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Optimization of Electroless Copper Plating on Polyethylene Films Modified by Surface Grafting of Vinyl Ether of Monoethanolamine

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Abstract

Metallized plastics have recently received significant interest for their useful applications in electronic devices such as for integrated circuits, packaging, printed circuits and sensor applications. In this work the metallized films were developed by electroless copper plating of polyethylene films grafted with vinyl ether of monoethanoleamine. There are several techniques for metal deposition on surface of polymers such as evaporation, sputtering, electroless plating and electrolysis. In this work the metallized films were developed by electroless copper plating of polyethylene films grafted with vinyl ether of monoethanoleamine. Polyethylene films were subjected to gamma-radiation induced surface graft copolymerization with vinyl ether of monoethanolamine. Electroless copper plating was carried out effectively on the modified films. The catalytic processes for the electroless copper plating in the presence and the absence of $SnCl_2$ sensitization were studied and the optimum activation conditions that give the highest plating rate were determined. The effect of grafting degree on the plating rate is studied. Electroless plating conditions (bath additives, pH and temperature) were optimized. Plating rate was determined gravimetrically and spectrophotometrically at different grafting degrees. The results reveal that plating rate is a function of degree of grafting and increases with increasing grafted vinyl ether of monoethanolamine onto polyethylene. It was found that pH 13 of electroless bath and plating temperature 40°C are the optimal conditions for the plating process. The increasing of grafting degree results in faster plating rate at the same pH and temperature. The surface morphology of the metallized films was investigated using scanning electron microscopy (SEM). The adhesion strength between the metallized layer and grafted polymer was studied using tensile machine. SEM photos and adhesion measurements clarified that uniform and adhered deposits were obtained under optimum conditions.

Introduction

Polymeric materials can substitute metals in many technical applications due to excellent mechanical properties, low density, easier processing and chemical inertness. At the same time metals have high electric conductivity, metallic lustre, some catalytic properties, which are not typical for polymers. In this connection the development of metal-polymer hybrids was an important research field in the recent years due to the wide applications of these materials in electronic industry such as integrated circuits, packing, printed circuit boards, sensors, *etc.* [1].

There are several techniques for metal deposition on surface of polymers such as evaporation, sputtering, electroless plating and electrolysis. However, due to surface inertness of the most polymers the adhesion strength between metals and plastics is inadequate for practical applications. Various methods were suggested to activate the surface of different polymeric materials. Niino and Yabe [2] reported about chemical surface modification of poly (tetrafluoroethylene) by excimer laser processing. Kurdi and co-workers [3] used low-pressure ammonia plasma treatment to activate the surface of polypropylene for subsequent metallization. Kang and co-workers

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[4-8] reported about Ar plasma treatment of poly (tetrafluoroethylene) and some polyimide films with subsequent plasma- or UV-graft polymerization of different monomers to modify a polymer surface. Charbonnier and co-workers [9] grafted nitrogen-containing groups on polycarbonate surface by laser irradiation through an ammonia atmosphere. Several authors [10,11] demonstrated the possibility of chemical activation for preparation of metallized polyimides and polyamides.

The radiation-induced graft polymerization of monomers onto polymer substrates is a technique that can be used for surface modification and impart desirable properties to polymer without significant affecting its original properties [12,13]. The grafting of functional monomers can ensure the formation of adhesive layer on the surface of a polymeric film, which can be successfully used for metallization.

Earlier [14,15] we demonstrated the possibility of polyethylene and polypropylene films modification by radiation grafting of vinyl ether of monoethanolamine (VEMEA). Due to the presence of amino- and ether-groups in the structure of VEMEA these grafted films were able to absorb a number of different metallic ions. This valuable property of the grafted films can be used for developing metallized polymeric materials through the electroless plating.

Electroless or autocatalytic metal plating is one of the conventional metallization methods in electronics. The advantages of this technique are very high selectivity, possibility to use a very thin seed layer, and the ability to plate into deep holes and cracks [16,17]. The electroless copper plating solution consists of water-soluble Cu^{2+} salt, Cu^{2+} complexing agent, reducing agent, pH adjustor, and rate additives.

Various reducing agents have been used in electroless baths, namely formaldehyde, dimethylboron, borohydride, hypophosphite and hydrazine. However, formaldehyde is mainly used in all commercial baths because of low cost, effectiveness and ease of control [16,17].

The overall electroless Cu^{2+} plating reactions using formaldehyde as a reducing agent can be described by the following equation (1):

$$Cu^{2+} + 2HCHO + 4OH^- \xrightarrow{Pd} \\ \xrightarrow{Pd} Cu + H_2 + 2H_2O + 2HCOO^- \quad (1)$$

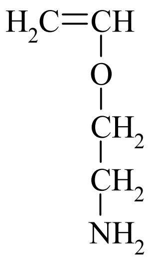
This reduction reaction takes place only in the presence of Pd as a catalyst. Two-step and one-step methods have been proposed to perform this catalytic activation process [4-8]. In the two-step method, the polymer surface was immersed successively in $SnCl_2$ and then in $PdCl_2$ solution. The one-step process is based on the catalyst composed of mixed Sn-Pd colloid. However $SnCl_2$ is not an active catalyst for electroless process. So it is important to develop Sn-free bath to avoid its side effects.

This work aims at the surface metallization of polyethylene (PE) grafted with VEMEA, optimization of plating and catalytic activation processes, and investigation of morphology and adhesion of metallized layer.

Experimental part

Materials

VEMEA as a commercial product of Alash Ltd. (Temirtau, Kazakhstan) was used in the present work. It was dried in the presence of dry K_2CO_3 and purified by double distillation in argon atmosphere.



$$H_2C{=}CH{-}O{-}CH_2{-}CH_2{-}NH_2$$

VEMEA

PE film classified as "for food packaging" obtained from Munai Plastik Ltd. (Kazakhstan) was used in this study and before experiments each sample was cleaned by treatment with acetone. All the chemicals used in this study were of analytical grade.

Methods and techniques

Synthesis of Grafted Films

PE films grafted with VEMEA at different irradiation dose were prepared by the methodology described in our previous publication [14]. The grafting was performed in sealed glass ampoules with polyethylene films immersed in monomer saturated with argon. MRX-γ-25M (Russia) equipped by ^{60}Co with the dose rate 0.3 Gy/s was used as a source of γ-irradiation. The dose rate was determined by a Fricke dosimeter. The grafted films were removed and washed in distilled water for several days in order to eliminate the unreacted monomer. The complete removal of impurities from the grafted films was confirmed gravimetrically and by FTIR. The grafted films were dried in a vacuum oven at 40°C for 2 hours.

Characterization of Grafted Films

The grafting of VEMEA onto PE was confirmed using FTIR spectroscopy as described in our previous publication [14]. The degree of grafting (*DG*) was determined gravimetrically and calculated by the following formula:

$$DG = [(m_{graft} - m_0)/m_0]\times 100\%,$$

where m_0 and m_{graft} are the weights of the films before and after grafting, respectively.

Metallization of Grafted Films

The metallization of grafted films was performed by two ways, *i.e.* by one- and two-step activation methods. In one-step method the grafted films were activated by immersion into solution of $PdCl_2$ for a certain time and then transferred into the plating bath. The solution composed of 5 g/L $CuSO_4$, EDTA 30 g/L, 10-15 g/L NaOH and 15 ml/L HCHO (40% aqueous solution of formaldehyde) was used as a bath for electroless plating. In two-step method prior to activation the grafted films were treated with solution of $SnCl_2$, then activated in solution of $PdCl_2$ and afterwards immersed into the plating bath.

Plating rate was determined gravimetrically by the weight gain and spectrophotometrically at wavelength 296 nm using UV-Vis spectrophotometer (UV2401PC-Shimadzu, Japan). The copper thickness was calculated from the weight gain according to Paunovic and Arndt assumption [18] that 1 mg/($cm^2\cdot h$) ≅ 1 μm/h.

The morphology of metallized films was investigated using SEM (Jeol, Superprob 733-Japan) combined with energy dispersion microanalyzer (INCA, Oxford instrument, UK).

Adhesion Measurements

The adhesion strength between the deposited copper layer and polymeric materials was determined as reported by Yang *et al.* [19]. The surface-modified PE films of area 1×1 cm were activated by direct immobilization in 0.1 M $PdCl_2$ solution for 20 min, and then rinsed with water. The surface-activated films were immersed into electroless Cu bath for an hour (bath composition $CuSO_4$ 5 g/l, Ethylene Diamine Teteraacetic Acid (EDTA) 30 g/l, and pH 13 with NaOH as adjustor, HCHO 10 ml/l). Metallized PE films were rinsed with distilled water, and then dried in a vacuum for 2 hours. The metallized films were adhered by Cu sheet backing (0.1 mm thickness) using a commercial adhesive (Super Glue, Oska, Japan) for the subsequent adhesion strength on tensile tester Model A50, Russia). All the measurements were carried out at a crosshead speed 1 cm/min. Each reported result was an average of 3 sample measurements.

Results and Discussion

Effect of Grafting Degree

The grafted films were obtained by irradiation of PE films immersed into VEMEA. After purification and drying, the films were weighed and the grafting degrees were determined gravimetrically as described in our previous publications [14,15]. As it was expected an increase in absorbed dose leads to increase in the grafting degree of the monomer.

The samples with different grafting degrees were metallized by one-step method according to the scheme shown in Fig. 1. The samples were activated by immersion in 0.1 g/L $PdCl_2$ solution for 25 min and then were placed into electroless Cu plating bath containing EDTA complexing compounds for an hour. The plating rate was determined gravimetrically and spectrometrically and the data obtained are shown in Table 1. The results of gravimetric and spectrophotometric determination of the plating rate are in good agreement and can be used simultaneously to ensure better accuracy. It is clearly seen that an increase in the grafting degree leads to a significant increase in the plating rate. The films with higher grafting degree exhibit better ability to absorb Pd^{2+} ions, which in turn will create greater concentration of catalytic centers on the material surface and facilitate the plating process.

Optimization of Activation Step

Good activation is a key to the entire electroless process. In order to optimize the activation stage we have studied the effects of operating conditions on the plating rate. Figures 1, 2 show the effects of activating time and concentration of the activator solution

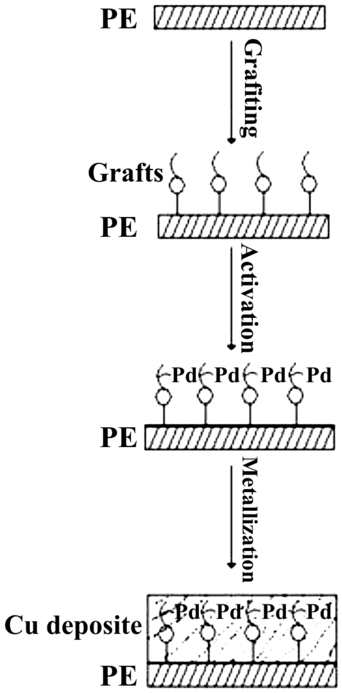


Fig. 1. Effect of activation time on the plating rate (activation solution 0.1 g/L $PdCl_2$).

Table 1

Dependence of plating rate on the grafting degree of VEMEA onto PE*

Grafting degree, %	Electroless plating rate, nm/hr	
	Gravimetric	Spectrophotometric
0	0	0
0.75	3.3	2.1
4.35	35.4	33.5
7.9	83.5	79.9

*Activation time 25 min, activation solution 0.1 g/L $PdCl_2$, EDTA plating bath, pH 13, T = 40°C

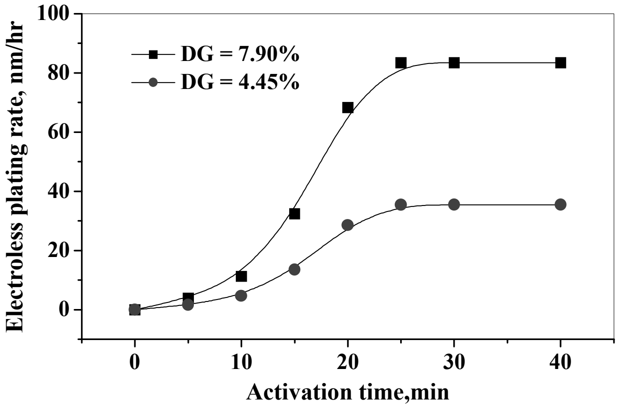


Fig. 2. Effect of $PdCl_2$ concentration on the plating rate (activation time 25 min).

on the plating rate. It is clear that the plating rate increases continuously with the increasing of immersion time up to 25 minutes. Then the plating rate comes to a plateau, which may be attributed to the complete saturation of substrate surface by Pd^{2+} ions. An increase in $PdCl_2$ concentration from 0 to 0.1 g/L results in greater plating rate (Fig. 2), but at concentrations higher than 0.1 g/L the saturation is observed as well.

The effect of $SnCl_2$ sensitization in activation stage prior to $PdCl_2$ treatment (two-step method) on the plating rate has been studied in comparison with the one-step method. In the two-step method, the polymer samples were immersed successively into $SnCl_2$ solution 5 min and then into $PdCl_2$ solution for 20 min during the sensitization stage the Sn^{2+} ions are absorbed by the films and after immersion into $PdCl_2$ the Pd^{2+} ions are reduced with the formation of catalytic surface of Pd metal atoms:

$$Pd^{2+} + Sn^{2+} \rightarrow Pd^0 + Sn^{4+} \qquad (2)$$

The results indicate that the two-step activation enhances the plating rate more effectively in comparison with the one-step method. It is well known that the electroless plating process is initiated mainly by Pd^0 [17]. On the other hand, the predominant species in the absence of $SnCl_2$ sensitization will be Pd^{2+} ions and their reduction will take place in alkaline solution of the plating bath consuming longer time to form catalytic surface with Pd^0. This fact helps to understand the observed incubation time of about 6 min to start Cu deposition on the grafted PE surface after activation in $PdCl_2$ solution in Sn-free process (Fig. 3). This time delay allows the reduction of Pd^{2+} complexes to Pd^0. For the surfaces activated via two-step process, immediate Cu deposition is observed, as Pd^0 is the predominant species on the surface.

Optimization of Electroless Plating Process

The goal of electroless plating process is to produce a continuous void free and tightly adherent deposit of Cu on a polymeric surface. Different electroless Cu baths prepared based on EDTA were studied to optimize the plating.

Operating Temperature

Figure 4 illustrates the effect of operating temperature on electroless plating rate. For all the grafting

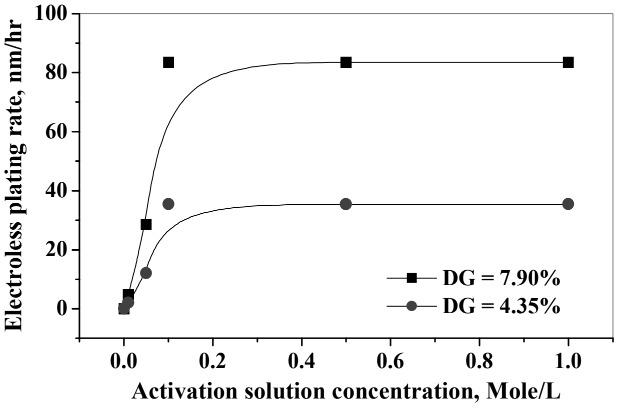


Fig. 3. Kinetics of Cu deposition with different activaton methods.

degrees the deposition rate increases with bath temperature up to 50°C then decreases due to the decomposition of bath at higher temperature. However, it is preferable to perform the plating process at 40°C in order to keep the high stability of the bath and to avoid the high temperature effects on the polymeric samples.

pH value

The effect of pH value on the electroless Cu plating at 40°C is shown in Fig. 5. pH values were changed by adding concentrated NaOH to the electroless plating bath. The deposition rate increases markedly with increasing pH, achieves the maximum at pH 13, and then decreases. This behavior can be explained by the following reasons [20,21]:

- An initial increase in the plating rate is due to the effect of OH^- ions as reactant in the total reaction as shown in the equation (1)
- A decrease in the plating rate is due to the consumption of OH^- via hydrolysis of formaldehyde to methylene glycol anions followed by its oxidation to formate ions as shown in the following equations:

$$HCHO + OH^- \rightarrow CH_2(OH)O^- \qquad (3)$$

$$CH_2(OH)O^- + 2OH^- \rightarrow$$
$$\rightarrow CHOO^- + 2H_2O + 2e^- \qquad (4)$$

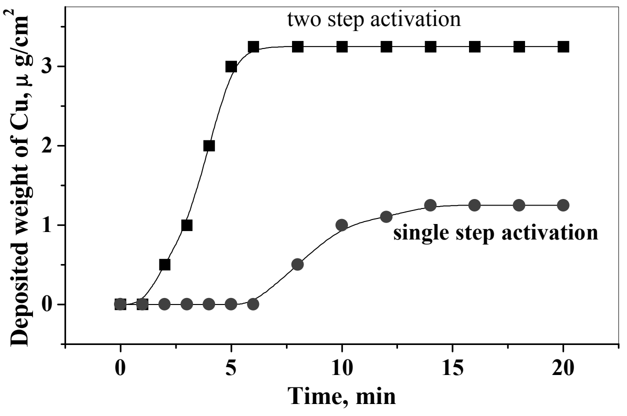


Fig. 4. Dependence of plating rate on the bath temperature (pH 13).

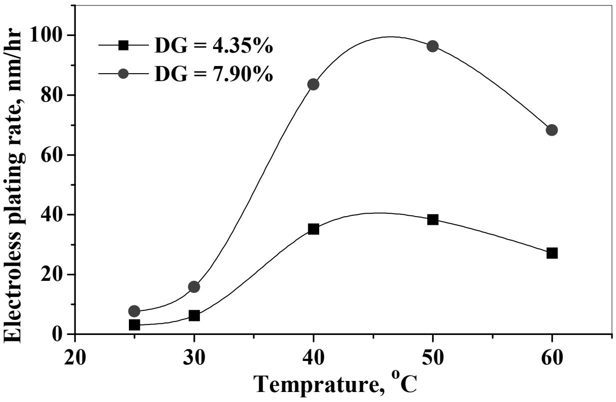


Fig. 5. Dependence of plating rate on pH (T = 40°C).

Plating Rate Additives

Different electroless plating baths containing small amounts of organic compounds including thiourea, pyridine and cytosine were prepared. The effect of these additives concentration on the plating rate at 40°C and pH 13 is shown in Fig. 6. The plating rate increases in presence of pyridine and cytosine and reaches the maximum at 60 mg/L of pyridine and 4 mg/L of cytosine. Then the plating rate decreases with the further addition of pyridine or cytosine. However, thiourea has an inhibiting effect on the plating rate, which decreases sharply even with addition of few amounts of thiourea. The initial increase in the plating rate by addition of pyridine and cytosine may be due to the presence of delocalized π-electron bond in their structure, which enhances the plating rate. This phenomenon is attributed to the greater adsorption ability of deposited copper than that of EDTA complexes at low concentrations of these compounds, which in turn facilitates the copper reduction and accelerates the deposition rate [19-21]. On the other hand, a decrease in the plating rate may be related to the excessive coverage of the sample surface, which makes the reduction of copper ions difficult or even impossible as was observed in the case of thiourea.

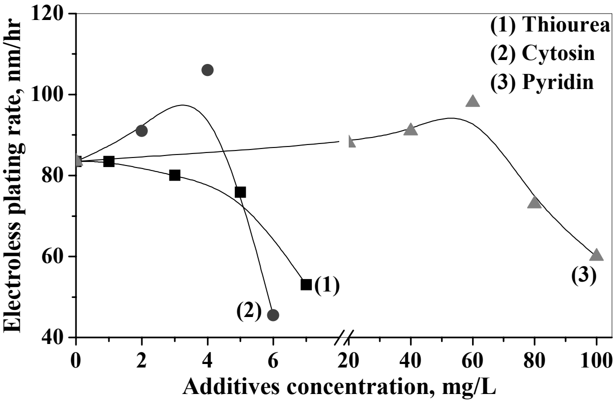


Fig. 6. Effect of organic additives on plating rate (EDTA plating bath, pH 13, T = 40°C).

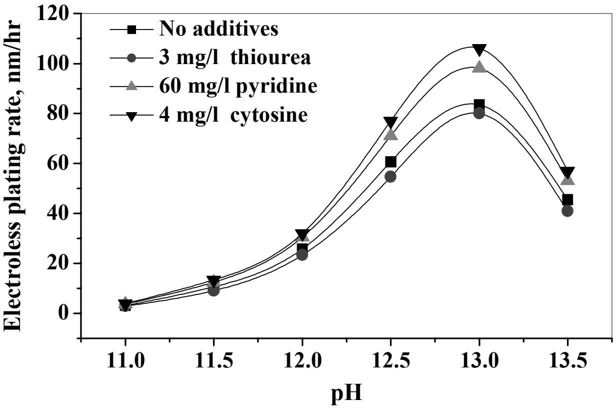


Fig. 7. Dependence of plating rate on pH in the presence of optimum concentration of organic additives (EDTA plating bath T = 40°C).

The influence of the optimal amounts of the studied organic additives on the plating rate at different pH values is demonstrated in Fig. 7. The results are similar to those of additive-free bath and show the previously discussed trend [20]. All the studied additives except thiourea can be used as plating rate accelerators or enhancers at pH 13.

Morphology of Films

The morphology of the polymeric films was investigated before and after metallization. Figure 8 (a, b) shows the grafted PE with VEMEA and the metallized film, respectively. The white clusters in Figure 8b represent metallic copper demonstrating good coverage and uniformity of the deposited layer. Moreover, the microanalysis of metallized films shows that the atomic percent of Cu metal is 98.9%.

Adhesion Measurements

One of the important characteristics of metallized films is the adhesion property. In this work, the adhesion strengths of electrolessly deposited Cu on the grafted modified PE films were determined by measuring the force required to separate the plated layer from the polymer surface. A simple test employing adhesive material (Super Glue) has been used to cement the plated layer to the Cu foil which gripped and pulled using a tensile testing machine and the adhesion strength is calculated as the force per unite area according to following equation: $\rho = F/A$.

It is shown that the adhesion strength increases with increasing of DG (Fig. 9). A number of mechanisms are probably responsible for the enhanced adhesion strength. During the electroless deposition of Cu in alkaline solution, the presence of covalently bonded amine groups on the PE grafted surface, the coordination bonding of the Pd catalyst to the surface legend, and the subsequent interaction of amine groups with the Cu are likely to have contributed to the high adhesion strength of the electrolessly deposits on the substrates. In addition, it has been reported about the spatial distribution of the grafted

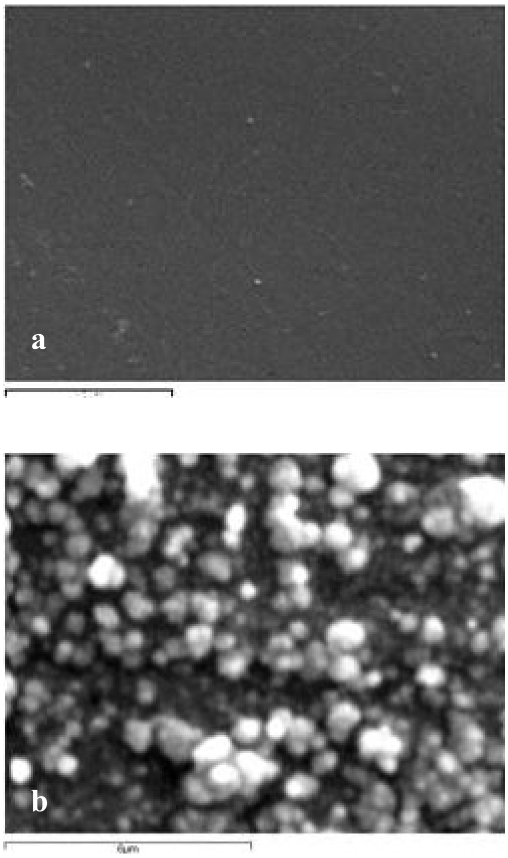


Fig. 8. SEM of (a) grafted and (b) metallized films.

chains into metal matrix [6,7]. Such distribution coupled with the strong interaction between the amine functional groups and metal, must have contributed to the observed adhesion strength enhancement.

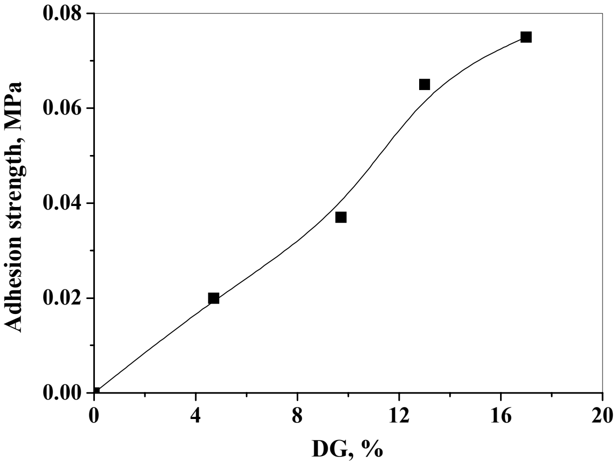


Fig. 9. Dependence of adhesion measurements on degree of grafting.

Conclusions

The electroless plating of polyethylene films grafted with vinyl ether of monoethanolamine resulting in formation of metallized materials has been studied in the present work. It was found that an increase in grafting degree of VEMEA onto PE films leads to a significant increase in the plating rate. The immersion of the grafted films into 0.1 g/L $PdCl_2$ for 25 min leads to the optimal plating characteristics for the single-step activation in the absence of $SnCl_2$ sensitization. Two-step activation is more effectively enhancing the plating rate in comparison with the single-step activation. The highest plating rate can be observed at pH 13 and working temperature 50°C, however it is preferable to perform the process at 40°C in order to keep the high stability of bath and to avoid the high temperature effects on the polymeric samples. The presence of 60 mg/L of pyridine and 4 mg/L of cytosine in the plating solution accelerates the metal deposition, whereas the presence of thiourea inhibits it. The adhesion of deposited layer increases with increase of grafting degree.

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