A study of tin-free activation process for electroless nickel plating on polyurethane foam

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Abstract – In the present study, a tin-free activation process has been studied for electroless nickel plating on polyurethane (PU) foam. The effect of HCl concentration (2-6 molar), PdCl\textsubscript{2} concentration (0.2-1.8 g/l), and the type of reducing agents (sodium hypophosphite and hydrazine) on the properties of the activated surface and the deposition of Ni were investigated by scanning electron microscope (SEM), energy dispersive X-ray spectrometer (EDX), X-ray photoelectron spectroscopy (XPS). The use of HCl concentration $\geq$ 6 M resulted in partial destruction of the PU foam. More uniform coating and higher amount of Ni deposit were obtained with the higher amount of PdCl\textsubscript{2} during activation. The XPS results revealed that the chemical state of nickel on the Ni/PU foam were Ni$^{2+}$.

Keyword: Electroless deposition; Palladium; Nickel; Catalyst; Polyurethane foam
1. Introduction

Polyurethane (PU) foams are porous materials available in a wide range of thermal and physical mechanical properties. PU foams have high energy absorption capacity and are particularly useful for, among many, shock absorbance, acoustic and thermal insulating applications, and filtering applications [1].

Electroless nickel plating is a widely used technique in industries which offers uniform deposition of nickel that exhibits good corrosion and wear resistance, decent electrical and thermal conductivity, and good solderability [2-3].

The conventional electroless plating of polymer substrates involves 3 steps: pretreatment, activation, and plating. The activation is the key to the subsequent successful electroless metal deposition [4]. The conventional activation process includes two-step method using sensitization solution of SnCl₂ and then activation solution of PdCl₂, or one-step method using a mixture of SnCl₂ and PdCl₂ [5-6]. However, these methods involve numerous problems such as the use of highly toxic tin and the uncontrollable process which results in the waste of Pd and the failure of plating [7].

In the present work, a tin free activation process has been studied for electroless nickel plating on PU foam. Particularly, sodium hypophosphite and hydrazine were investigated as potential Sn replacement for reduction of Pd. Furthermore, the use of hydrochloric acid (HCl) for chemically roughening the PU’s surface was also explored as a route to enhance mechanical adhesion between the deposited metal and the PU. Hence, the effects of HCl concentration, PdCl₂ concentration, and the type of reducing agents on the electroless nickel plating on PU foam were examined. The chemical compositions and morphology of the substrate surface were characterized by X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectrometer (EDX), and scanning electron microscopy (SEM).

2. Experimental

2.1. Etching and activating

The PU foam sample (1x1x1 cm³) was cleaned in distilled water and dip in acetone for 5 min at room temperature, then cleaned in distilled water again. After cleaning, etching was performed on PU foams by dripping in hydrochloric acid solutions (2M, 4M, 6M) for 1 hr. After etching, the samples were cleaned in distilled water and dip in acetone for 5 min, filtered to remove excess acetone, and then dried. Subsequently, the PU foams were immersed in a solution of palladium chloride (PdCl₂: (0.2, 1, 1.8) g/l, HCl : 2 g/l) at 40 °C for 10 min with ultrasonic vibration. Then it was rinsed and reduced in a reducing agent (sodium hypophosphite or hydrazine) at 40 °C for 2 min.

<table>
<thead>
<tr>
<th>Reagent</th>
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<th>Quantity per 300 ml plating bath</th>
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<tbody>
<tr>
<td>tri Sodium-Citrate</td>
<td>Na₃C₆H₅O₇</td>
<td>10.5 g</td>
</tr>
<tr>
<td>Ammonium Sulfate</td>
<td>(NH₄)₂SO₄</td>
<td>9 g</td>
</tr>
<tr>
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The color of the solution turned to black, as the formation of Pd nanoparticles was obtained [8].

2.2. Preparation of Ni/PU foam

Nickel deposition was achieved by dipping the activated PU foam into an electroless nickel plating bath (300 ml for each sample) for 1 hr at 85°C. The bath was maintained at pH of 9.8 ± 2.0 to ensure a high cation exchange. The chemical compositions of the bath are given in Table 1.

2.3. Characterization

The chemical composition on the surface of PU foam was determined by XPS using an Amicus photoelectron spectrometer with Mg Kα X-ray source. The binding energy was calibrated with the C 1s peak at 285.0 eV. The particle morphology and elemental distribution were obtained using a JEOL JSM-35CF scanning electron microscope operated at 20 kV.

3. Results and discussion

3.1. Effect of HCl concentration on PU foam

The typical SEM images of PU foam before and after etching/activation are presented in Fig. 1(a)-(f). The quality of the deposited metal layers, in the electroless deposition on non-metallic surface, is noted to be dependent on the adhesion between the Pd activation particles and the PU’s surface. Electroless deposition also requires sufficient surface cleaning pre-treatment to increase the adhesion of Pd(+2) ions to the polymer’s surface [9]. In the conventional activation by PdCl₂ and SnCl₂ process, the surface was treated with 30% sodium hydroxide (NaOH) at 60°C for 10 min. High surface roughness with some cracks were observed over the surface of PU foam after conventional activation (Fig. 1(b)). On the contrary, the tin-free activation did not result in an obvious surface roughness. Comparing to the original PU foam in Fig. 1(a), the surface morphology of the PU foam after etching with 4M HCl for 1 hr (Fig. 1(c)) and the PU foam after etching and PdCl₂ activation (Fig. 1(e)), was quite smooth and was not significantly different from the ones after etching.

Table 1. Ni plating bath formulation for the PU foams

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Fig. 1. SEM micrographs of the top-layer morphology of PU foam, etching/activation: (a) PU foam; (b) PU foam + Pd-Sn; (c) PU foam + HCl 4M; (d) PU foam + HCl 2M/activation; (e) PU foam + HCl 4M/activation and (f) PU foam + HCl 6M/activation.

There were no significantly differences in the morphologies of PU foam after etching/activation with different concentrations of hydrochloric acid as shown in Fig. 1(d)-(f). However, the use of HCl concentration ≥ 6 M resulted in partial destruction of the PU foam.

3.2 Effect of PdCl₂ concentration during the activating process on nickel plating

The SEM images of the PU foam after electroless nickel deposition prepared by etching with 4M HCl for 1 hr, activated by PdCl₂ solution and reduced in sodium hypophosphite are shown in Fig. 2 (a)-(f). It can be seen from Fig.2 that the three dimensional network of the PU foam microstructure was not much altered after electroless nickel plating. The nickel layer was not evident in the SEM images when the PU foam was prepared by etching with 4M HCl for 1 hr and activated by PdCl₂ 0.2 g/l as shown in Fig. 2(a) and Fig. 2(b). Increasing the amount of PdCl₂ during activation to 1.0 g/l and 1.8 g/l resulted in more uniformly coating of nickel layer on the surface as shown in Fig 2(c) and Fig. 2(e), respectively. Fig. 3 shows the EDX spectra of Ni, O, and C elements on the Ni/PU foam prepared with different amounts of PdCl₂ in the activating solution. It is clearly seen that the amount of Ni deposit increased with increasing amount of PdCl₂ in the activating solution.
3.3 XPS analysis

The chemical states of nickel on the Ni/PU foam prepared by tin-free activation electroless deposition were investigated by XPS technique and the results are shown in Fig. 4. The Ni 2p peak is always characterized by a complex shape due to the presence of multiplet splitting, shake-up and plasmon loss structures [10]. In the present work, the binding energy of Ni 2p was observed in the range of 856.9-862.6 eV and was attributed to Ni$^{2+}$ ions according to the literature [11-12]. It is thus suggested nickel on the Ni/PU foams’ surface is present mostly in the form of nickel oxide.

3.4 Effect of reducing agent on nickel plating

Hydrazine and sodium hypophosphite were selected as the reducing agents for Pd during the activating process in order to demonstrate the effect of reducing agent on the plating efficiency. Here, the plating efficiency is evaluated by the deposition rate testing. The deposition rate was calculated by the following equation:

$$v = \frac{(m_2-m_1)}{m_1 t}$$

where $m_1$ and $m_2$ are the masses of the specimen before and after electroless plating procedure, respectively; $t$ is the stabilizing time of electroless plating bath [13].

The effect of reducing agent on the deposition rate is shown in Fig. 5. The results indicate that the use of hydrazine provided slower plating rate than sodium hypophosphite. Furthermore, both reducing agents appear to give optimum deposition rate near the early stage of plating, after which the plating gradually declined. The plating time deposition was optimized at 60 min. According to the experimental results, the deposition rate was low after 60-120 min. Moreover, it was found that the bath decomposed easily after plating for 60 min.

4. Conclusions

Electroless nickel deposition on PU foam was successfully achieved by a tin-free etching/activation process to avoid the use of highly toxic tin. The rate of deposition and the amount of Ni deposit were significantly increased with increasing amount of PdCl$_2$ during activation. The optimum conditions were determined to be (i) etching with 4M HCl for 1 hr (ii) activation with PdCl$_2$ solution 1.8 g/l, and (ii) plating time 60 min with sodium hypophosphite as a reducing agent.
References