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Modification of Polyethylene of Various Density by Layers of Copper Sulfide

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Polyethylene films of high, medium and low density were modified by layers of copper sulfide obtained using sorption-diffusion method. For the inclusion of elemental sulfur into polyethylene a solution of high polythionic acid, $H_2S_{33}O_6$, was used. The concentration of sulfur sorbed in the polyethylene increased with the decrease of crystalline volume fraction and the increase of the temperature of polythionic acid solution and the duration of the sulfuration. On treating sulfured polyethylene with a copper salt solution, a copper sulfide layer was formed. The amount of copper increased with the decrease of density and crystalline volume fraction of the polyethylene, and with increase of sorbed sulfur concentration.

Keywords: high polyhionic acid, polyethylene, sulfuration, layer of copper sulfide.

INTRODUCTION

Copper sulfide layers and coatings on various polymers as composite materials are widely used in modern advanced technology. Coated polymers may be used as conductive substrates for electroless or electrolytic deposition of metal films [1] or semiconductor layers [2]. An intermediate layer of Cu_xS between the polymer substrate and metal coating improves the peal strength considerably [3]. Cu_xS coatings might also be used as solar radiation absorbers [4, 5], solar cells [6] and solar radiation control coatings [7]. These coatings are applicable in architectural windows to control the amount of visible and infrared components of solar radiation entering buildings [8, 9]. Recently, Cu_xS thin layers on dielectrics were used as resistive gas sensors [10, 11]. Such sensors are developed for the detection of various gases in air at the working temperatures tending to room temperature.

Copper sulfide, Cu_xS ($x = 1 \div 2$), layers on polymeric materials may be formed by various methods. Sorption-diffusion is a simple and promising method for obtaining composites. Copper sulfide layers are formed in the surface matrix of a polymer as a result of the chemical reaction between diffused sulfur – containing particles and cuprous or cupric ions. Most polymers, including polyethylene, absorb different compounds of sulfur, which can act as sulfuration agents. For the sulfuration of dielectrics various solutions were proposed, e.g. the solution of elemental rhombic (α) sulfur in carbon disulfide, CS_2 or acetone, CH_3COCH_3 [12]; the aqueous solutions of sodium polysulfides, Na_2S_n ($n \approx 4.8$) [13] and of polythionic acids, $H_2S_nO_6$ ($n = 6 \div 45$) [14, 15]. The solutions of polythionic acids are suitable for sulfuring the majority of polymers. Recently it has been reported [14] that copper sulfide layers on the polyethylene of low density can be formed using highly sulfured polythionic acids.

The aim of the present work was to investigate the processes of sulfuration and formation of copper sulfide layers on a polyethylene film (PE) of various density and thickness by use of high polythionic acid.

EXPERIMENTAL

Films of the high (HDPE 1, HDPE 2), middle (MDPE 3) and low (LDPE 4) density polyethylene were used as substrates. Their thickness was measured by a Peacock micrometer and found to be: HDPE 1 – 155 ±10 μm, HDPE 2 – 18 ±2 μm, MDPE 3 – 26 ±1 μm, LDPE 4 – 140 ±5 μm. The density of the polyethylenes was measured by a flotation method using a series of water/acetone mixtures at 293 K temperature. Dimensions of the samples were 15×75 mm. Before sulfuration the surface of polyethylene film was cleaned in the 4 % solution of Prewocell WOF-100, degreased in benzene and washed in distilled water.

For the inclusion of sulfur into the polyethylenes a $0.002\ mol \cdot l^{-1}$ solution of polythionic acid was used. It was prepared according to the equation [16]:

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

where $n = 3m + 3$.

Then, on the basis of data of sulfite [17, 18] and cyanic [19] decomposition of polythionates, the average number of sulfur atoms (n) in a molecule of polythionic acid was established.

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 and then used in analysis and further experiments. The sulfur diffused into the polyethylene samples was extracted by acetone, and its amount in the extract was determined by a spectrometric cyanide method [20] using a Specord UV VIS spectrophotometer ($\lambda = 450$ nm).

Later on, the samples of sulfured PE were treated with the copper (I – II) salt solution consisting of $0.4\ mol \cdot l^{-1}$ $CuSO_4$ and $0.1\ mol \cdot l^{-1}$ hydroquinone (reducing agent). This mixture was iodometrically established to be that of univalent and bivalent cooper salts, containing $0.34\ mol \cdot l^{-1}$

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Cu (II) salt and 0.06 mol·l^{-1} Cu (I) salt independently on temperature [14]. After being immersed in the copper (I – II) salt solution, the sample was rinsed with distilled water and used for analysis. The amount of copper in the sulfide film after fusing in the concentrated nitric acid was determined by an atomic Perkin-Elmer spectrometer (λ = 325 nm).

The transverse sections of PE with the layers of copper sulfide were investigated using a JXA–50 electron microscope (Jeol).

ANALYSIS AND RESULTS

Semi-hydrophilic polymer (polyamide) sorbs polythionate ions from a solution of polythionic acid [15] while hydrophobic polymer (polyethylene of low density) sorbs elemental sulfur from this solution [14]. Elemental sulfur separates during polythionic acids decomposition [17, 21] and diffuses into polyethylene bulk. A molecule of polythionic acid contains chain of bivalent sulfur atoms, $HO_3S–(S–S)_x–SO_3H$. Therefore, the greater number of bivalent sulfur atoms (x) and number of sulfur atoms (n) in a molecule, the greater amount of elemental sulfur after sulfuration is found in the PE samples. It has previously been found [14], that polyethylene contains rhombic cyclic octasulfur S_8.

In this study the dependence of sulfur concentration (c_S, mg·cm^{-3}) in the polyethylene of various density and thickness on a temperature of a polythionic acid solution and time of the treatment was investigated. The $H_2S_nO_6$ solutions with n = 33 and the temperatures 313, 333 and 353 K were used. With the increase of the temperature (Figure 1) and time of the treatment, the concentration of sulfur in the PE of various density increases as well (Figure 2).

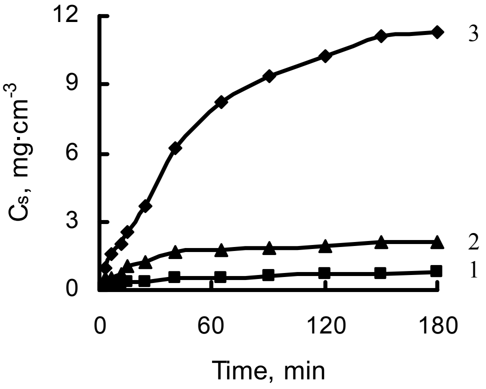

Fig. 1. Dependence of sulfur concentration in HDPE 1 on its immersion time in a solution of $H_2S_{33}O_6$ and temperature (K): 1 – 313, 2 – 333, 3 – 353

At higher temperature (333 – 353 K) the decomposition of $H_2S_nO_6$ happens significantly faster than at 313 K temperature, and the amount of elemental sulfur liberated during the decomposition also increases. Thus, polyethylenes can sorb greater amount of elemental sulfur.

PE films of high, medium and low density same as other polyolefines can sorb elemental sulfur well only in their amorphous phase in the state of high elasticity.

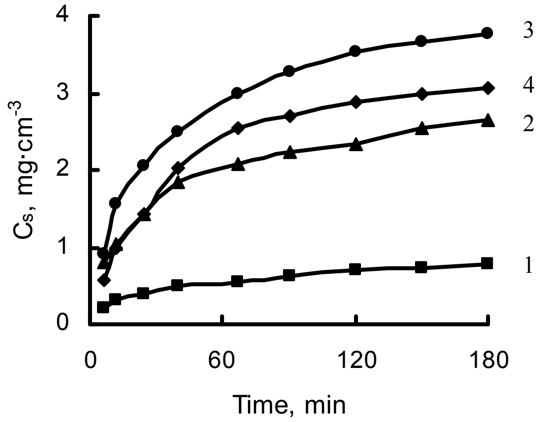

Fig. 2. Dependence of sulfur concentration in PE 1 – 4 on time when treating it with solution of $H_2S_{33}O_6$ at 313 K. The samples of polyethylenes: 1 – HDPE 1, 2 – HDPE 2, 3 – MDPE 3, 4 – LDPE 4

Crystalline regions of a polyethylene are denser than amorphous regions. Therefore, different values of sorbed sulfur in the polyethylenes might be caused by different part of an amorphous and a crystalline phase in PE 1 – 4. In this study the dependence of sulfur concentration in the polyethylenes on a crystalline volume fraction v_c, calculated from density ρ of polymer [22] was determined:

$$V_c = \frac{\rho - \rho_a}{\rho_c - \rho_a}, \tag{2}$$

where: ρ_c and ρ_a – densities of the crystalline and the amorphous phases.

Those densities for polyethylenes are ρ_c = 1.000 g·cm^{-3} and ρ_a = 0.855 g·cm^{-3} [23]. The values of ρ and v_c of PE 1 – 4 samples are presented in Table 1.

Table 1. Some characteristics of polyethylene films of various density

Marking	Thickness, μm	Density, g·cm^{-3}	Crystalline volume fraction
HDPE 1	155±10	0.962	0.738
HDPE 2	18±2	0.960	0.724
MDPE 3	26±1	0.940	0.586
LDPE 4	140±5	0.919	0.441

The data obtained show that the highest concentrations of sorbed sulfur in the interval of temperatures 313 – 333 K were in LDPE 4 and MDPE 3 samples. In these samples the values of the crystalline volume fraction (Table 1) are lower than those in high density HDPE 1 and HDPE 2 samples. The part of crystalline phase in low density polyethylene is less than amorphous phase. The highest sulfur concentrations at the temperature of 353 K were in the samples of very thin MDPE 3 and HDPE 2 films, but the amounts of sulfur found in the samples of HDPE 2 and MDPE 3 were 3 or 2 times smaller than that in LDPE 4 and HDPE 1 ones.

There were revealed, that the concentration of the sulfur sorbed in the polyethylenes increases when the temperature increases and crystalline volume fraction decreases. According to the experimental data obtained in this study, the temperature of the polythionic acid solution has a great influence on the sulfur concentration in the PE. This influence is greater in the case of high density polyethylene film. As the temperature of a solution is raised a polyethylene becomes thermoplastic and rubbery; segmental motion of PE continually increases, primarily in the amorphous regions [24]. Thus, at high temperatures (333 and 353 K) polyethylenes, especially HDPE 1 and HDPE 2, become more elastic. Low density polyethylene is produced in the free radical process and hence has a very high degree of branching; therefore both crystalline areas and density are lower [25]; and into channels of more amorphous phase can get more molecules of elemental sulfur. Maximum sulfur concentrations close to saturation ($c_{S\infty}$, mg·cm^{-3}) in the polyethylenes found when samples were sulfured in polythionic acid solutions at 353 K. The sulfur concentrations close to saturation found in PE 1 – 4 are 2 – 7 times higher, than those found in the samples of PE 1 – 4 sulfured in 333 K solutions: $c_{S\infty}$ for HDPE 1 were 11.3 mg·cm^{-3} (353 K) and 2.1 mg·cm^{-3} (333 K); for HDPE 2 – 30.6 and 4.4 mg·cm^{-3}; for MDPE 3 – 43.4 and 6.8 mg·cm^{-3}; for LDPE 4 – 16.5 and 7.5 mg·cm^{-3}.

It takes place for two reasons:

- at high temperature (353 K) $H_2S_{33}O_6$ decomposes much faster, therefore more liberated elemental sulfur diffuses into polymer bulk,
- at higher temperature of $H_2S_{33}O_6$ solution a polyethylene becomes more elastic, thus S_8 molecules of a large diameter (4.73 Å) easily penetrate into polymer bulk.

In this study, the interaction of PE 1 – 4 sulfured in a solution of higher polythionic acid with a solution of a Cu (I – II) salt was studied. The copper sulfide layer forms as a result of heterogeneous redox reactions between Cu$^+$, Cu^{2+} and S_8. Depending on the initial concentration of sulfur in the PE 1 – 4 and the conditions of treatment with the solution of copper salt, light brown, brown or even black copper sulfide layers were obtained.

The dependences of the amount of copper (m_{Cu}, mg·10^{-2}·cm^{-2}) in a sulfide layer on the time of PE treatment with the solution of higher polythionic acid (Figure 3), and the temperature of the polythionic acid solution were studied (Figure 4). It was determined that the amount of copper in the layer is dependent on the concentration of sulfur in the PE and the density of polyethylenes.

The highest values of copper amount were obtained in sulfide layers of low density LDPE 4 samples: 14.5 mg·10^{-2}·cm^{-2} (PE sulfured at 313 K), 35.2 mg·10^{-2}·cm^{-2} (333 K) and 51.2 mg·10^{-2}·cm^{-2} (353 K). As seen from Fig. 2, m_{Cu} 7 – 11 times higher in LDPE 4 than in medium density MDPE 3 and high density HDPE 1 and HDPE 2 samples. LDPE 4 is less crystalline, between its macromolecules are more cavities varied in size, therefore Cu$^+$ and Cu^{2+} ions easily penetrate into the amorphous phase channels and there react with sorbed elemental sulfur. Diffusion of the cuprous and cupric ions leads to formation Cu_xS in the polymer matrix, and diffusion of sulfur through the formed layer leads to deposition Cu_xS on the polymer surface. Due to sooner diffusion of Cu$^+$, Cu^{2+} ions the main part of sulfide deposits in the matrix of LDPE 4 (till 40 μm); the remaining part (till 3 μm) is outer layer forming on the polyethylene surface.

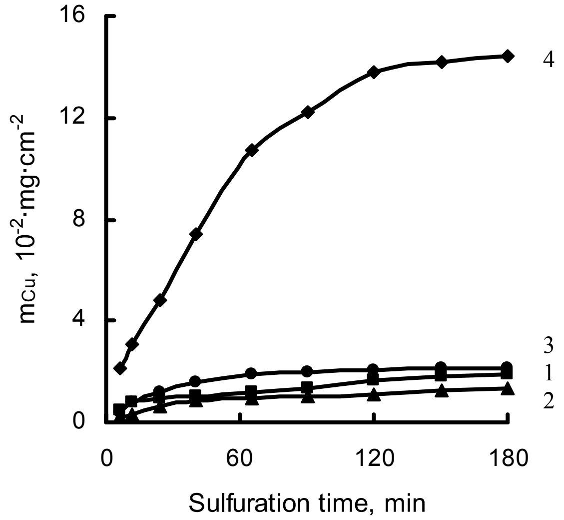

Fig. 3. Dependence of copper amount in sulfide layer on PE 1 – 4 on time when treating it with solution of $H_2S_{33}O_6$ at 313 K. The period of sulfured PE 1 – 4 treatment with the copper (I – II) salt solution at 353 K – 10 min. The samples of polyethylenes: 1 – HDPE 1, 2 – HDPE 2, 3 – MDPE 3, 4 – LDPE 4

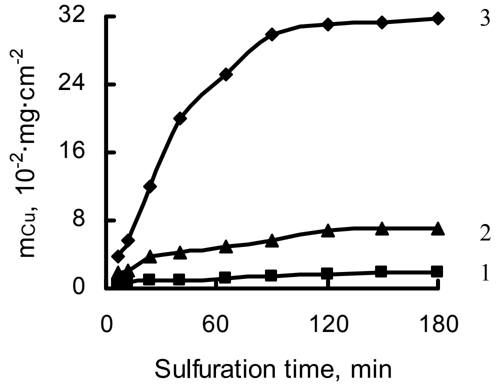

Fig. 4. Dependence of copper amount in sulfide layer on HDPE 1 on time when treating it with solution of $H_2S_{33}O_6$. The period of sulfured HDPE 1 treatment with the copper (I – II) salt solution at 353 K – 10 min. The temperature of sulfuration solution (K): 1 – 313, 2 – 333, 3 – 353

Cu_xS layer separates the reactants (sulfur in the polyethylene and Cu$^+$, Cu^{2+} ions in the copper salt solution); therefore the reaction continues due their diffusion though the formed layer. It seems likely that the formed compact sulfide layer decelerates further the increase in the amount of copper in samples of HDPE 1, HDPE 2 and MDPE 3.

The highest values of m_{Cu} were obtained in the samples of PE 1 – 4 treated in $H_2S_{33}O_6$ solution at the temperature of 353 K: 30.5 mg·10^{-2}·cm^{-2} for HDPE 1, 20.9 mg·10^{-2}·cm^{-2} for HDPE 2, 29.1 mg·10^{-2}·cm^{-2} for MDPE 3 and 51.2 mg·10^{-2}·cm^{-2} for LDPE 4. In this case the values of copper amount in LDPE 4 samples are only about 1.5 times higher. Obviously, due to considerably higher concentration of sulfur in PE 1 – 4 more cuprous and cupric ions reacted with sulfur.

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

The obtained results showed that solution of high polythionic acid is good sulfuring agent for polyethylene films of any density and thickness. The regularities established enable a proper choice of the formation of copper sulfide layers on the polymer surface and in the polymer bulk.

CONCLUSIONS

1. High polythionic acid, $H_2S_{33}O_6$, solution can be used for the insertion of sulfur into polyethylene of high, medium and low density.
2. The concentration of sulfur sorbed in the polyethylenes increases with the decrease of crystalline volume fraction and the increase of the temperature of polythionic acid solution and the sulfuration time.
3. A copper sulfide layer is formed by treating PE containing sorbed elemental sulfur with a Cu (I – II) salt solution.
4. The amount of copper in the sulfide layer increased with the decrease of density and crystalline volume fraction of the polyethylenes, and with increase of sorbed sulfur concentration. The amount of copper is related to the thickness of the polyethylene film too.

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