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Electrochemical and Optical Method for Analysing the Metallic Layers Deposited on ABS-Type Polymers

The paper presents optical and electrochemical methods of analysis in view of studying the metal layers deposited on the surface of ABS plastic materials. We used optical microscopy in order to observe the quality of the deposits on the surface of polymers, as well as the study of the influence of different factors on the metallisation process. Moreover, we realised also the electrochemical study of the metallic layers deposited on the ABS polymers through the interpretation of the polarisation curves in view of observing the main phenomena occurring on the surface of the polymers.

Keywords: *ABS polymers, conductibilised plastic, electrochemical*

1. Introduction

The chemical and optical methods of analysis were used for the investigation of the properties of the metal layer deposited on the surfaces of the ABS-type polymers, chemically and electrochemically conductibilised.

The electrochemical determinations consisted in the characterisation, through linear voltameter, of the process of chemical conductibilisation of ABS plastic materials coppering, and the characterisation of the process of electrochemical depositing of metals (copper and nickel covering) on the conductibilised surfaces.

By means of the voltmetric method we aimed at experimentally obtaining the current-potential dependency, by applying the variation of potential as perturbing dimension and recording the system response through its current variation.

We chose to plot the polarisation curves because through this method we can rigorously determine the currents corresponding to the hydrogen release and those

corresponding to the global cathodic process (the cathodic depositing of copper and the hydrogen release).

The optical microscope analysis was performed with the purpose of observing the deposits quality, as well as the main phenomena taking place on the surface of the metallised plastic material. The results have an informative character and they may constitute an eliminating criterion if one is particular about the aesthetics of the surface.

2. The electrochemical experiments of depositing metal layers on the ABS-type polymers

For determinations we used a Princeton electrochemical cell (fig. 1) coupled to a computer-aided Parstat 2273 potentiostat-galvanostat. The electrochemical system functions with 3 types of electrochemical electrodes (working electrode, reference electrode and counter-electrode) [1], [4] in an acid CuSO_4 electrolyte.

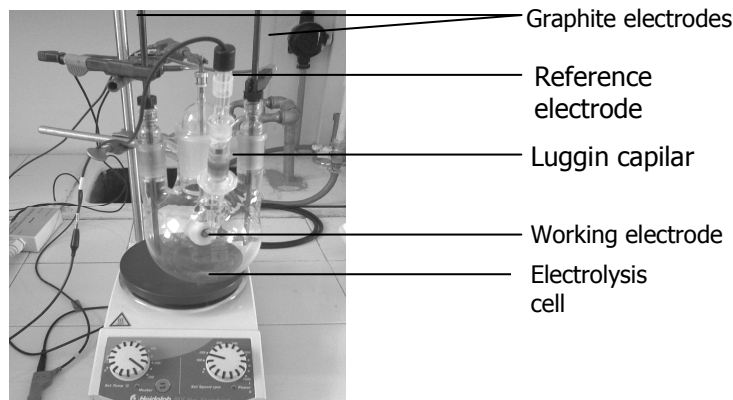


Figure 1. Princenton electrolysis cell

As working electrode we used plastic pills (ABS) conductibilised by chemical and electrochemical copper covering, with an 1 cm^2 active surface (fig.2).

The reference electrode was the calomel saturated electrode (ESC), and as counter-electrode (auxiliary electrode) we used two graphite bars symmetrically placed to the working electrode.

The process taking place on the surface of the plastic material, previously chemically conductibilised and cathodically polarised in a Na_2SO_4 solution, is the molecular hydrogen release (H_2), visible through the apparition of gas bubbles on the

respective surface. We remark that the H_2 release increases with the displacement of the electrode potential towards more negative values.



Figure 2 Electrochemically conductibilised plastic material pills (ABS)

In order to study the kinetics of the cathodic copper depositing we used as support electrolyte a Na_2SO_4 solution with the concentration of 0.5 M.

3. Results and discussions

The polarisation curve in a Na_2SO_4 solution corresponding to the chemically conductibilised plastic material represents the hydrogen release curve. When adding $CuSO_4 \cdot 5H_2O$ 8 g/L (2 g/L Cu^{2+}) to the Na_2SO_4 solution in the case of the cathodic polarisation there occurs a limit current due to the fact that all ions arriving at the surface of the material are discharged. The shape of the voltametric curve depends on the determinant speed's slow stage (fig.3).

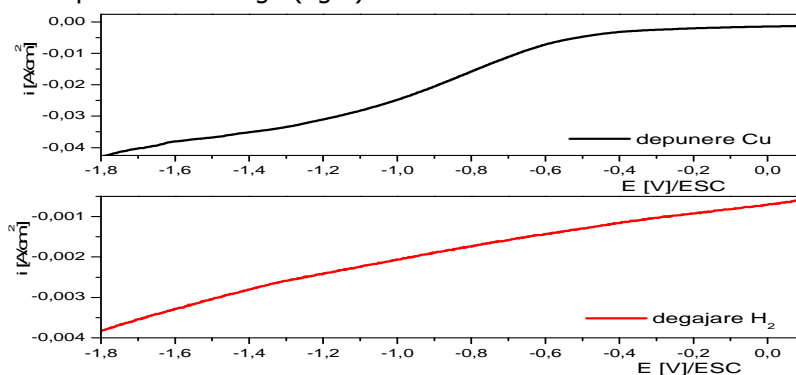


Figure 3. The cathodic curve of the copper depositing on the chemically conductibilised ABS (electrolyte - Na_2SO_4 and $CuSO_4 \cdot 5H_2O$ 8 g/L) and the cathodic curve of hydrogen release (Na_2SO_4 electrolyte)

In the case of low current densities, the determining speed is the transfer of charge, the current density exhibiting an exponential variation depending on potential, according to the Buttlar-Volmer relation [3], [5]. In the case of high current densities, the slow stage is represented by the transport of the electro-active species from the solution to the electrode, the shape of the curve being determined by Fick's laws of diffusion [5], the value of the current density heading towards a limit (limit diffusion current).

In the case of the polarisation curve on the electrochemically conductibilised and graphitised ABS pill (fig.4), the occurrence of the cathodic peak is due to the fact that when reaching the discharge potential of the Cu^{2+} ions their concentration is higher than the concentration in the mass of the electrolyte solution.

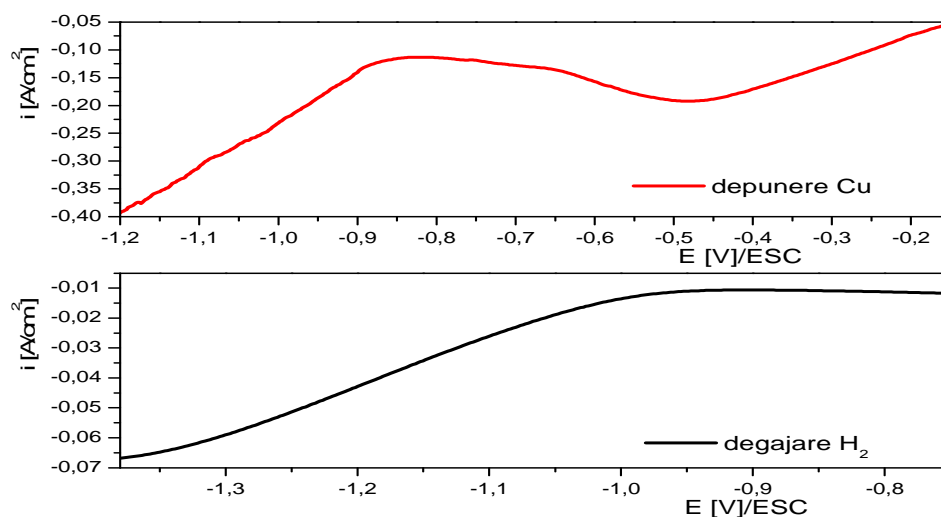


Figure 4. The cathodic curve of copper depositing on the graphitised ABS (electrolyte Na_2SO_4 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 200g/L) and the cathodic curve of hydrogen RELEASE (electrolyte Na_2SO_4)

When the Cu^{2+} concentration in the solution increases up to 50g/L we witness a poignant increase of the cathodic peak, which, in the range of the 2 g/L Cu^{2+} concentration, is almost undetectable on the polarisation curve (fig. 5).

Thus, in the case of the 2 g/l Cu^{2+} concentration, the depositing on the surface of the ABS plastic material is non-uniform, whereas for a 50 g/l Cu^{2+} concentration, the depositing is compact on the entire surface of the part, which can be remarked during the optical examination of the surface. (fig. 6).

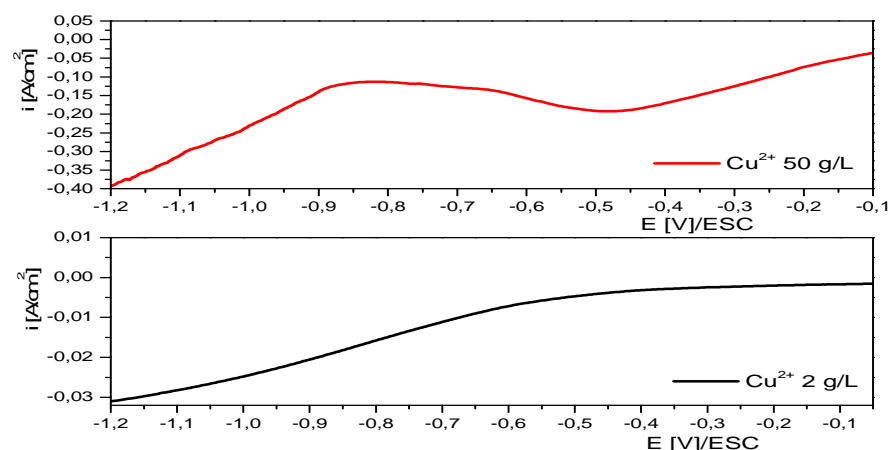


Figure 5. The influence of the difference of Cu^{2+} ions concentration upon the polarisation curves

Also, we studied, with the help of the optical microscope, the metallic depositing in view of observing the main phenomena occurring on the surface of the metallised polymer [2].

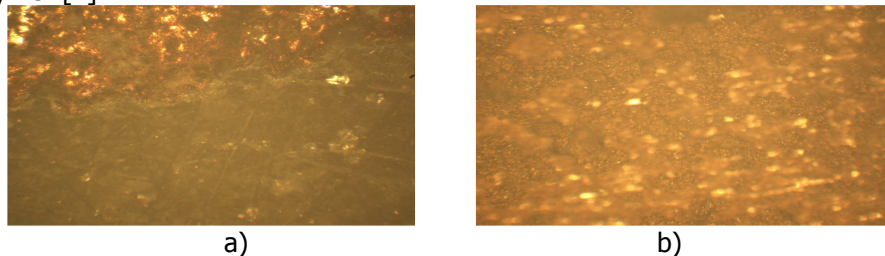


Figure 6 The influence of the Cu^{2+} concentration upon the depositing of
a) 2 g/L Cu^{2+} ; b) 50 g/L Cu^{2+}

We remarked as important the manner of obtaining the support material (cast or plastified ABS), as well as the presence of inhibitors in the solution of metal depositing on the polymeric support. This is relevant during the microscopic analysis. (fig. 7).

Both in the case of the cast polymer and in the case of the plastified one, the support material is visible. The copper is deposited more uniformly in the case of cast ABS, whereas on the surface of the plastified ABS there remain relatively large surfaces on which the copper depositing has not occurred.

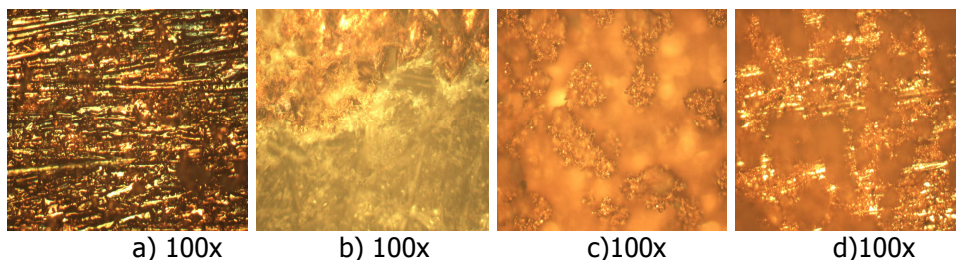


Figure 7 The influence of the manner of obtaining the ABS material upon the deposits (fig.a and b) and the lack of inhibitors on the metallic deposit (fig. c and d)
a) cast ABS; b) plastified ABS; c) deposits on peaks; d) deposits in depths

The advantage of the depositing on plastified ABS is the obtaining of a shiny deposit (fig.6b). We found that in the absence of inhibitors (levelling / shine agents) in the composition of the electrolyte, the Cu depositing takes place preponderantly on the micro-peaks at the level of the support material, with the formation of spongy macro-crystalline deposits. This phenomenon is due to the fact that the Cu^{2+} ions are firstly adsorbed on the micro-peaks and then in the depths on the ABS surface.

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