskas M., USSR Pat. 895542, 1982.
17. Ancutienė I., Janickis V. and Grevys S., *Lithuanian Republic Pat*. LT 4111 B, 1997.
18. Foss O., Structures of Compounds Containing Chains of Sulfur Atoms. In: H.J. Emeleus and A.G. Sharpe (eds.), *Advances in Inorganic Chemistry and Radiochemistry,* Academic Press, NY, 2 (1960), pp. 237–278.
19. Janickis J., Valančiūnas J. and Tučaitė O., *Zh. Neorg. Khim.*, **3**, 2087 (1958) (in Russian).
20. Janickis J., Valančiūnas J., Zelionkaitė V., Janickis V. and Grevys S., *Trans. Lithuanian Acad. Sci. Ser. B* (Lithuania), **3**, 83 (1975) (in Russian).
21. Baranauskas M., ebrauskas A., Šalkauskas M. and Prokopčikas M., *Trans. Lithuanian Acad. Sci. Ser. B* (Lithuania), **2**, 3 (1983) (in Russian).
22. ebrauskas A. and Lazauskienė R., *Chemistry* (Lithuania), **4**, 25 (1993) (in Russian).
23. Ancutienė I., Janickis V., Grevys S. and ebrauskas A., *Chemistry* (Lithuania), **4**, 3 (1996).
24. ebrauskas A., *Chemistry* (Lithuania), **1**, 182 (1991) (in Russian).
25. Maciulevičius R., Janickis V. and Ivanauskas R., *Chemistry* (Lithuania), **11**, 141 (2000).
26. Blasius E., Horn G., Knöchel A., Münch J. and Wagner H., Analytical Chemistry of Sulfur Compounds. In: G. Nickless (ed.), *Inorganic Sulfur Chemistry*, Elsevier Publishing, Amsterdam (1968), pp. 199–239.
27. Babko A. and Pilipenko A., Photometric analysis. Method for determination of non-metals, Khimiya, Moscow (1974) (in Russian).
28. Martynov M.A. and Vylegzhanina K.A., Radiography of polymers, Khimiya, Leningrad (1972) (in Russian).
29. Ancutienė I., Janickis V. and Grevys S., *Chemistry* (Lithuania), **2**, 3 (1997).
30. Janickis V., Doctoral dissertation, Polytechnical Institute, Kaunas 1983.
31. Donohue J., The Structures of the Elements, Wiley, NY (1974).
32. Alberty R.A. and Silbey R.J., Physical Chemistry, Wiley, NY (1996).
33. Malkin A.J. and Tchalych A.E., Diffusion and viscosity of polymers. Methods of measurement, Khimiya, Moscow (1979) (in Russian).
34. Tchalych A.E., Diffusion in systems of polymers, Khimiya, Moscow (1987) (in Russian).
35. ebrauskas A., *Chemical Technology* (Lithuania), **1**, 39 (1996) (in Lithuanian).