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Formation of Cu_xS Layers on Polypropylene Sulfurized by Molten Sulfur

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The processes of formation of electrically conductive layers of copper sulfides Cu_xS by the sorption–diffusion method on polypropylene (PP) using molten sulfur as sulfurizing agent was investigated. The amount of sorbed sulfur increased with the increase of the duration of treatment. Copper sulfide layers were formed on the surface of polypropylene after the treatment of sulfurized polymer with Cu(II/I) salt solution. The amount of copper sulfide in layer increased with the increase of treatment duration in copper salt solution. XRD spectra of PP films treated for 3 min with molten sulfur and then with Cu(II/I) salt solution for the different time showed that the copper sulfide phases, mostly digenite, $Cu_{2-x}S$ and α-chalcocite, Cu_2S were formed in the layers. Electromotive force measurement results confirmed the composition of formed Cu_xS layers on PP. The phase composition of layers also changed after the annealing. The value of electrical resistance of copper sulfide layers on PP varied from 20 Ω/cm^2 to 80 Ω/cm^2 and after annealing at 80 °C – in the interval of 10 Ω/cm^2 – 60 Ω/cm^2.

Keywords: polypropylene, sulfurization, electroconductive layers, copper sulfide, XRD.

1. INTRODUCTION

In recent years, polypropylene (PP) has been widely used in various fields of industry because of its excellent mechanical properties, such as light weight, low cost and readily-recyclable characteristics. In spite of these outstanding characteristics, PP is often unsuitable in some applications, such as painting, coating, bonding and metallization due to its inherent low surface energies [1]. For these applications, the improvement of hydrophilic property of PP surface is necessary [2 – 4].

The surfaces of polymers modified by different metallic sulfides have unique electric, optic, catalytic and magnetic properties. They are used in galvanic metallization, in manufacture of selective gas sensors, which serve at room temperature; they can absorb radio waves and serve as polaroids of infrared spectra or active sorbents [5 – 10].

Electrically conductive layers can be prepared by the sorption-diffusion method [11]. By this method the surface of a polymer film is initially treated by the solution containing sulfurization agent and then by the aqueous solution of metal salt. Sodium polysulfides [11], polythionic acids and polythionates [12, 13], thiourea [14 – 16], and sulfur in carbon disulfide solution [17] have already been used for sulfurization of polymer foils by different methods. The sulfurization process using cited agents is prolonged, many of them are quite harmful, and sometimes their preparation is complicated.

This work reports the preparation of electroconductive Cu_xS layers on polypropylene (PP) films using molten sulfur as the sulfurization agent.

The aim of this work was to form Cu_xS layers on PP film and to characterize chemical composition of the formed layers by X-ray diffraction (XRD) technique.

2. EXPERIMENTAL

15 mm × 45 mm size samples of non-oriented PP film of 150 μm thicknesses (KWH Plast, Finland) were used for the experiments. Before sulfurization process the surface of the PP samples was treated at 90 °C with etching solution (H_2SO_4/H_3PO_4 (1:1) and saturated with CrO_3). The etched PP film was sulfurized by molten sulfur at 135 °C for 1 min – 7 min in a glass reactor. The sulfurized PP films were treated with aqueous 0.4 mol/l Cu(I/II) salt solution at 80 °C for 0.5 min – 12 min [16].

The sheet resistance of Cu_xS layers was measured with a MS8205F (Mastech, China) constant current numerical measuring device with special electrodes. The electrodes were produced from two nickel-plated copper plates. The electrodes were fixed with 1 cm spacing and the dielectric material was placed between them. The concept of sheet resistance is used to characterize formed thin Cu_xS layers.

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

X-ray diffraction analysis of sulfur and copper sulfide layers was performed employing ДРОН-6 X-ray diffractometer (Russia), radiation CuK_α Ni filter, monochromator angular, current in a tube 30 μA, working voltage 30 kV. X-ray diffraction data were analyzed with Search Match, Xfit as well as Excel computer programs.

3. RESULTS AND DISCUSSION

In order to receive the copper sulfide layers on PP film with the low sheet resistance it was necessary to find the optimal conditions of the sulfurization process. It was established [16] that optimum etching temperature of the etching solution for PP of 150 μm thickness is 90 °C and

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duration 25 min – 30 min.

Etched PP was sulfurized for 1 min – 7 min in the molten sulfur at 135 °C. During this process sulfur was sorbed on PP film surface. The amount of sulfur on PP increased with increasing treatment duration in molten sulfur (Fig. 1). It was established that amount of sulfur increased until the 3-rd min of sulfurization, and then it decreased practically negligibly. Probably, the decrease of sulfur amount on the PP was caused by the starting desorption process.

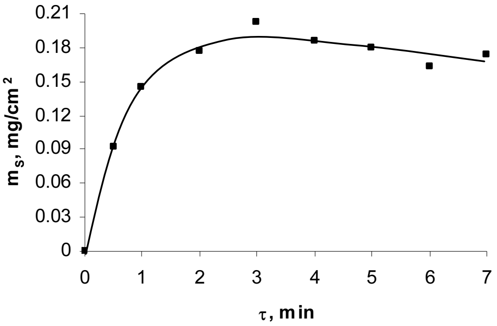

Fig. 1. Changes of sulfur amount in the PP films sulfurized at 135 °C in molten sulfur

Maximal amount of sulfur (0.2 mg·cm^{-2}) in PP sulfurized by molten sulfur for 3 min in comparison with the one treated in thiourea solution at 90 °C for 7 h (0.09 mg·cm^{-2}) [14] was more than twice bigger.

Cu_xS layers were formed on PP [16] sulfurized for 3 min and containing sulfur amount from 0.166 mg·cm^{-2} to 0.188 mg·cm^{-2}. The sulfurized PP films were treated with aqueous 0.4 mol/l Cu(I/II) salt solution at 80 °C for 0.5 min – 12 min. The amount of copper sulfide in the layers (Fig. 2) increased until 6 min of treatment with Cu(I/II) salt solution.

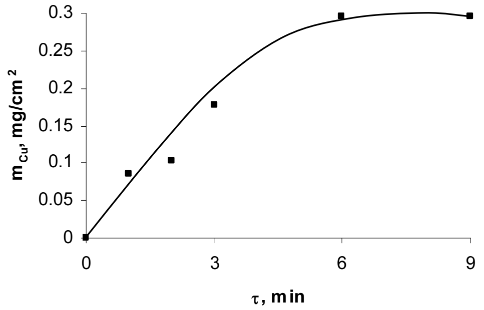

Fig. 2. Changes of copper sulfide amount in the PP films with Cu_xS layers

Sheet resistances were in interval of (20 – 80) Ω·cm^{-2} of the formed Cu_xS layers (Fig. 3, curve 1). After annealing in the thermostat at 80 °C for 0.5 h the sheet resistances of the layers decreased to average 20 Ω (Fig. 3, curve 2). The lowest resistances were measured after PP treatment in molten sulfur at 135 °C for 3 min and then in Cu(I/II) salt solution for 1 min.

Due to the different reaction rates, the composition of the formed Cu_xS layers can vary, i. e., x value can vary in the interval of $1 < x < 2$. Electromotive force of copper sulfide phases varies in the interval 0 mV – 290 mV [18].

The results of electromotive force measurement showed that when duration of the interaction of sulfurized PP with Cu(I/II) salt solution was increased, the electromotive force values of Cu_xS layers increased from 170 mV (after treatment for 0.5 min) to 160 mV (after treatment for 1 min) and then decreased to 150 mV, and after 3 min they became almost constant and were ~150 – 160 mV (Fig. 4, curve 1). Cu_xS layers corresponded predominantly to djurleite and chalcocite ($1.91 < x < 2$). It can be assumed [18] that composition of the formed layers is close to Cu_2S.

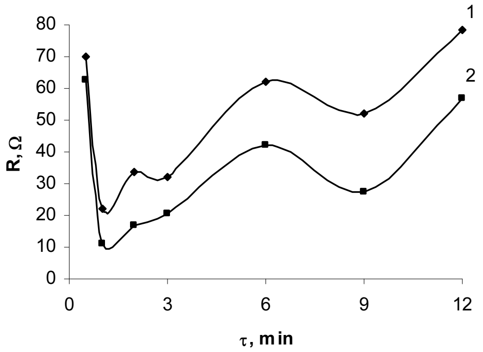

Fig. 3. Dependence of surface sheet resistances of the Cu_xS layers on the duration of treatment in Cu(I/II) salt solution: 1 – Cu_xS layers formed on PP films sulfurized for 3 min in molten sulfur, 2 – after annealing at 80 °C for 30 min

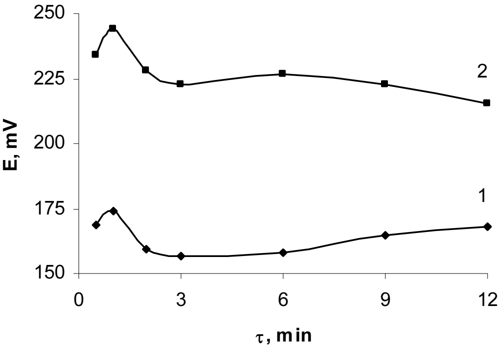

Fig. 4. Electromotive forces of the Cu_xS layers on PP films sulfurized for 3 min in molten sulfur and treated in Cu(I/II) salt solution (1) and then annealed at 80 °C for 30 min (2)

It was found that the electromotive force of the samples annealed for 0.5 hours at 80 °C increased and reached 234 mV and 244 mV, respectively (corresponded to spioncopite and geerite, ($1.4 < x < 1.65$)). When the samples were treated in Cu(I/II) salt solution longer, the electromotive force became almost constant 225 mV (corresponded to geerite ($1.36 < x < 1.4$)) (Fig. 4, curve 2). Electromotive force of the annealed samples with Cu_xS layers increased to an average of 60 mV. From these data, it can be concluded that the duration of treatment with Cu(I/II) salt solution and annealing conditions had effect on the electromotive force value. In the case of the duration of the annealing, it was found that the electromotive force and sheet resistance of Cu_xS layer became stable when the samples were kept in thermostat for 0.5 h at 80 °C.

X-ray diffraction analysis of the sulfurized PP films showed that S_{18} [71-569] ($d = 0.386$; 0.313; 0.257 nm) was diffused into PP surface. After treatment in Cu(I/II) salt solution, copper sulfide phases: digenite, $Cu_{2-x}S$ [2-1292] or α-chalcocite, Cu_2S [2-1294] ($d = 0.195$ nm), were found on PP films. After annealing the samples at 80 °C in thermostat for 30 min, the following copper sulfide phases were found on PP surface: covellite, CuS [6-464] (*d* = 0.305; 0.281; 0.189 nm), talnakhite, $Cu_{34}S_{32}$ [71-2438] (*d* = 0.306 nm), and digenite, $Cu_{2-x}S$ [2-1292] (*d* = 0.195 nm).

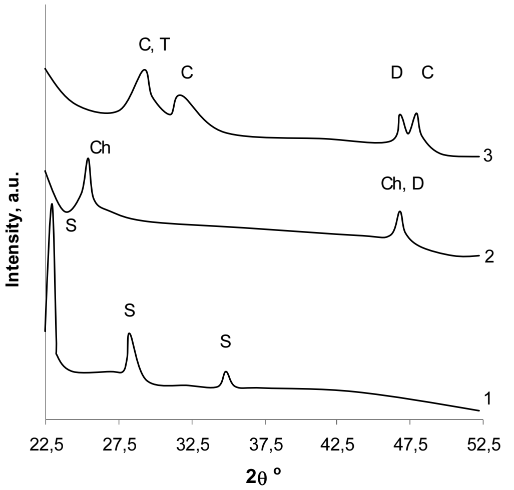

Fig. 5. X-ray diffraction patterns of the sulfurized (1), modified with Cu_xS layers PP film (2) and this film annealed at 80 °C for 30 min (3). C – covellite, Ch – chalcocite, D – digenite, T – talnakhite, S – sulfur

4. CONCLUSIONS

1. The molten sulfur was used for sulfurization of PP for the first time. Amount of sulfur on PP increased by increasing treatment duration in molten sulfur at 135 °C till 3 min, and it was more than twice bigger in comparison with the one when PP was sulfurized in thiourea solution.
2. The amount of copper sulfide in the layers on PP increased until 6 min of treatment in Cu(I/II) salt solution.
3. X-ray diffraction data of the sulfurized for 3 min PP films showed that S_{18} was sorbed on PP surface. After treatment in Cu(I/II) salt solution, copper sulfide phases: digenite or chalcocite were found on PP films. After annealing the following copper sulfide phases were found on PP surface: covellite, talnakhite, and digenite.
4. Electromotive force values of the formed Cu_xS layers varied from 150 mV to 170 mV. After annealing of the samples for 0.5 hours at 80 °C they increased and varied in the interval of 225 mV – 244 mV.
5. The electrical sheet resistance of Cu_xS layers on PP varied from 20 $\Omega\cdot cm^{-2}$ to 80 $\Omega\cdot cm^{-2}$, after annealing at 80 °C they were in the interval of (10 – 60) $\Omega\cdot cm^{-2}$.

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