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Potentiometric Control of Metal Concentration for Chelation Kinetics of Modified Polyimide Films

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Abstract

Interaction of modified polyimide films with agrentium nitrate solutions of various concentrations was studied. Sorption of Ag ions by films is divided into three steps: formation of Ag ion layer on the border of film surface; diffusion inside the films; and final saturation of film by Ag ions. The data are confirmed by calculation of weight of the sorbed Ag ions onto the films with various thicknesses. Electrochemical Ag loading of PI films includes two parallel reactions: film dissolution accompanied by chelation.

Introduction

The metallization of plastic, in particular of polyimide films, is included into the number of perspective directions of the modern technology. Polymer composite materials, with metal loading, find wide application in airspace, electronics and other perspective areas of engineering. In this regard, among the various polymeric materials the interest is focused on polyimides (PI), which have high thermal and radiation resistance and excellent physico-mechanical properties [1,2].

The present investigation is to study the first stage of plating process of such modified films - interaction of the modified polyimide film with solutions of silver nitrate.

Experimental

Absorption kinetics of Ag cations into a modified surface layer of PI films has been studied between 10^{-4}-10^{-2} M concentration range under potentiometric control of silver ion concentration.

Kapton 75 HN, 100 HN, 200 HN with thickness 12.5; 25; 37.5 mm relatively were used. The films were modified in alcohol-aqueous solutions of potassium alkali.

Ion-selective electrodes on the basis of Ag_2S and silver wire, coated with AgCl were used. A standard AgCl electrode was employed with a salt bridge. Background electrolyte and bridge electrolyte were 0.1 N potassium nitrate.

The hydrolyzed films with size 1.5×4 cm (surface 12 sq.cm) were immersed into an electrochemical cell (volume 25 cm^3) filled with argentium nitrate. The solution was stirred gently at constant rate. The measurement of the potential of the indicator electrode was recorded with digital pH-meter MERATRONIC 5170 (ELWRO) under 0.1 mV precision during 2-5 hours until full absorption of Ag ions by the film is ensured.

Theoretical

Sorption of Ag ions from the solution occurs due to chemical interactions Ag cations with a surface layer of the modified film. During the process, kinetics of chelation can follow such steps as shown in Fig. 1.

It should be noticed that the modified layer is able to dissolve. Due to the affinity of Ag to the modified

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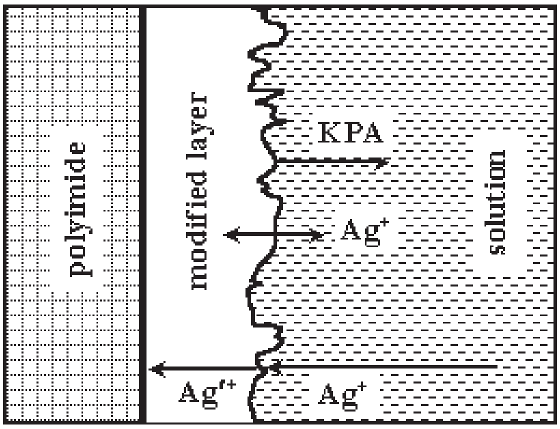


1. Diffusion of Ag ions into the surface layer
2. Interaction of Ag cations with surfaces of the film (adsorption and adhesion)
3. Diffusion of Ag cations in solid phase of the film.

Fig. 1. Three main stages of the diffusion of silver ions into PI film.

polymer is high, the equilibrium on the interface of film-solution should be shifted definitely to diffusion of Ag cations into the film, thus the solution becomes poor of Ag ions.

Because the potential of indicator electrode is linked to the concentration of Ag ions in the solution:

$$E = E_0 + \frac{RT}{nF} \cdot \ln C_{Ag^+} \quad (1)$$

that the Ag concentration in the solution could be calculated through a change of the potential.

The rate of chelation can be determined through kinetics of ion exchange on the interface of film-solution, so at irreversible sorption it could be as concentration of Ag in the solution:

$$\frac{dc}{dt} = -KC \quad (2)$$

where K is constant of absorption rate.

$$C = C_0 \cdot e^{-Kt} \quad (3)$$

On the other hand at any limitation of the diffusion in the solution that is:

$$\frac{dc}{dt} = -S \cdot D \frac{C}{\delta \cdot V} \quad (4)$$

where D – diffusion coefficient; d – thickness of diffusion layer; S – surface of electrode; V – electrode volume and after integration:

$$C = C_0 \cdot e^{-\frac{SD}{\delta v}t} \quad (5)$$

If the limitation of chelation rate can be controlled by rate of Ag diffusion to the film surfaces, that the same expression of the dependence between Ag concentration and time can be used. The exponent coefficient is a constant of diffusion rate on the interface of film-solution in the case of reduced reaction rate or coefficient. That represents a thickness of the diffusion layer, as well as a ratio of film square and solution volume at reduced rate of diffusion. Measured potential of the electrode is bound with concentration of Ag ions in the solution through the Nernst equation:

$$E = E_0 + \frac{RT}{nF} \lg C_0 - \frac{RT}{nF} K\tau \quad (6)$$

Thus, at such way of the kinetics there are linear plots of the curve $E - \tau$.

In this case it is supposed that film capacity after Ag ion sorption is higher than the total amount of Ag ions in the solution. Otherwise, only the initial plots of the curve $E - \tau$ should be taken into account.

Anyway, in all cases the process is considered as irreversible, however that is not true. If the process is reversible then the dissolution of Ag from the film is monomolecular.

Thus,

$$\frac{dC}{dt} = -K_1 C + K_2 C_1 = K_1 C + K_2 (C_0 - C) \cdot \frac{V_S}{V_f} \quad (7)$$

where K_1 – constant of direct reaction, K_2 – constant of back reaction, C – concentration of Ag ions in the solution, C_0 – the initial concentration of Ag ions in the solution, C_1 – concentration of Ag-ions in the film, V_S and V_f – volumes of solution and film respectively.

After integration that is:

$$C = C_0 \frac{\frac{K_2 V_S}{K_1 K_f} + \exp(-(K_1 - K_2 \frac{V_S}{V_f}) \cdot t}{1 - \frac{K_2 V_S}{K_1 V_f}} \quad (8)$$

that is more casual case which take into account the reversibility of reaction and film volume, but more complicated for calculation.

Results and Discussion

A series of kinetics curves were obtained for following films: Kapton 75 HN, 100 HN, 200 HN between 10^{-4}-10^{-2} M concentration range of silver nitrate. Typical example curve of Kapton 100HN is shown in Fig. 2. One of such series is demonstrated in Fig. 3.

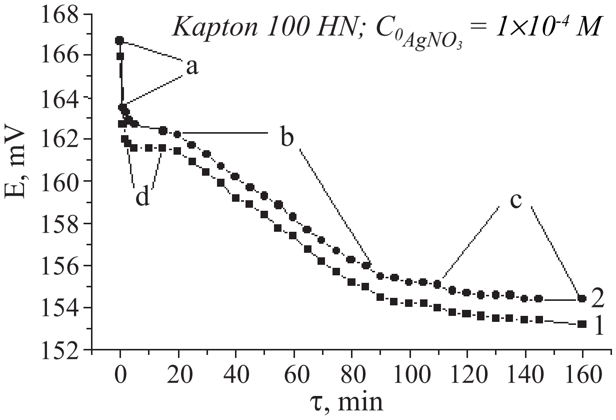
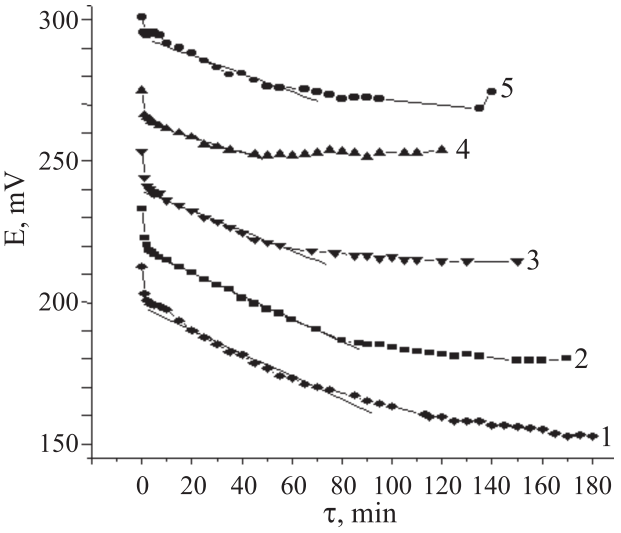


Fig. 2. Potentiometric measurement of Ag concentration in the solution during chelation of the modified PI film.



1–10^{-4} M, 2–4×10^{-4} M, 3–10^{-3} M, 4–4×10^{-3} M, 5–10^{-2} M

Fig. 3. Kinetics of chelation of Kapton 75 HN films.

We can see that the curves follow the following few steps:

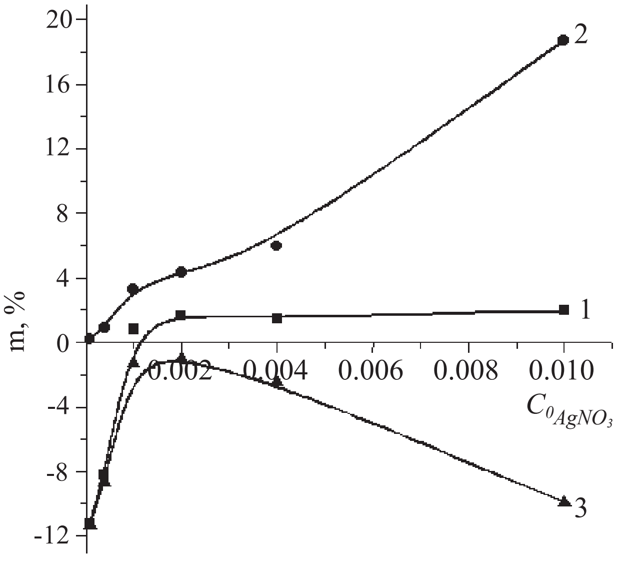
1. Sharp drop of the potential at the initial step (a);
2. Gradual linear decreasing (b), which corresponds to linear dependence of $\lg C_{Ag}$ vs time. In some curves there is a strong division on lag step (d), which corresponds to constant concentration of Ag ions in the solution;
3. Transition of the potential to the constant level relating to saturation of films by Ag ions.

The curves change in the dependence on concentration of chelating solution, but slope of the curves with a linear decrease of the potential (b) remains the same through all curves. The coefficient calculated from the linear portion of the plot points out that it can be concerned with the reduced step of the diffusion in the solution. However further studies alone can establish this point.

A bent of the linear plots at the final step of the process is due to excees of the film capacity about Ag ions, which can not diffuse into the film. That is also confirmed by elongation of the linear plot at decreasing silver concentration.

A high rate of Ag vanishing from the solution at the initial time, which prevails the rate of diffusion, can be speculated as dissolution of potassium polyamate. That leads to the formation of Ag complexes into the solution out of the potentiometic control. Such behaviour could be confirmed by the measurement of film weight.

The study of the films weight before and after chelation shows it rises at Ag concentration more than 10^{-3} M (Fig. 4, curve 1). The decrease of weight manifests the dissolution of potassium salts, which are a part of the modified layers.



Kapton 200 HN
1 - total change of film weight
2 - change of film weight due to its dissolution
3 - content of Ag in the film

Fig. 4. Relative change of PI film weight after chelation.

The substitution of K on Ag ions leads to the decrease of modified layer dissolution, so the process includes two parallel reactions: film dissolution accompanying its chelation. The reason of weight decrease is perhaps due to lack of Ag ions in the undersurface layer, otherwise it is observed the formation of a non-soluble compound at diffusion control of the process.

The presence of two opposite diffusion currents near the surface layer (Ag compounds and modified polymer, between them the reaction occurs) leads to pulse character of the process. That is sometimes observed with the formation of a non-soluble product on the basis of Ag complexes.

Acknowledgment

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